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FINAL QUALITY ASSURANCE PROJECT PLAN FOR REMEDIAL
INVESTIGATION/FEASIBILITY STUDY OPERABLE UNIT 3 (OU3) VOLUME II OF IV NIROP
FRIDLEY MN
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0003

**Final
Quality Assurance Project Plan
for
Operable Unit 3
Remedial Investigation/Feasibility Study**

**Naval Industrial Reserve
Ordnance Plant
Fridley, Minnesota**

Volume III of IV



**Southern Division
Naval Facilities Engineering Command**

Contract Number N62467-94-D-0888

Contract Task Order 0003

June 1997

**FINAL
QUALITY ASSURANCE PROJECT PLAN
FOR
OPERABLE UNIT 3 REMEDIAL INVESTIGATION/FEASIBILITY STUDY**

**NAVAL INDUSTRIAL RESERVE ORDNANCE PLANT
FRIDLEY, MINNESOTA**

VOLUME III OF IV

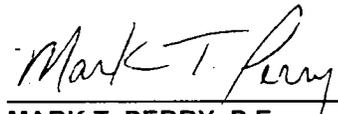
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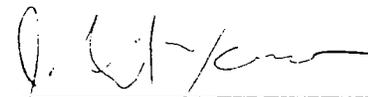
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PREFACE

This Quality Assurance Project Plan (QAPP) is Volume III of the four-volume Work Plan.

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ACRONYMS/ABBREVIATIONS

AA	Atomic Absorption
B&R Environmental	Brown & Root Environmental
BFB	Bromofluorobenzene
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFU	Colony Forming Units
CLEAN	Comprehensive Long-Term Environmental Action, Navy
CLP	Contract Laboratory Program
COC	Chain of Custody
CRDL	Contract Required Detection Limit
CRQL	Contract Required Quantitation Limit
CVAA	Cold Vapor Atomic Absorption
DFTPP	Decafluorotriphenyl phosphine
DPT	Direct-Push Technology
DRO	Diesel Range Organics
DQO	Data Quality Objective
EC	Electron Capture
Fe(II)	Ferrous (Reduced) Iron
FFA	Federal Facilities Agreement
FOL	Field Operations Leader
FS	Feasibility Study
FSP	Field Sampling Plan
FTMR	Field Task Modification Request
GC	Gas Chromatograph
GFAA	Graphite Furnace Atomic Absorption
GRO	Gasoline Range Organics
HBV	Health Based Value
HRL	Health Risk Limit
ICP	Inductively Coupled Plasma
LCS	Laboratory Control Sample
LIMS	Laboratory Information Management System
MCL	Maximum Contaminant Level
MDL	Method Detection Limit
MPCA	Minnesota Pollution Control Agency
MS	Mass Spectrophotometer
MS/MSD	Matrix Spike/Matrix Spike Duplicate
NEESA	Naval Energy and Environmental Support Activity
NFESC	Naval Facilities Engineering Service Center
NIROP	Naval Industrial Reserve Ordnance Plant
NIST	National Institute of Science and Technology
NTU	Nephelometric Turbidity Units
ORP	Oxidation Reduction Potential
OU1	Operable Unit 1
OU2	Operable Unit 2
OU3	Operable Unit 3
PARCC	Precision, Accuracy, Representativeness, Comparability, Completeness
PCB	Polychlorinated Biphenyl
PQL	Practical Quantitation Limit
QA	Quality Assurance

ACRONYMS/ABBREVIATIONS (Continued)

QAM	Quality Assurance Manager
QAPP	Quality Assurance Project Plan
QC	Quality Control
QN	Quality Notice
RA	Risk Assessment
RAS	Routine Analytical Services
RI	Remedial Investigation
RPD	Relative Percent Difference
SDG	Sampling Delivery Group
SOP	Standard Operating Procedure
SOW	Statement of Work
SO ₄ ²⁻	Sulfate
SRM	Standard Reference Materials
TAL	Target Analyte List
TCL	Target Compound List
TOC	Total Organic Carbon
TSS	Total Suspended Solids
UCL	Upper Ninety-Five Percent Confidence Limit
U.S. EPA	United States Environmental Protection Agency
VOC	Volatile Organic Compound
%R	Percent Recovery

1.0 PROJECT DESCRIPTION

This project description outlines the overall scope of a Remedial Investigation (RI) to be performed for Operable Unit 3 of the Naval Industrial Reserve Ordnance Plant (NIROP) located in Fridley, Minnesota. Operable Unit 3 includes contaminant sources in all environmental media (soil and groundwater) at the site. The Quality Assurance Project Plan presents the organization, objectives, planned activities, and specific Quality Assurance/Quality Control (QA/QC) procedures associated with the Work Plan (and addenda) for the RI. Specific protocols for sampling, sample handling and storage, chain-of-custody, and laboratory and field analyses are described. All QA/QC procedures are structured in accordance with applicable technical standards, and U.S. EPA Region V and Minnesota Pollution Control Agency requirements, regulations, guidance, and technical standards.

1.1 INTRODUCTION

This Quality Assurance Project Plan (QAPP) has been prepared by Brown & Root Environmental (B&R Environmental) on behalf of the United States Navy Southern Division Naval Facilities Engineering Command and the NIROP, Fridley, Minnesota. This QAPP and other associated documents, including Work, Field Sampling, and Health and Safety Plans constitute the project planning documents for the OU3 RI.

1.1.1 Overall Project Objectives

The general project objectives for the Fridley Operable Unit 3 (OU3) Remedial Investigation (RI) are outlined in the Federal Facilities Agreement (FFA) for the NIROP. Attachment A of the FFA outlines the general project objectives as follows:

"(1) identify all source areas of contamination; (2) identify the extent and magnitude of soil, subsoil, surface water, and groundwater contamination; (3) gather all necessary data to support the Feasibility Study (FS) and Risk Assessment (RA), and; (4) provide information and data needed for the selection and implementation of response actions at the site."

The FFA goes on to state (Section IV, Task A, Part 2) that RI Work Plans (upon implementation) are intended to:

"(1) provide for the complete characterization of the site and its actual or potential hazard to public health, welfare and the environment; (2) produce sufficient data and information to allow the Navy to submit the review of Alternatives Report; and, (3) produce data of sufficient quantity and adequate technical content to assess possible alternative response actions during the FS."

These general project objectives, except for surface water evaluation which was addressed in the Operable Unit 1 (OU1) RI, have provided the basis for the development of specific Data Quality Objectives (DQOs), as discussed in Section 4.0 of the attendant Work Plan (Volume I), as well as the scope of work for the OU3 RI.

1.1.2 Project Status/Phase

The RI at NIROP Fridley has been undertaken on an operable unit basis. The first operable unit (OU1) included site groundwater and surface water. The OU1 RI was completed by RMT Inc. in June 1987. The second operable unit (OU2) included all facility soils (unsaturated zone) other than those beneath the plant building footprint. The RI for OU2 was completed by RMT Inc. in September, 1993. The third operable unit (OU3) includes potential source areas at the facility. This QAPP and all attendant project planning documents apply to OU3. OU2 has been made a subset of OU3. All conclusions from the OU2 RI will be included in the OU3 FS.

The OU3 RI will be completed in a phased manner. The first phase will include chemical and physical characterization of the soils and shallow groundwater beneath the plant. The second phase will include additional groundwater characterization to delineate potential contaminant migration associated with any potential source areas identified during Phase I.

1.1.3 QAPP Preparation Guidelines

This Quality Assurance Project Plan has been prepared in accordance with the general guidance outlined in the United States Environmental Protection Agency (U.S. EPA) Region V Model Superfund Quality Assurance Project Plan dated January 1996. Additional guidance regarding the QAPP contents was provided by representatives of U.S. EPA Region V and the Minnesota Pollution Control Agency (MPCA) during a teleconference held on February 20, 1996. Representatives of U.S. EPA Region V, the MPCA, the United States Navy Naval Facilities Engineering Command (Southern Division), and B&R Environmental participated in the teleconference.

1.2 FACILITY DESCRIPTION

A brief discussion of the NIROP, including its location, size and borders, regional geology, hydrogeology, hydrology, topography, etc. is provided in the remainder of this section. The majority of this information is contained in the Work Plan for the OU3 RI, and specific sections of the Work Plan are referenced as appropriate.

1.2.1 Location

The NIROP Fridley is located approximately 700 feet east of the Mississippi River in the City of Fridley, Anoka County, Minnesota. A site location map for the facility is provided as Figure 2-1 of the Work Plan for the Naval Industrial Reserve Ordnance Plant (Volume I).

1.2.2 Facility Size and Borders

The NIROP encompasses approximately 83 acres. The facility is bordered on the east by the Burlington Northern rail yard, on the north by various industrial facilities, on the west by East River Road, and on the south by United Defense, LP.

1.2.3 Topography

The NIROP is located on a broad, flat, alluvial terrace of the Mississippi River at an elevation of approximately 835 feet (National Geodetic Vertical Datum of 1929). Slopes across the site are five percent or less (Envirodyne Engineers, Inc., June 1983 Initial Assessment Study, Naval Industrial Reserve Ordnance Plant, Minneapolis, Minnesota).

1.2.4 Local Hydrology and Hydrogeology

Detailed information regarding regional geology, hydrogeology, and hydrology are provided in Sections 2.7.1, 2.7.2, and 2.7.3 of the Work Plan (Volume I).

1.3 FACILITY HISTORY

Detailed discussions of the general history of the NIROP and past data collection activities at the facility are included in the Work Plan (Volume I). Specific sections of the Work Plan are cited and incorporated by reference in the remainder of this section, as applicable.

1.3.1 General History

The NIROP has been in operation since 1940 and is a production facility for Naval ordnance. Items produced at the facility have included gun mounts and advanced missile launching systems. Additional general background regarding historical industrial activities at the NIROP is provided in Section 2.4 of the Work Plan for the facility (Volume I).

1.3.2 Past Data Collection Activities

A chronological history of events at the NIROP, including past data collection activities is provided in Section 2.5 of the Work Plan (Volume I). A concise summary of historical events including previous investigations is provided in Table 2-1 of the Work Plan (Volume I).

1.3.3 Current Status

At the current time, the Remedial Investigations for Operable Units 1 and 2 have been completed. A feasibility study of alternatives was completed for Operable Unit 1, and, as a result of the feasibility study, a Record of Decision was signed requiring implementation of a containment system (active pumping) to prevent continued offsite migration of TCE in groundwater. Operable Unit 3 includes potential source areas at the facility.

1.4 PROJECT OBJECTIVES

This section outlines the overall project objectives for the OU3 RI at NIROP, Fridley. Specific objectives and associated tasks are discussed in Section 1.4.1. Project target parameters and intended data uses are discussed in Section 1.4.2. Data Quality Objectives are developed in Section 1.4.3.

1.4.1 Specific Objectives and Associated Tasks

Four primary objectives, as discussed in Section 1.1.1, are identified for the NIROP Fridley OU3 RI. A phased investigation will satisfy these objectives as previously discussed in Section 1.1.2. The specific objectives for each phase of the OU3 RI are outlined in the following subsections.

1.4.1.1 Phase I

Characterize the soils beneath the production facility from the standpoint of potential direct contact impacts on human health (utility and construction workers) under existing site conditions and under a benchmark future condition (industrial land use).

Characterize the soils beneath the production facility from the standpoint of potential sources of groundwater contamination. Groundwater contamination is considered any concentration exceeding a U.S. EPA Maximum Contaminant Level (MCL) or a MPCA Health Risk Limit (HRL). The more conservative value (MCL or HRL) will be used. If neither a MCL nor a HRL exist for a parameter, then a state Health Based Value (HBV) will apply.

Characterize stratigraphy to define potential preferential flow conduits for groundwater contamination and/or dense non-aqueous phase liquids.

Tasks necessary to accomplish the objectives of Phase I include the collection of near-surface and subsurface soil samples, and shallow groundwater samples from beneath the building footprint.

1.4.1.2 Phase II

Characterize stratigraphy and groundwater beneath the production facility in order to locate contaminant sources and obtain information needed to evaluate remediation alternatives.

Tasks necessary to accomplish the objectives of Phase II include the installation of groundwater monitoring wells within the building, and collection and analysis of groundwater samples from the newly installed wells.

1.4.2 Project Target Parameters and Intended Data Uses

This section discusses the field and laboratory analytical information to be generated during the course of the OU3 RI. Field parameters and intended data uses are discussed in Section 1.4.2.1. Laboratory parameters and intended data uses are discussed in Section 1.4.2.2.

1.4.2.1 Field Parameters

Field parameters will include those associated with the completion of soil borings, installation and development of monitoring wells, and groundwater sampling and analysis. Field measurements will include only those completed using simple field instrumentation, field test kits, a portable colorimeter, and a field gas chromatograph (GC).

Field measurements of total volatile organics will be completed using a Photoionization Detector or Flame Ionization Detector. These measurements will be used to determine appropriate subsurface sample horizons to be submitted for laboratory analysis and in safety monitoring to determine breathing zone conditions for site workers.

Field parameters including pH, specific conductance, turbidity, dissolved oxygen, and temperature will be completed for all aqueous phase samples using a water quality meter as discussed in Section 7.5.2 of the FSP. These measurements will be used to support monitoring well development and purging of stagnant water from well casings. Specific conductance and pH will also be used as general indicators of water quality.

Additional water parameters will include oxidation-reduction potential (ORP), dissolved ferrous (reduced) iron, dissolved reduced manganese, and hydrogen sulfide (as sulfide). (Note that ORP is sometimes referenced as Eh.) These measurements, along with pH, dissolved oxygen, temperature, and several laboratory parameters, will be used to assess the natural attenuation of chlorinated solvents in the groundwater system at the NIROP Fridley. In addition to measurement using the water quality meter, dissolved oxygen will also be measured using a field test kit. ORP will be measured using a water quality meter. The remaining field parameters (dissolved ferrous iron, dissolved reduced manganese, and hydrogen sulfide) will be measured using a portable colorimeter. Tables 1-1 and 1-2 provide a summary of field parameters and associated ranges and increments of detection.

TABLE 1-1
RANGES AND INCREMENTS OF DETECTION
FIELD PARAMETERS FOR GROUNDWATER QUALITY TESTING
NIROP FRIDLEY, MINNESOTA

Parameter	Method	Range/Increment
pH	meter	0-14 / 0.01 units
Specific Conductance	meter	0-100 / 0.01 millimhos/cm
Turbidity	meter	0-800 / 0.1-1 NTU
Dissolved Oxygen	meter	0-19.9 / 0.01-0.1 mg/L
Temperature	meter	0-50 / 0.1-1°C

TABLE 1-2
ANALYTICAL DETECTION LIMITS
FIELD PARAMETERS FOR EVALUATION OF NATURAL ATTENUATION
NIROP FRIDLEY, MINNESOTA

Parameter	Method	Range / Increment
pH	meter	0 to 14 / 0.01 units
Dissolved Oxygen	modified Winkler titration test kit	0.02 to 10 / 0.02 mg/L
Temperature	meter	-5.0 to 50 / 0.4°C
Oxidation Reduction Potential	meter	-1500 to 1500 mV / 2% of reading plus 1 count
Dissolved Ferrous Iron	10-phenanthroline method ⁽¹⁾	0 to 5 / 0.01 mg/L
Dissolved Reduced Manganese	PAN method ⁽¹⁾	0 to 0.8 / 0.001 mg/L
	Periodate oxidation method ⁽¹⁾	0 to 20 / 0.1 mg/L
Hydrogen Sulfide (as sulfide)	Methylene Blue Method ⁽¹⁾	0 to 0.6 / 0.001 mg/L

(1) Portable colorimeter

On-site analysis of soil samples will also be performed using a field GC for the volatile organic compounds shown in Table 1-3. As further discussed in Section 7.3.1 of the FSP, soil samples will be collected at 4-foot intervals (using direct-push technology or DPT) or 5-foot intervals (during installation of permanent monitoring wells) down to the termination depths of the borings for purge-and-trap field GC analysis. The results of these analyses will be used to evaluate the vertical distribution of contaminated soil during drilling, to guide the sampling effort, and to quantitatively evaluate the protection of groundwater. The soil sample with the highest field GC result in the 2- to 12-foot interval, as well as the soil sample from the 0- to 2-foot interval, of the DPT borings will be collected and submitted for analysis by the fixed-base laboratory.

1.4.2.2 Laboratory Parameters

Laboratory parameters will include Target Compound List (TCL) volatile and semivolatile organics and polychlorinated biphenyls, Target Analyte List (TAL) metals and cyanide, hexavalent chromium, sulfate, total suspended solids (TSS), total hardness (as CaCO_3), alkalinity (as CaCO_3), nitrate, nitrite, dissolved chloride, dissolved bromide, dissolved phosphate, dissolved methane, and total organic carbon (TOC). Pyridine will also be added to the semivolatile Target Compound List since this compound was a constituent in some of the products used at the site. Total hardness, TSS, and alkalinity will be used for engineering analysis during the feasibility study. The TCL and TAL compounds/analytes will be used to support decision making via direct comparison with the preliminary health-based numeric decision rules outlined in Section 4.0 of the Work Plan. It should be noted that SW-846 Method 8260A, modified by using a 25 mL purge volume, will be used for the analysis of TCL volatiles for groundwater samples. This method will be used in place of standard Contract Laboratory Program (CLP) protocol in order to achieve lower quantitation limits for volatile organic compounds in groundwater, since these are the compounds of primary concern at the site. This low-concentration method will also be used for the analysis of all trip blanks associated with the OU3 investigation. Analytical methods are further discussed in Section 7. Representative soil samples will be analyzed for hexavalent chromium to evaluate the speciation of total chromium. As detailed in Standard Operating Procedure LTL-7014 (Appendix A) matrix spike results of the hexavalent chromium analyses may also necessitate fixed-base laboratory analysis of soil samples for pH, ORP, ferrous iron, and sulfides. Based on holding time requirements, as presented in Table 4-1 of the FSP, analyses for these four parameters will be performed immediately upon receipt by the laboratory for each hexavalent chromium sample designated for matrix spike analysis. Representative soil samples will be analyzed for TOC to evaluate the availability of carbon sources for bioremediation options. The remaining parameters (sulfate, nitrate, nitrite, dissolved chloride, dissolved bromide, dissolved phosphate,

TABLE 1-3

PRACTICAL QUANTITATION LIMITS - FIELD GC VOLATILE ORGANIC ANALYSIS
 NIROP FRIDLEY, MINNESOTA

Parameter	Soil Samples
	PQL(1)
Volatile Organic Compounds	µg/kg
Acetone	5
Benzene	1
Bromoform	1
Bromomethane	5
2-Butanone	5
Carbon disulfide	1
Carbon tetrachloride	1
Chlorobenzene	1
Chloroethane	5
Chloroform	1
Chloromethane	5
1,1-Dichloroethane	1
1,2-Dichloroethane	1
1,1-Dichloroethene	1
cis-1,2-Dichloroethene	1
trans-1,2-Dichloroethene	1
Ethylbenzene	1
2-Hexanone	5
4-Methyl-2-pentanone	5
Methylene chloride	1
Styrene	1
1,1,2,2-Tetrachloroethane	1
1,1,1-Trichloroethane	1
1,1,2-Trichloroethane	1
Trichloroethene	1
Tetrachloroethene	1
Toluene	1
Vinyl chloride	5
m,p-Xylenes	1
o-Xylene	1

1 PQL Practical Quantitation Limit.

and dissolved methane) will be used in conjunction with the field parameters previously discussed to assess the natural attenuation of chlorinated solvents in the groundwater system at the NIROP Fridley. Tables 1-4 through 1-6 provide a summary of all target laboratory analytes and associated Contract Required Quantitation and Method Detection Limits (TCL organics via CLP protocol), Contract Required and Instrument Detection Limits (TAL inorganics), and Practical Quantitation and Method Detection Limits (non-CLP parameters). Quantitation and detection limits are further discussed in Section 7.2.1.

1.4.3 Data Quality Objectives

Data quality objectives for the Fridley OU3 RI were developed in accordance with current U.S. EPA guidance. The DQO development process is outlined in detail in Section 4.0 of the attendant Work Plan (Volume I).

1.5 SAMPLE NETWORK DESIGN AND RATIONALE

The sample network design and rationale is discussed in detail in Section 2.0 of the attendant Field Sampling Plan (Volume II). Figures displaying the location of all proposed borings and monitoring wells are provided in Section 2.0 of the Field-Sampling Plan.

1.6 PROJECT SCHEDULE

The project schedule is provided in Section 6.0 of the attendant project Work Plan (Volume I).

TABLE 1-4
ANALYTICAL DETECTION LIMITS - TCL ORGANICS
NIROP FRIDLEY, MINNESOTA
PAGE 1 OF 4

Parameter	PQL(1)	CRQL(2)	MDL(3)	
	AQ(4)	SO(5)	AQ	SO
Volatile Organic Compounds	µg/L	µg/kg	µg/L	µg/kg
Acetone	5	10	2.88	1.72
Benzene	1	10	0.076	0.14
Bromodichloromethane	1	10	0.13	0.09
Bromoform	1	10	0.15	0.13
Bromomethane	1	10	0.37	2.40
2-Butanone	5	10	0.70	1.26
Carbon disulfide	1	10	0.20	0.16
Carbon tetrachloride	1	10	0.10	0.07
Chlorobenzene	1	10	0.12	0.11
Chloroethane	1	10	0.19	2.24
Chloroform	1	10	0.17	2.08
Chloromethane	1	10	0.15	2.31
Dibromochloromethane	1	10	0.12	0.19
1,1-Dichloroethane	1	10	0.16	2.33
1,2-Dichloroethane	1	10	0.11	0.14
1,1-Dichloroethene	1	10	0.17	0.53
cis-1,2-Dichloroethene ⁽⁷⁾	1	10	0.14	2.04
trans-1,2-Dichloroethene ⁽⁷⁾	1	10	0.17	2.06
1,2-Dichloropropane	1	10	0.14	0.13
cis-1,3-Dichloropropene	1	10	0.15	0.19
trans-1,3-Dichloropropene	1	10	0.11	0.18
Ethylbenzene	1	10	0.11	0.10
2-Hexanone	5	10	0.50	0.85
4-Methyl-2-pentanone	5	10	0.59	0.62
Methylene chloride	2	10	1.74	7.92
Styrene	1	10	0.078	0.08
1,1,2,2-Tetrachloroethane	1	10	0.23	0.14
1,1,1-Trichloroethane	1	10	0.13	0.08
1,1,2-Trichloroethane	1	10	0.15	0.14
Trichloroethene	1	10	0.15	0.09
Tetrachloroethene	1	10	0.12	0.24
Toluene	1	10	0.13	0.18
Vinyl chloride	0.3	10	0.22	2.26
Xylenes (total)	1	10	0.13	0.16

TABLE 1-4
ANALYTICAL DETECTION LIMITS - TCL ORGANICS
NIROP FRIDLEY, MINNESOTA
PAGE 2 OF 4

Parameter	CRQL(2)		MDL(3)	
	AQ(4)	SO(5)	AQ	SO
Semivolatile Organic Compounds	µg/L	µg/kg	µg/L	µg/kg
Acenaphthene	10	330	0.24	4.9
Acenaphthylene	10	330	0.24	4.4
Anthracene	10	330	0.42	6.6
Benzo(a)anthracene	1 ⁽⁶⁾	330	0.16	7.2
Benzo(a)pyrene	1 ⁽⁶⁾	330	0.15	8.7
Benzo(b)fluoranthene	1 ⁽⁶⁾	330	0.47	13.7
Benzo(g,h,i)perylene	10	330	0.49	10.8
Benzo(k)fluoranthene	5 ⁽⁶⁾	330	0.31	8.6
Bis(2-chloroethoxy)methane	10	330	0.24	6.7
Bis(2-chloroethyl)ether	1 ⁽⁶⁾	330	0.21	3.2
Bis(2-ethylhexyl)phthalate	10	330	0.87	10.3
4-Bromophenyl-phenylether	10	330	0.27	9.9
Butylbenzylphthalate	10	330	0.12	7.7
Carbazole	10	330	0.24	6.1
4-Chloro-3-methylphenol	10	330	0.33	11.1
4-Chloroaniline	10	330	1.06	38
2-Chloronaphthalene	10	330	0.44	8.4
2-Chlorophenol	10	330	0.19	5.6
4-Chlorophenyl-phenylether	10	330	0.35	6.6
Chrysene	10	330	0.19	5.1
Dibenz(a,h)anthracene	1 ⁽⁶⁾	330	0.12	7.6
Dibenzofuran	10	330	0.27	5.5
3,3'-Dichlorobenzidine	10	330	1.93	79.7
Diethylphthalate	10	330	0.17	8.2
Di-n-butylphthalate	10	330	0.18	7.0
Di-n-octylphthalate	10	330	0.40	6.7
4,6-Dinitro-2-methylphenol	25	830	1.19	116
2,4-Dinitrophenol	10 ⁽⁶⁾	830	1.08	15
2,4-Dinitrotoluene	2 ⁽⁶⁾	330	0.22	12.4
1,2-Dichlorobenzene	10	330	0.51	5.4
1,3-Dichlorobenzene	10	330	0.60	3.2
1,4-Dichlorobenzene	10	330	0.51	3.6
2,4-Dichlorophenol	10	330	0.26	10.5

TABLE 1-4
ANALYTICAL DETECTION LIMITS - TCL ORGANICS
NIROP FRIDLEY, MINNESOTA
PAGE 3 OF 4

Parameter	CRQL(2)		MDL(3)	
	AQ(4)	SO(5)	AQ	SO
Semivolatile Organic Compounds	µg/L	µg/kg	µg/L	µg/kg
Dimethylphthalate	10	330	0.21	12.2
2,4-Dimethylphenol	10	330	1.18	67
2,6-Dinitrotoluene	2 ⁽⁶⁾	330	0.29	27.0
Fluoranthene	10	330	0.41	5.6
Fluorene	10	330	0.16	4.4
Hexachlorobenzene	1 ⁽⁶⁾	330	0.26	9.5
Hexachlorobutadiene	1 ⁽⁶⁾	330	0.54	4.0
Hexachlorocyclopentadiene	10	330	1.38	6.7
Hexachloroethane	2 ⁽⁶⁾	330	0.57	5.2
Indeno(1,2,3-cd)pyrene	1 ⁽⁶⁾	330	0.06	7.0
Isophorone	10	330	0.18	8.2
2-Methylnaphthalene	10	330	0.41	6.4
2-Methylphenol	3 ⁽⁶⁾	330	0.69	9.4
4-Methylphenol	10	330	0.43	8.6
Naphthalene	10	330	0.38	5.7
2-Nitroaniline	25	830	0.26	10.3
3-Nitroaniline	25	830	1.16	89.3
4-Nitroaniline	25	830	3.14	81
Nitrobenzene	10	330	0.55	9.2
2-Nitrophenol	10	330	0.34	10.9
4-Nitrophenol	25	830	1.74	4.2
N-nitroso-di-n-propylamine	10	330	0.30	8.0
N-nitrosodiphenylamine	10	330	0.29	12.5
2,2'-Oxybis(1-chloropropane)	10	330	0.26	9.8
Pentachlorophenol	10 ⁽⁶⁾	830	1.2	6.3
Phenanthrene	10	330	0.24	6.4
Phenol	10	330	0.28	30.1
Pyrene	10	330	0.20	6.8
1,2,4-Trichlorobenzene	10	330	0.54	8.1
2,4,5-Trichlorophenol	25	830	0.28	9.3
2,4,6-Trichlorophenol	10	330	0.15	4.8
Pyridine ⁽⁸⁾	10	330	0.65	83

TABLE 1-4
ANALYTICAL DETECTION LIMITS - TCL ORGANICS
NIROP FRIDLEY, MINNESOTA
PAGE 4 OF 4

Parameter	CRQL(2)		MDL(3)	
	AQ(4)	SO(5)	AQ	SO
Polychlorinated biphenyls	µg/L	µg/kg	µg/L	µg/kg
Aroclor-1016	0.5 ⁽⁶⁾	33	0.081	5.36
Aroclor-1221	1.0 ⁽⁶⁾	67	0.092	9.58
Aroclor-1232	0.5 ⁽⁶⁾	33	0.17	4.34
Aroclor-1242	0.5 ⁽⁶⁾	33	0.3	6.65
Aroclor-1248	0.5 ⁽⁶⁾	33	0.091	18
Aroclor-1254	0.5 ⁽⁶⁾	33	0.1	22
Aroclor-1260	0.5 ⁽⁶⁾	33	0.084	3.36

- 1 PQL Practical Quantitation Limit.
- 2 CRQL Contract Required Quantitation Limit; as specified in OLM03.1, unless otherwise noted.
- 3 MDL Method Detection Limit; as provided by Laucks Testing Laboratories, Inc.
- 4 AQ Aqueous (groundwater) samples.
- 5 SO Solid (soil) samples.
- 6 CRQL revised to reflect laboratory's "true" reporting limit since standard CRQL for this compound exceeds MPCA HRL or other MPCA groundwater criterion.
- 7 1,2-Dichloroethene is typically reported as total 1,2-dichloroethene based on CLP requirements. The cis- and trans-isomers of 1,2-dichloroethene will be individually reported for the OU3 RI.
- 8 Pyridine is not part of the CLP TCL list but will be included in the semivolatile analysis of the OU3 RI samples since this compound was a component of products used at the NIROP Fridley.

TABLE 1-5
ANALYTICAL DETECTION LIMITS - TAL INORGANICS
NIROP FRIDLEY, MINNESOTA

Parameter	CRDL(1)		IDL(2)	
	AQ(3)	SO(4)	AQ	SO
Target Analyte List Metals	µg/L	mg/kg	µg/L	mg/kg
Aluminum	200	40	68	13.6
Antimony	60	12	12	2.4
Arsenic	10	2	1.9	0.38
Barium	200	40	0.5	0.1
Beryllium	5	1	0.3	0.06
Cadmium	5	1	3	0.6
Calcium	5000	1000	54	10.8
Chromium	10	2	5	1
Cobalt	50	10	2	0.4
Copper	25	5	2	0.4
Cyanide	10	10	2.686 ⁽⁵⁾	0.0238 ⁽⁵⁾
Iron	100	20	22	4.4
Lead	3	0.6	0.79	0.16
Magnesium	5000	1000	55	11
Manganese	15	3	1	0.2
Mercury	0.2	0.1	0.025	0.025
Nickel	40	8	3	0.6
Potassium	5000	1000	96	19.2
Selenium	5	1	1	0.2
Silver	10	2	3	0.6
Sodium	5000	1000	20	4
Thallium	10	2	0.78	0.16
Vanadium	50	10	3	0.6
Zinc	20	4	2	0.4

- 1 CRDL Contract Required Detection Limit; as specified in ILM04.0.
- 2 IDL Instrument Detection Limit, unless otherwise noted; as provided by Laucks Testing Laboratories, Inc.
- 3 AQ Aqueous (groundwater) samples.
- 4 SO Solid (soil) samples.
- 5 MDL Method Detection Limit; as specified by Laucks Testing Laboratories, Inc.

TABLE 1-6
ANALYTICAL DETECTION LIMITS
BIOLOGICAL/ENGINEERING/MISCELLANEOUS PARAMETERS
NIROP FRIDLEY, MINNESOTA

Parameter	Aqueous Samples (mg/L)	
	PQL ⁽¹⁾	MDL ⁽²⁾
Total Suspended Solids	2	NA ⁽³⁾
Alkalinity (as CaCO ₃)	2	NA
Hardness (as CaCO ₃)	1	NA
Sulfate	1	0.057
Nitrate	0.2	0.01
Nitrite	0.1	0.025
Dissolved Chloride	1	0.1
Dissolved Bromide	1	0.012
Dissolved Phosphate	1	0.12
Dissolved Methane (ng/L)	15	5.03
	Solid Samples (mg/Kg) ⁽⁴⁾	
Total Organic Carbon	200	24
Hexavalent Chromium	2	0.6
pH (pH units)	±0.1 ⁽⁵⁾	NA
Ferrous Iron	estimated at 1 ⁽⁵⁾	NA
Sulfide	estimated at 40 ⁽⁵⁾	NA
Oxidation Reduction Potential (mV)	±10 mV ⁽⁵⁾	NA

- 1 PQL Practical Quantitation Limit; as provided by Laucks Testing Laboratories, Inc.
- 2 MDL Method Detection limit; as provided by Laucks Testing Laboratories, Inc.
- 3 NA MDL determination not applicable to this method.
- 4 Units for solid sample results are mg/kg unless otherwise noted.
- 5 PQL not applicable. Values shown represent sensitivity for the parameter.

2.0 PROJECT ORGANIZATION

The project organization for the OU3 Remedial Investigation/Feasibility Study is provided in Section 7.0 (Project Management) of the attendant Work Plan (Volume I). A project organization chart, management responsibilities, quality assurance responsibilities, laboratory responsibilities, and field responsibilities are discussed in Sections 7.1 through 7.5 of the Work Plan, respectively.

3.0 QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

The overall Quality Assurance (QA) objective for this project is to develop and implement procedures for field sampling, chain-of-custody, laboratory analysis, and reporting that will provide results which are legally defensible in a court of law. Intended data uses are described in Section 1.4.2 of this QAPP. Specific procedures for sampling, chain-of-custody, laboratory instrument calibration, laboratory analysis, reporting of data, internal quality control, audits, preventive maintenance of field and laboratory equipment, and corrective action are described in other sections of this QAPP. The PARCC parameters (precision, accuracy, representativeness, comparability, and completeness) are qualitative and/or quantitative statements regarding the quality characteristics of the data used to support project objectives and ultimately, environmental decisions. These parameters are discussed in the remainder of this section. Specific routine procedures used to assess the quantitative parameters (precision, accuracy, and completeness) are provided in Section 12.0.

3.1 PRECISION

3.1.1 Definition

Precision is a measure of the amount of variability and bias inherent in a data set. Precision describes the reproducibility of measurements of the same parameter for samples under similar conditions. The equation for determining precision for this project is described in detail in Section 12.2.

3.1.2 Field Precision Objectives

Field duplicate precision monitors the consistency with which environmental samples were obtained and analyzed. Field duplicate results for solid matrix samples are considered to be precise if the relative percent difference (RPD) is less than or equal to 50 percent. Field duplicate results for aqueous matrix samples are considered to be precise if the RPD is less than or equal to 30 percent. Field precision is assessed through the collection and measurement of field duplicates at a rate of 1 duplicate per 10 analytical samples.

3.1.3 Field GC Precision Objectives

Precision for field GC analyses will be measured through the use of field duplicates and laboratory duplicates. Field duplicates, as specified in Section 3.1.2, will be collected at a rate of one duplicate per ten environmental samples. Laboratory duplicate analysis for field GC analyses will be performed by analyzing two aliquots of the same sample at a frequency of one duplicate per 20 environmental samples. Sampling personnel will identify samples to be used for laboratory duplicate analysis on the chain-of-custody report (COC) and will supply extra volume for such samples. If any of the three largest component peaks for the target compounds listed in Table 1-3 in the field or laboratory duplicate sample are above the PQL in both analyses but exhibit a Relative Percent Difference (RPD) exceeding 150%, or if any site-specific target compound is detected in one analysis at a level greater than 5-times the PQL but is not detected in the duplicate analysis, the Field Operations Leader (FOL) shall be informed and a third aliquot or a fresh sample obtained from the same location shall be analyzed. Further detail regarding laboratory and field duplicate analysis for the field GC is provided in Sections 5.9.5 and 5.9.6, respectively, in the field GC SOP (Appendix C).

3.1.4 Laboratory Precision Objectives

Laboratory precision Quality Control samples will be analyzed with a frequency of 5 percent (i.e., one quality control sample per 20 environmental samples) for organic analyses and a frequency of 10 percent (i.e., one quality control sample per 10 environmental samples) for inorganic analyses. Laboratory precision is measured via comparison of calculated Relative Percent Difference (RPD) values and Precision Control Limits specified in the analytical method or by the laboratory's QA/QC Program.

Five distinct types of analyses will be completed for environmental samples collected during the OU3 RI at the NIROP Fridley, as follows (Laucks Testing Laboratories, Inc., SOPs are provided in Appendix A):

- Target Compound List (TCL) organic analyses via OLM03.1 and SOP LTL-8260A. As discussed in Section 1.4.2.2, analysis for volatiles in aqueous samples only will be performed via SOP LTL-8260A with a 25 mL sample volume. The remaining TCL organic analyses will be performed via OLM03.1. Analysis for PCBs will be modified to focus on PCB-only analyses as described in the Addendum to Laucks SOP LTL-8082 (also provided in Appendix A).
- Target Analyte List (TAL) inorganic/cyanide analysis via ILM04.0.

- Total Organic Carbon (TOC), hexavalent chromium, pH, ORP, sulfide, and ferrous iron analyses of soil via SOPs LTL-7014, LTL-9113, LTL-9128, LTL-9301, and LTL-7601.
- Characteristic analyses to evaluate natural attenuation of chlorinated solvents including sulfate, nitrate, nitrite, dissolved chloride, dissolved bromide, dissolved phosphate, and dissolved methane via SOPs LTL-9110 and AM18.
- General water quality analyses including total suspended solids, hardness (as CaCO_3), and alkalinity (as CaCO_3) via SOPs LTL-9202, LTL-9009, and LTL-9005.

Precision for TCL organic analysis will be measured via the RPDs for matrix spike/matrix spike duplicate samples. Precision for TAL inorganic analysis will be measured via RPDs for laboratory duplicates. Precision for dissolved methane will be measured via the RPD for field duplicates. Precision for the remaining parameters will be measured via the RPD results for laboratory duplicate samples. Tables 3-1 through 3-3 present RPD Precision Control Limits.

3.2 ACCURACY

3.2.1 Definition

Accuracy is the degree of agreement between an observed value and an accepted reference value. The equation for determining accuracy for this project is described in detail in Section 12.1.

3.2.2 Field Accuracy Objectives

Accuracy in the field is assessed through the use of rinsate and trip blanks and is ensured through the adherence to all sample handling, preservation and holding times. Accuracy and precision requirements for field measurements (e.g., pH) are ensured through calibration as discussed in Section 9.1 of the Field Sampling Plan.

3.2.3 Field GC Accuracy Objectives

Accuracy for field GC analyses will be measured through the use of matrix spikes, QC check standards, and blanks. Matrix spike analyses will be performed at a frequency of 5% (one matrix spike per twenty

TABLE 3-1
PRECISION CONTROL LIMITS (RPDS)⁽¹⁾
MATRIX SPIKE/MATRIX SPIKE DUPLICATE SAMPLES
ORGANIC ANALYSIS VIA OLM03.1^(2,3)
NIROP FRIDLEY, MINNESOTA

Chemical	Aqueous Samples	Solid Samples
VOLATILE ORGANICS		
1,1-Dichloroethene	20	22
Trichloroethene	20	24
Benzene	20	21
Toluene	20	21
Chlorobenzene	20	21
SEMIVOLATILE ORGANICS		
Phenol	42	35
2-Chlorophenol	40	50
1,4-Dichlorobenzene	28	27
N-Nitroso-di-n-propylamine	38	38
1,2,4-Trichlorobenzene	28	23
4-Chloro-3-methylphenol	42	33
Acenaphthene	31	19
4-Nitrophenol	50	50
2,4-Dinitrotoluene	38	47
Pentachlorophenol	50	47
Pyrene	31	36
PCBs		
Aroclor 1016	35	50
Aroclor 1260	35	50

- 1 RPD - Relative Percent Difference as described in Section 12.0.
- 2 U.S. EPA (U.S. Environmental Protection Agency) CLP, 1994. Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration, OLM03.1.
- 3 As noted previously, volatile analysis for aqueous samples will be performed using SOP LTL-8260 (Appendix A).

TABLE 3-2
PRECISION CONTROL LIMITS (RPDS)(1)
LABORATORY DUPLICATE SAMPLES
INORGANIC ANALYSIS VIA ILM04.0(2)
NIROP FRIDLEY, MINNESOTA

Chemical	Aqueous Samples	Solid Samples
INORGANICS		
Aluminum	20	35
Antimony	20	35
Arsenic	20	35
Barium	20	35
Beryllium	20	35
Cadmium	20	35
Calcium	20	35
Chromium	20	35
Cobalt	20	35
Copper	20	35
Iron	20	35
Lead	20	35
Magnesium	20	35
Manganese	20	35
Mercury	20	35
Nickel	20	35
Potassium	20	35
Selenium	20	35
Silver	20	35
Sodium	20	35
Thallium	20	35
Vanadium	20	35
Zinc	20	35
Cyanide	20	35

- 1 RPD - Relative Percent Difference as described in Section 12.0.
- 2 U.S. EPA (U.S. Environmental Protection Agency) CLP, 1995. Statement of Work for Inorganics Analysis, Multi-Media, Multi-Concentration, ILM04.0.

TABLE 3-3

**PRECISION CONTROL LIMITS (RPDS)⁽¹⁾
 BIOLOGICAL/ENGINEERING/MISCELLANEOUS PARAMETERS
 LABORATORY DUPLICATE SAMPLES
 NIROP FRIDLEY, MINNESOTA**

Parameter	Aqueous Samples
Total Suspended Solids	20
Alkalinity(as CaCO ₃)	10
Hardness (as CaCO ₃)	15
Sulfate	10
Nitrate	10
Nitrite	30
Dissolved Chloride	11
Dissolved Bromide	30 ⁽³⁾
Dissolved Phosphate	30 ⁽³⁾
Dissolved Methane	NA ⁽²⁾
	Solid Samples
Total Organic Carbon	33
Hexavalent Chromium	20 ⁽⁴⁾
pH	±0.5 pH units
Ferrous Iron	qualitative confirmation
Sulfide	qualitative confirmation
Oxidation-Reduction Potential	20 ⁽³⁾

- 1 RPD - Relative Percent Difference as described in Section 12.0.
- 2 Not Applicable.
- 3 Default limits; insufficient data points available to generate statistical laboratory control limits.
- 4 Default limits specified by SW-846 Method 3060A.

environmental samples). Sampling personnel will identify samples to be used for matrix spike analysis on the COC and will supply extra volume for such samples. Matrix spike samples will be spiked with each of the target compounds shown in Table 1-3. Accuracy control limits of 50 to 150 percent will be used to assess matrix spike recovery for target compounds. Further information regarding matrix spikes for field GC analysis is provided in Section 5.9.4 of the field GC SOP (Appendix C).

A QC check standard solution containing all target compounds listed in Table 1-3 will be analyzed with each initial calibration. Accuracy control limits for QC check standard Percent Recoveries (%Rs) will be 50 to 150 percent. Analysis of the QC check standard solution is further discussed in Section 5.9.1 of field GC SOP (Appendix C).

Equipment rinsate blanks (one per ten environmental samples, with a minimum of one per day), trip blanks (one per cooler), and method or laboratory reagent blanks (after each initial and continuing calibration) will also be analyzed to assess accuracy. These types of blanks are described in more detail in Section 3.6 of this QAPP. Further detail regarding control limits and corrective actions for these blanks for PGC analysis is provided Sections 5.9.2 and 5.9.3 of the field GC SOP (Appendix C).

Retention time monitoring and control, as fully described in Section 5.9.7 of the field GC SOP (Appendix C), will also be performed to monitor the accuracy of qualitative analyte identification.

3.2.4 Laboratory Accuracy Objectives

Accuracy in the laboratory is measured through the comparison of a spiked sample result against a known or calculated value expressed as a percent recovery (%R). Percent recoveries are derived from the analysis of known amounts of compounds spiked into deionized water (i.e., laboratory control sample analysis), or into actual samples (i.e., surrogate or matrix spike analysis). Laboratory control sample analysis measures the accuracy of laboratory operations. Surrogate and matrix spike analyses measure the accuracy of laboratory operations as affected by matrix. Laboratory control sample analyses are performed with a frequency of one per twenty associated samples of like matrix. Matrix spike analyses will be performed with a frequency of one per twenty associated samples of like matrix for organic analyses and with a frequency of one per ten associated samples of like matrix for inorganic analyses. Surrogate spike analysis is performed for all organic chromatographic analyses. Laboratory accuracy is assessed via comparison of calculated percent recovery (%R) values with Accuracy Control Limits specified in the analytical method or by the laboratory's QA/QC Program.

Five distinct types of analyses will be completed for environmental samples collected during the OU3 RI at the NIROP Fridley, as follows (Laucks Testing Laboratories, Inc., SOPs are provided in Appendix A):

- Target Compound List (TCL) organic analyses via OLM03.1 and SOP LTL-8260A. As discussed in Section 1.4.2.2, analysis for volatiles in aqueous samples only will be performed via SOP LTL-8260A with a 25 mL sample volume. The remaining TCL organic analyses will be performed via OLM03.1. Analysis for PCBs will be modified to focus on PCB-only analyses as described in the Addendum to Laucks SOP LTL-8082 (also provided in Appendix A).
- Target Analyte List (TAL) inorganic/cyanide analysis via ILM04.0.
- Total Organic Carbon (TOC), hexavalent chromium, pH, ORP, sulfide, and ferrous iron analyses of soil via SOPs LTL-7014, LTL-9113, LTL-9128, LTL-9301, and LTL-7601.
- Characteristic analyses to evaluate natural attenuation of chlorinated solvents including sulfate, nitrate, nitrite, dissolved chloride, dissolved bromide, dissolved phosphate, and dissolved methane via SOPs LTL-9110 and AM18.
- General water quality analyses including total suspended solids, hardness (as CaCO_3), and alkalinity (as CaCO_3) via SOPs LTL-9202, LTL-9009, and LTL-9005.

Accuracy for Target Compound List organic analysis will be measured via the percent recoveries for surrogate spikes and matrix spike/matrix spike duplicates. Accuracy for Target Analyte List Inorganic analysis will be measured via percent recoveries for matrix spikes and laboratory control samples. Accuracy the remaining analytes will be measured via percent recoveries for matrix spikes and laboratory control samples, as applicable. Tables 3-4 and 3-5 present control limits for matrix and surrogate spike recoveries, respectively, for TCL organics. Tables 3-6 and 3-7 present control limits for matrix spike and laboratory control samples, respectively, for TAL inorganics. Tables 3-8 and 3-9 present control limits for matrix spikes and laboratory control samples, respectively, for the remaining, non-CLP parameters.

TABLE 3-4
ACCURACY CONTROL LIMITS (%R)⁽¹⁾
MATRIX SPIKE/MATRIX SPIKE DUPLICATE SAMPLES
ORGANIC ANALYSIS VIA OLM03.1^(2,3)
NIROP FRIDLEY, MINNESOTA

Chemical	Aqueous Samples	Solid Samples
VOLATILE ORGANICS		
1,1-Dichloroethene	60-140	59-172
Trichloroethene	60-140	62-137
Benzene	60-140	66-142
Toluene	60-140	59-139
Chlorobenzene	60-140	60-133
SEMIVOLATILE ORGANICS		
Phenol	12-110	26-90
2-Chlorophenol	27-123	25-102
1,4-Dichlorobenzene	36-97	28-104
N-Nitroso-di-n-propylamine	41-116	41-126
1,2,4-Trichlorobenzene	39-98	38-107
4-Chloro-3-methylphenol	23-97	26-103
Acenaphthene	46-118	31-137
4-Nitrophenol	10-80	11-114
2,4-Dinitrotoluene	24-96	28-89
Pentachlorophenol	9-103	17-109
Pyrene	26-127	35-142
PCBs		
Aroclor 1016	40-160	40-160
Aroclor 1260	39-149	40-160

- 1 %R - Percent Recovery as described in Section 12.0.
- 2 U.S. EPA (U.S. Environmental Protection Agency) CLP, 1994. Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration, OLM03.1.
- 3 As noted previously, volatile analysis for aqueous samples will be performed using SOP LTL-8260 (Appendix A).

TABLE 3-5
ACCURACY CONTROL LIMITS (%R)⁽¹⁾
SURROGATE SPIKES
ORGANIC ANALYSIS VIA OLM03.1^(2,3)
NIROP FRIDLEY, MINNESOTA

Chemical	Aqueous Samples	Solid Samples
VOLATILE ORGANICS		
Toluene-d8	60-140	84-138
Bromoflourobenezene	60-140	59-113
1,2-Dichloroethane-d4	60-140	70-121
SEMIVOLATILE ORGANICS		
Nitrobenzene-d5	35-114	23-120
2-Fluorobiphenyl	43-116	30-115
Terphenyl-d14	33-141	18-137
Phenol-d5	10-110	24-113
2-Fluorophenol	21-110	25-121
2,4,6-Tribromophenol	10-123	19-122
2-Chlorophenol-d4	33-110 ⁽⁴⁾	20-130 ⁽⁴⁾
1,2-Dichlorobenzene-d4	16-110 ⁽⁴⁾	20-130 ⁽⁴⁾
PCBs		
Tetrachloro-m-xylene	30-150	30-150
Decachlorobiphenyl	30-150	30-150

- 1 %R - Percent Recovery as described in Section 12.0.
- 2 U.S. EPA (U.S. Environmental Protection Agency) CLP, 1994. Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration, OLM03.1.
- 3 As noted previously, volatile analysis for aqueous samples will be performed using SOP LTL-8260 (Appendix A).
- 4 Advisory limits only.

TABLE 3-6
ACCURACY CONTROL LIMITS (%R)⁽¹⁾
MATRIX SPIKE SAMPLES
INORGANIC ANALYSIS VIA ILM04.0⁽²⁾
NIROP FRIDLEY, MINNESOTA

Chemical	Aqueous Samples	Solid Samples
INORGANICS		
Aluminum	75-125	NS ⁽³⁾
Antimony	75-125	75-125
Arsenic	75-125	75-125
Barium	75-125	75-125
Beryllium	75-125	75-125
Cadmium	75-125	75-125
Calcium	NS ⁽³⁾	NS ⁽³⁾
Chromium	75-125	75-125
Cobalt	75-125	75-125
Copper	75-125	75-125
Iron	75-125	75-125
Lead	75-125	75-125
Magnesium	NS ⁽³⁾	NS ⁽³⁾
Manganese	75-125	75-125
Mercury	75-125	75-125
Nickel	75-125	75-125
Potassium	NS ⁽³⁾	NS ⁽³⁾
Selenium	75-125	75-125
Silver	75-125	75-125
Sodium	NS ⁽³⁾	NS ⁽³⁾
Thallium	75-125	75-125
Vanadium	75-125	75-125
Zinc	75-125	75-125
Cyanide	75-125	75-125

- 1 %R - Percent Recovery as described in Section 12.0.
- 2 U.S. EPA (U.S. Environmental Protection Agency) CLP, 1995. Statement of work for Inorganics Analysis, Multi-Media, Multi-Concentration, ILM04.0.
- 3 No spike required.

TABLE 3-7
ACCURACY CONTROL LIMITS (%R)⁽¹⁾
LABORATORY CONTROL SAMPLES
INORGANIC ANALYSIS VIA ILM04.0⁽²⁾
NIROP FRIDLEY, MINNESOTA

Chemical	Aqueous Samples	Solid Samples
INORGANICS		
Aluminum	80-120	TBD ⁽³⁾
Antimony	80-120 ⁽⁴⁾	TBD
Arsenic	80-120	TBD
Barium	80-120	TBD
Beryllium	80-120	TBD
Cadmium	80-120	TBD
Calcium	80-120	TBD
Chromium	80-120	TBD
Cobalt	80-120	TBD
Copper	80-120	TBD
Iron	80-120	TBD
Lead	80-120	TBD
Magnesium	80-120	TBD
Manganese	80-120	TBD
Mercury	80-120 ⁽⁵⁾	TBD
Nickel	80-120	TBD
Potassium	80-120	TBD
Selenium	80-120	TBD
Silver	80-120 ⁽⁴⁾	TBD
Sodium	80-120	TBD
Thallium	80-120	TBD
Vanadium	80-120	TBD
Zinc	80-120	TBD
Cyanide	NA ⁽⁶⁾	TBD

- 1 %R - Percent Recovery as described in Section 12.0.
- 2 U.S. EPA (U.S. Environmental Protection Agency) CLP, 1995. Statement of Work for Inorganic Analysis, Multi-Media, Multi-Concentration, ILM04.0.
- 3 TBD - To Be Determined at time of analysis based on EPA LCS lot number.
- 4 Advisory limits only.
- 5 LCS analysis for mercury is not required by CLP protocol, but will be performed for this project.
- 6 NA - Not Applicable.

TABLE 3-8
ACCURACY CONTROL LIMITS (%R)⁽¹⁾
BIOLOGICAL/ENGINEERING/MISCELLANEOUS PARAMETERS
MATRIX SPIKE SAMPLES
NIROP FRIDLEY, MINNESOTA

Analytical Method	Aqueous Samples
Total Suspended Solids	NA ⁽²⁾
Alkalinity(as CaCO ₃)	NA
Hardness (as CaCO ₃)	NA
Sulfate	81-115
Nitrate	79-117
Nitrite	50-150
Dissolved Chloride	73-121
Dissolved Bromide	50-150 ⁽³⁾
Dissolved Phosphate	50-150 ⁽³⁾
Dissolved Methane	NA
Solid Samples	
Total Organic Carbon	63-119
Hexavalent Chromium	75-125 ⁽⁴⁾
pH	NA
Ferrous Iron	NA
Sulfide	NA
Oxidation-Reduction Potential	NA

- 1 %R - Percent Recovery as described in Section 12.0.
- 2 NA - Not Applicable.
- 3 Default limits; insufficient data points available to generate statistical laboratory control limits.
- 4 Default limits specified by SW-846 Method 3060A.

TABLE 3-9
ACCURACY CONTROL LIMITS (%R)⁽¹⁾
BIOLOGICAL/ENGINEERING/MISCELLANEOUS PARAMETERS
LABORATORY CONTROL SAMPLES
NIROP FRIDLEY, MINNESOTA

Analytical Method	Aqueous Samples
Total Suspended Solids	NA ⁽²⁾
Alkalinity(as CaCO ₃)	88-112
Hardness (as CaCO ₃)	87-115
Sulfate	90-110
Nitrate	90-110
Nitrite	90-110
Dissolved Chloride	90-110
Dissolved Bromide	90-110
Dissolved Phosphate	90-110
Dissolved Methane	NA
Solid Samples	
Total Organic Carbon	80-120
Hexavalent Chromium	NA
pH	NA
Ferrous Iron	NA
Sulfide	NA
Oxidation-Reduction Potential	NA

- 1 %R - Percent Recovery as described in Section 12.0.
- 2 NA - Not Applicable.

3.3 COMPLETENESS

3.3.1 Definition

Completeness is a measure of the amount of usable, valid, analytical data obtained, compared to the amount expected to be obtained. Completeness is typically expressed as a percentage. The equation for completeness is presented in Section 12.3.

The ideal objective for completeness is 100 percent (i.e., every sample planned to be collected is collected; every sample submitted for analysis yields valid data). However, samples can be rendered unusable during shipping or preparation (e.g., bottles broken or extracts accidentally destroyed); errors can be introduced during analysis (e.g., loss of instrument sensitivity, introduction of ambient laboratory contamination), or strong matrix effects can become apparent (e.g., extremely low matrix spike recovery). These instances result in data that do not meet QC criteria. Based on these considerations, 95 percent is considered an acceptable target for the data completeness objective. Completeness will be calculated for the OU3 RI as a whole since it is anticipated that all samples will be collected within a four-month period. If critical data points are lost, resampling and/or reanalysis may be required.

One hundred percent of the fixed-base laboratory data for the OU3 RI will be validated in accordance with the Region 5 Standard Operating Procedures for Validation of CLP Organic and Inorganic Data and the U.S. EPA Contract Laboratory Program National Functional Guidelines for Organic and Inorganic Data Review. Data rejected as a result of the validation process will be treated as incomplete data.

3.3.2 Field Completeness Objectives

Field completeness is a measure of the amount of valid field measurements obtained from all the field measurements taken in the project. Field completeness for this project is expected to be greater than 90 percent.

3.3.3 Laboratory Completeness Objectives

Laboratory completeness is a measure of the amount of valid laboratory measurements obtained from all the laboratory measurements taken in the project. Laboratory completeness for this project is expected to be greater than 95 percent.

3.4 REPRESENTATIVENESS

3.4.1 Definition

Representativeness is an expression of the degree to which the data accurately and precisely depict the actual characteristics of a population or environmental condition existing at an individual sampling point. Use of standardized sampling, handling, analytical, and reporting procedures ensures that the final data accurately represent actual site conditions.

3.4.2 Measures to Ensure Representativeness of Field Data

Representativeness is dependent upon the proper design of the sampling program and will be satisfied by ensuring that the Field Sampling Plan (FSP) is followed and that proper sampling techniques are used.

3.4.3 Measures to Ensure Representativeness of Lab Data

Representativeness in the laboratory is ensured by using the proper analytical procedures, meeting sample holding times, and analyzing and assessing field duplicate samples. The sampling network for the OU3 RI was designed to provide data representative of facility conditions. During development of this network, consideration was given to past waste disposal practices, existing analytical data, physical setting and processes, and constraints inherent to the CERCLA program. The rationale of the sampling network is discussed in detail in the Field Sampling Plan (FSP).

3.5 COMPARABILITY

3.5.1 Definition

Comparability is defined as the confidence with which one data set can be compared to another (e.g., between sampling points; between sampling events). Comparability is achieved by using standardized sampling and analysis methods, and data reporting formats (including use of consistent units of measure and reporting of solid matrix sample results on a dry-weight basis). Additionally, consideration is given to seasonal conditions and other environmental variations that could exist to influence data results.

3.5.2 Measures to Ensure Comparability of Field Data

Comparability is dependent upon the proper design of the sampling program and will be satisfied by ensuring that the FSP is followed and that proper sampling techniques are used. It is also dependent on recording field measurements using the correct units. Field measurements for this project include pH, specific conductance, temperature, turbidity, dissolved oxygen, dissolved ferrous iron, dissolved reduced manganese, hydrogen sulfide, oxidation-reduction potential, and volatile organic compounds by field GC analysis. The units used for the field measurements for this project are as follows:

- pH is measured to the nearest 0.1 standard pH unit.
- Specific conductance is measured in millimhos (the inverse of the ohm).
- Temperature is measured in degrees Celsius.
- Turbidity is measured in nephelometric turbidity units (NTU).
- Dissolved oxygen is measured in mg/L.
- Dissolved ferrous iron is measured in mg/L.
- Dissolved reduced manganese is measured in mg/L.
- Hydrogen sulfide is measured in mg/L.
- Oxidation Reduction Potential is measured in mV.
- Volatile organics by field GC are measured in $\mu\text{g}/\text{kg}$.

3.5.3 Measures to Ensure Comparability of Lab Data

Planned analytical data will be comparable when similar sampling and analytical methods are used and documented. Results will be reported in units that ensure comparability with previous data and with current state and Federal standards and guidelines. Organic chemicals will be reported in $\mu\text{g}/\text{L}$ for aqueous samples and $\mu\text{g}/\text{kg}$ for solid samples. Metals and cyanide will be reported as $\mu\text{g}/\text{L}$ for aqueous samples and mg/kg for solid samples. Total organic carbon and hexavalent chromium will be reported in mg/kg (solid samples). Oxidation-reduction potential and pH in soils will be reported in standard pH units and mV, respectively. Ferrous iron and sulfide will be reported as qualitatively present or absent in soils. The remaining biological/engineering parameters will be reported in mg/L (aqueous samples). Detection/reporting limits are further discussed in Sections 7.2.1 and 1.4.2.2

3.6 LEVEL OF QUALITY CONTROL EFFORT

Trip blank, rinsate blank, ambient condition blank, source water blank, method blank, duplicate, standard reference materials (SRM) and matrix spike samples will be analyzed to assess the quality of the data resulting from the field sampling and analytical programs. In addition, duplicate measurements will be completed for field parameters.

External QC measures (i.e., field quality control samples) consist of field duplicates, ambient condition blanks, trip blanks, source water blanks, and equipment rinsate blanks. Information gained from these analyses further characterizes the level of data quality obtained to support project goals. Each of these types of field quality control samples undergo the same preservation, analysis, and reporting procedures as the related environmental samples. Each type of field quality control sample is discussed below.

Field duplicates are either two samples collected independently at a sampling location (e.g., surface water), or a single sample homogenized and split into two portions (where volatile organic compounds (VOCs) are to be analyzed, the VOC sample aliquots are containerized first to avoid loss of constituents, then the remaining sample matrix is homogenized.) Field duplicates are collected and analyzed for chemical constituents to measure the precision of the sampling and analysis methods employed. The general level of the QC effort will be one field duplicate for every 10 or fewer investigative samples.

Trip blanks and ambient condition blanks, consisting of distilled water, will be submitted to the Laucks Testing Laboratories, Inc., to provide the means to assess the quality of the data resulting from the field sampling program. Ambient blank samples are analyzed to check for interfering contaminants that could potentially be present in ambient air at the sampling site (e.g., volatile compounds or particulates). Ambient blanks will be collected based on conditions at the time of sampling at the discretion of the Field Operations Leader (FOL), with a minimum of one ambient blank being collected during the RI. Trip blanks pertain to volatile organic compounds (VOCs) only. Trip blanks are used to assess the potential for contamination of VOCs resulting from contaminant migration into sample bottles/jars during sample shipment and storage. Trip blanks are prepared by the laboratory prior to the sampling event, shipped to the site with the sample containers, and kept with the investigative samples throughout the sampling event. They are then packaged for shipment with other VOC samples and sent for analysis. There should be one trip blank included in each sample shipping container that contains VOCs. At no time after trip blank preparation are their sample containers opened before they reach the laboratory.

Equipment rinsate blanks are obtained under representative field conditions by collecting the rinse water generated by running analyte-free water through sample collection equipment after decontamination and prior to use. One rinsate blank will be collected per each type of sampling equipment used (i.e., bailer, split-spoon sampler, hand tools, etc.) per day that sampling is conducted. A sampling event is matrix specific, therefore an equipment blank must be collected for each matrix sampled. If pre-cleaned, dedicated, or disposable sampling equipment is used, one rinsate blank must be collected as a "batch blank." Rinsate blanks are analyzed for the same chemical constituents as the associated environmental samples.

Source water blanks consist of potable waters used in decontamination and steam cleaning activities. Source water blanks are analyzed for all organic and inorganic constituents under investigation as a means of determining whether the source waters used in decontamination activities have introduced contaminants to the environmental samples. Source water blanks will be collected at a rate of one per each potable water source.

Method blank samples are generated within the laboratory and used to assess contamination resulting from laboratory procedures. Laboratory duplicate samples are analyzed for inorganic parameters to check for sampling and analytical reproducibility. Matrix spikes provide information about the effect of the sample matrix on the digestion and measurement methodology. Laboratory duplicates and matrix spikes for inorganic analyses will be analyzed with a frequency of ten percent (one per every ten or fewer investigative samples per matrix (i.e., groundwater, soil)). All matrix spikes for organic analyses are performed in duplicate and are hereinafter referred to as MS/MSD samples.

MS/MSD samples are investigative samples. Soil MS/MSD samples require no extra volume for VOCs or extractable organics. However, extra sample volume must be collected for aqueous MS/MSD samples for VOCs and extractable organics. Specifically, 4 extra 40 mL bottles for VOCs, 2 extra 1000 mL bottles for semivolatiles, and 2 extra 1000 mL bottles for PCBs are required. One MS/MSD sample will be collected/designated for every 20 or fewer investigative samples per sample matrix (i.e. groundwater, soil) for organic analyses.

The level of QC effort for testing of Target Compound List (TCL) organics (volatiles in soil samples and semivolatiles) will conform to the Statement of Work (SOW/OLM03.1). Modifications for PCB-only analysis are provided in the Addendum to Laucks SOP LTL-8082 (Appendix A). The level of QC effort for TCL volatiles in aqueous samples will conform to SOP LTL-8260 (Appendix A). The level of QC effort for

all inorganic parameters will exceed method requirements in that matrix spike and laboratory duplicate analyses will be performed after every 10 investigative samples instead of after every 20 investigative samples. . With this exception, the level of QC effort for testing of inorganics (metals and cyanide) will conform to the Statement of Work (SOW/ILM04.0) and the level of QC effort for testing of all non-CLP analytes will conform to the SOPs provided in Appendix A.

4.0 SAMPLING PROCEDURES

Field sampling procedures for the Operable Unit 3 Remedial Investigation are discussed in detail in the attendant Field Sampling Plan (Volume II). The specific sampling information components required by U.S. EPA Region V as outlined in the CERCLA model Quality Assurance Project Plan and their location in the Field Sampling Plan (FSP) are as follows:

- Field sampling by matrix - Section 2.0 of the FSP
- Field quality control sample collection/preparation procedures - Section 8.0 of the FSP
- Sample containers, preservatives, and volume requirements - Section 4.0 of the FSP
- Decontamination procedures - Section 6.0 of the FSP
- Sample packaging and shipping procedures - Section 5.0 of the FSP

In addition, Sections 7 through 11 of the Field Sampling Plan address the following sampling procedures and field investigation tasks:

- Mobilization/demobilization - Section 7.1
- Monitoring well installation - Section 7.4
- Monitoring well development - Section 7.4.1
- Groundwater sampling - Section 7.5
- Water level measurements - Section 7.4.2
- Soil sampling procedures - Section 7.3
- Surveying - Section 7.6
- Aquifer testing - Section 7.7
- Waste handling - Section 7.8
- Quality control sample procedures - Section 8.0
- Field measurements/screening - Section 9.0
- Preventive maintenance procedures/schedule - Section 10.0
- Sample disposal - Section 11.0

Standard Operating Procedures regarding sampling and record keeping are included as Appendices to the Field Sampling Plan.

5.0 CUSTODY PROCEDURES

Custody is one of several factors which is necessary for the admissibility of environmental data as evidence in a court of law. Custody procedures help to satisfy the two major requirements for admissibility: relevance and authenticity. Sample custody is addressed in three parts: field sample collection, laboratory analysis, and final evidence files. Final evidence files, including all originals of laboratory reports and purge files, are maintained under document control in a secure area. A sample or evidence file is under custody if:

- the item is in the actual physical possession of an authorized person, or;
- the item is in view of the person after being in his or her possession, or;
- the item was placed in a secure area to prevent tampering; or
- the item is in a designated and identified secure area with access restricted to authorized personnel only.

The chain-of-custody (COC) report is a multi-part, standardized form used to summarize and document pertinent sample information, such as sample identification and type, matrix, date and time of collection, preservation, and requested analyses. Furthermore, through the sequential signatures of various sample custodians (e.g., sampler, airbill number, laboratory sample custodian), the COC report documents sample custody and tracking. Custody procedures apply to all environmental and associated field quality control samples obtained as part of the data collection system.

5.1 FIELD CUSTODY PROCEDURES

The FOL (or designee) is responsible for the care and custody of the samples collected until they are relinquished to the analyzing laboratory or entrusted to a commercial overnight courier. COC reports are completed for each sample shipment. The reports are filled out in a legible manner, using waterproof ink, and are signed (and dated) by the sampler. Pertinent notes, such as whether the sample was field filtered, or whether the sample is suspected to be high in contaminant concentration, are also indicated on the COC report. Information similar to that contained in the COC report is also provided on the sample label, which is securely attached to the sample bottle. In addition, sample tags will be affixed to the sample bottles and will be returned by the analytical laboratory for inclusion in the final evidence file. COC report forms and sample labels are generally supplied by the laboratory subcontractor. In accordance with

NFESC guidelines, samples for chemical constituents analysis must be sent (for next-day receipt) to the laboratory within 24-hours of collection.

The field GC will be located in a building at the NIROP Fridley, typically within five minutes driving time from all sample collection locations. Samples, along with completed COC reports, will be hand-delivered by field personnel to the GC analyst. At times, the analyst may also pick up samples from the collection sites. The Field Operations Leader is responsible for maintaining COC procedures until the time of sample delivery or pickup. After that time, the analyst is responsible for maintaining COC procedures and for refrigeration of all samples until all analyses have been successfully completed.

Full details regarding sample chain-of-custody (including use of custody seals and sample shipment protocols) are contained in B&R Environmental SOP SA-6.1, which is provided in as an appendix to the attendant Field Sampling Plan (Volume II). B&R Environmental SOP SA-6.2, also provided in the FSP, discusses maintenance of site logbooks, site notebooks, and other field records. Additionally, each of the various sampling SOPs incorporated into the FSP contains a section that addresses relevant sample documentation (i.e., completion of sample logsheets, etc.). All sample records are eventually docketed into the B&R Environmental project central file.

5.2 LABORATORY CUSTODY PROCEDURES

When samples are received by the laboratory subcontractor, the laboratory's sample custodian will examine each cooler's custody seals to verify that they are intact and that the integrity of the environmental samples has been maintained. The custodian will then open the cooler and measure its internal temperature. The temperature reading will be noted on the Supplemental Sample Receipt Log, as further discussed below. The sample custodian will then sign the COC report and examine the contents of the cooler. Sample container breakages or discrepancies between the COC report and sample label documentation will be recorded. With the exception of samples for volatiles analysis, the pH of chemically preserved samples will be checked using Hydrion paper and recorded. (The pH of volatile samples will be checked and recorded after analysis to prevent loss of volatile compounds.) A Laucks Testing Laboratories, Inc., CLP Sample Receipt Log and Supplemental Sample Receipt Log, as shown in Appendix 3 of LTL 4002 (Appendix A), are also completed. All problems or discrepancies noted during this process are to be promptly reported to the B&R Environmental Project Manager. Samples are then logged into the laboratory's laboratory information management system (LIMS). Other pertinent issues relating to sample custody, such as interlaboratory chain-of-custody procedures, and specific procedures

for sample handling, storage, dispersment for analysis, and remnant disposal, are discussed in the laboratory SOPs included in Appendix A.

5.3 FINAL EVIDENCE FILES

The B&R Environmental central file will be the repository for all documents which constitute evidence relevant to sampling and analysis activities as described in this QAPP. B&R Environmental is the custodian of the evidence file and maintains the contents of these files for the RI, including all relevant records, reports, logs, field notebooks, pictures, subcontractor reports and data reviews in a secure, limited access location and under custody of the B&R Environmental facility manager. The control file will include at a minimum:

- field logbooks
- field data and data deliverables
- photographs
- drawings
- soil boring logs
- laboratory data deliverables
- data validation reports
- data assessment reports
- progress reports, QA reports, interim project reports, etc.
- all custody documentation (tags, forms, airbills, etc.)

Upon completion of the contract, all pertinent files will be relinquished to the custody of the United States Navy.

6.0 CALIBRATION PROCEDURES AND FREQUENCY

All instrumentation used to perform chemical measurements must be properly calibrated prior to use in order to obtain valid and usable results. The requirement to properly calibrate instruments prior to use applies equally to field instruments as it does to fixed laboratory instruments. Field instrument calibration is discussed in Section 6.1. Laboratory instrument calibration is discussed in Section 6.2.

6.1 FIELD INSTRUMENT CALIBRATION

With the exception of the field GC, field instrument calibration is discussed in Section 9.1 of the attendant Field Sampling Plan. A summary of the requirements specific to calibration of the field GC for on-site analysis of volatile organic compounds is provided in the following paragraphs.

All compounds listed in Table 1-3 will be included in the calibration standards for field GC analysis. Standard solutions for field GC analysis will be purchased as manufacturer-certified solutions, if available. Otherwise, stock solutions will be prepared from pure standard materials. Standards for field GC analysis are further discussed in Section 5.5 of the field GC SOP (Appendix C).

A five-point initial calibration is required before any samples are analyzed. The Percent Relative Standard Deviation (%RSD) for all target compounds shown in Table 1-3 must be less than or equal to 30 percent. A mid-point continuing calibration is required at the beginning and end of every 12-hour period of sample analysis or after every 20 analytical runs, whichever is more frequent. Continuing Calibration Percent Differences (%Ds) for site-specific target compounds must not exceed 25 percent. Initial and continuing calibration procedures, acceptance criteria, and corrective action are further described in Section 5.8 of the field GC SOP included in Appendix C.

6.2 LABORATORY INSTRUMENT CALIBRATION

Calibration procedures for laboratory balances and thermometers are described in SOP LTL-1005 and SOP LTL-1006, respectively, included in Appendix A. Method- and instrument-specific calibration and tuning criteria for particular analyses are described briefly below. The frequency of calibration will be performed according to the requirements of the specific methods.

6.2.1 Volatile Organic Compound Analyses

For the analysis of volatile organic compounds in aqueous samples, the GC/MS system will be tuned and calibrated in accordance with the requirements associated with a 25 mL sample volume as specified in SOP LTL-8260 (Appendix A). For the analysis of volatile organic compounds in soil samples, the GC/MS system will be tuned and calibrated in accordance with the Contract Laboratory Program Statement of Work (OLM03.1). For either matrix, a bromofluorobenzene (BFB) instrument performance check (tuning check) must be run prior to the initial and each continuing calibration and must meet all method-specified criteria before analyses may continue. Initial calibration is required before any samples are analyzed and must include a blank and a minimum of five different concentrations as specified in the methods. A continuing calibration check, including the mid-range standard and a blank, must be performed at the beginning of each 12-hour shift during which analyses are performed.

6.2.2 Semivolatile Organic Compound Analyses

For semivolatile organic compounds, the GC/MS system will be calibrated in accordance with the CLP SOW (OLM03.1). A decafluorotriphenyl phosphine (DFTPP) instrument performance check (tuning check) must be run prior to the initial and each continuing calibration and must meet all method-specified criteria before analyses may continue. Initial calibration is required before any samples are analyzed and must include a blank plus five different concentrations as specified in the method. Standards for pyridine will be included in the initial and continuing calibrations at concentrations specified by the SOW for semivolatile compounds. A continuing calibration check, including the mid-range standard and a blank, must be performed at the beginning of each 12-hour shift during which analyses are performed.

6.2.3 PCB Analyses

For PCB analyses, the GC system will be calibrated in accordance with the CLP SOW (OLM03.1) with some modifications since only PCBs, and not pesticides, are being analyzed. Initial calibration is required before any samples are analyzed. The initial calibration and calibration verification procedures and frequencies will be performed as described in SOP LTL-8082 and the Addendum to SOP LTL-8082 (Appendix A).

6.2.4 Metals Analyses

6.2.4.1 Inductively Coupled Argon Plasma (ICP) Analyses

Inductively coupled plasma spectrometry (ICP) systems will be calibrated in accordance with the EPA CLP protocols outlined in ILM04.0. Initial calibration is required each day before any samples are analyzed and consists of a calibration blank and at least one standard. Following initial calibration, an initial calibration verification sample (obtained from a different source than the solutions used for calibration), an initial calibration blank, and interference check samples are analyzed. A continuing calibration verification sample and a continuing calibration blank are run every 2 hours or every 10 samples, whichever occurs first. Interference check samples must be analyzed a minimum of twice per 8-hour working shift. A continuing calibration verification sample, a continuing calibration blank, and interference check samples are also run after analysis of the last sample.

If any of the continuing calibration samples fail to yield a response within 10% of the true value, initial calibration will be repeated, and all field samples analyzed since the last in-control calibration standard will be reanalyzed.

6.2.4.2 Furnace Atomic Absorption Analyses

Furnace atomic absorption analyses will be calibrated in accordance with the EPA CLP protocols outlined in ILM04.0. Initial calibration is required each day before any samples are analyzed and consists of a calibration blank and at least three calibration standards covering the range of concentrations of interest. The correlation coefficient of the regression of concentration versus response should be 0.995 or greater. Immediately following initial calibration, an initial calibration verification sample (obtained from a different source than the solutions used for calibration) and an initial calibration blank are analyzed. A continuing calibration verification sample and a continuing calibration blank are run every two hours or every ten samples, whichever occurs first. A continuing calibration verification sample and a continuing calibration blank are also run after analyses of the last sample.

If any of the continuing calibration samples fail to yield a response within 10% of the true value, initial calibration will be repeated, and all field samples analyzed since the last in-control calibration standard will be reanalyzed.

6.2.5 Engineering/Biological/Miscellaneous Parameters

Calibration and standardization requirements for the remaining required parameters are described in the applicable SOPs included in Appendix A.

7.0 ANALYTICAL AND MEASUREMENT PROCEDURES

Geoprobe groundwater samples, monitoring well groundwater samples, soil samples, and field Quality Control samples (e.g., trip blanks, rinsate blanks, etc.) collected during the NIROP Fridley Operable Unit 3 (OU3) Remedial Investigation (RI), will be analyzed by Laucks Testing Laboratories, Inc., 940 South Harney Street, Seattle, Washington 98108; (206) 767-5060; FAX (206) 767-5063. The laboratory maintains Standard Operating Procedures (SOPs) for all required analyses. Analysis for dissolved methane will be performed by Microseeps, 220 William Pitt Way, Pittsburgh, PA 15238; (412) 826-5245; Fax (412) 826-3433.

The analytical methods to be used for analysis of the OU3 RI samples have been selected based on existing information regarding the NIROP plant building. During a previous investigation at the East Plating Shop, various metals, cyanide, volatile and semivolatile organics, PCBs, and petroleum hydrocarbons were detected in environmental matrices (soil and/or groundwater). Furthermore, based on the industrial nature of operations at the facility, it is possible that multiple types of chemicals could have been released via drywells, sumps, etc.

Although the presence of volatile organic constituents in the groundwater is a primary concern for the facility, information regarding the types of chemicals released is currently insufficient to develop a focused analytical program. Therefore, the suite of analyses for the OU3 RI is comprehensive and is inclusive of TCL volatiles, semivolatiles, and PCBs as well as TAL metals and cyanide. The only CLP analytical fraction not planned for analysis is the TCL pesticides fraction. Based on the nature of operations at the facility, there is no reason to believe that pesticides will be present in the soil or groundwater beneath the plant.

The NIROP OU3 RI is focused on source characterization. Based on existing analytical data for both the East Plating Shop and downgradient groundwater, it is anticipated that concentrations will be relatively high in source areas within the building. A low-level EPA method was chosen for the analysis of volatile organics in aqueous samples, since these compounds are of primary concern at the site. Standard CLP and EPA methods were chosen for the remaining parameters. With the exceptions noted in Section 7.2.1, the Contract Required Quantitation and Detection Limits (CRQLs and CRDLs) will be adequate for these parameters for the purposes of source characterization. Field measurements and analytical procedures are discussed in more detail in the remainder of this section.

7.1 FIELD MEASUREMENT PROCEDURES

Field measurements to be completed during the OU3 field investigation will include those completed in support of health and safety considerations, well development and purging, general chemical and physical characterization of groundwater, selection of soil samples for laboratory analysis, and evaluation of the natural attenuation of chlorinated solvents in groundwater. Chemical/physical parameters to be measured using field instrumentation or field test kits include volatile organics as methane equivalents, temperature, specific conductance, hydronium ion concentration (pH), dissolved oxygen, turbidity, oxidation-reduction potential, dissolved ferrous iron, dissolved reduced manganese, and hydrogen sulfide (groundwater samples). Measurement of field parameters is discussed in Section 9.0 (Field Measurements/Screening) of the Field Sampling Plan provided as Volume II of this deliverable. Calibration of field instruments is discussed in Section 9.1 of the Field Sampling Plan. Analysis for volatile organic compounds on-site using a field GC will also be performed. A SOP for field GC analysis is included in Appendix C.

7.2 LABORATORY ANALYTICAL AND MEASUREMENT PROCEDURES

Table 7-1 provides a summary of the laboratory analytical methods and associated laboratory SOPs for the OU3 RI. With the exception of TCL volatiles in aqueous samples, all samples for TCL volatile and semivolatile organics and TAL metals and cyanide will be analyzed in accordance with the CLP analytical procedures set forth in the U.S. EPA Statement of Work for organics analysis (OLM03.1) and inorganic analysis (ILM04.0), respectively. TCL volatile organic compounds in aqueous samples will be analyzed using SW-846 Method 8260A with a 25 mL sample volume as specified in SOP LTL-8260 (Appendix A) in order to achieve lower quantitation limits. Samples for TCL PCB analysis will be analyzed in accordance with OLM03.1 with the modifications provided in the Addendum to SOP LTL-8082 (Appendix A). These modifications focus the calibration and other quality control measures on PCB analysis since pesticide analysis will not be performed. Non-CLP methods will be used for quantitation of the remaining parameters. Standard Operating Procedures for these analyses are included in Appendix A.

It should be noted that the 10% frequency requirement for matrix spikes and laboratory duplicates for inorganic analyses which is specified in this QAPP exceeds the requirements stated in the CLP SOWs and laboratory SOPs. The more stringent frequency requirement, as specified in this QAPP, will override the requirements stated in the SOWs and SOPs and must be met for the OU3 RI project samples. In addition, the laboratory will note in the data package narratives the presence of peaks during volatile or semivolatile analysis which indicate the presence of petroleum compounds.

7.2.1 List of Project Target Compounds and Detection Limits

A complete list of the target compounds/analytes, Contract Required Quantitation and Detection Limits, Practical Quantitation Limits, and laboratory method and instrument detection limits is provided in Section 1.4 of this QAPP. The method detection limits shown have been experimentally determined using Laucks Testing Laboratories, Inc., SOP LTL-1011 which is included in Appendix A and is based on the method found in 40 CFR Part 136 Appendix B (FR Vol. 49, No. 209, pages 198-199). The instrument detection limits shown have been experimentally determined as specified in the CLP Statement of Work (ILM04.0). With the exceptions noted in the following paragraph, data generated through use of CLP protocols will be reported to the Contract Required Quantitation Limit (CRQL) for organics analysis and the Contract Required Detection Limit (CRDL) for inorganics analysis. All environmental data generated through use of non-CLP methods will be reported to the analyte's Practical Quantitation Limit (PQL), if applicable. An analyte's PQL is an expression of the method detection limit with consideration given to required adjustments to ensure that precision and accuracy requirements of the method are attainable. Results for ferrous iron and sulfide spot tests will be reported as qualitatively present or absent.

Contract Required Quantitation Limits for several semivolatile organic compounds and PCBs have been revised as noted in Table 1-4. These revisions have been made to reflect the laboratory's "true" reporting limits for compounds for which the standard CRQL exceeds MPCA HRL or other state criteria.

All solid sample results will be reported on a dry-weight basis. Quantitation and detection limits will also be adjusted, as necessary, based on dilutions and sample volume.

7.2.2 List of Associated Quality Control Samples

In addition to the field quality control samples (field duplicates, trip blanks, rinsate blanks, etc.) discussed in Section 3.0 of this Quality Assurance Project Plan, laboratory quality control samples including matrix spike/matrix spike duplicate samples, method blanks, preparation blanks, laboratory control samples, etc. will be analyzed. Laboratory Quality Control samples are discussed in additional detail in Sections 3.0 and 8.0 of this QAPP.

TABLE 7-1

SUMMARY OF ORGANIC AND INORGANIC ANALYTICAL PROCEDURES
 SOLID AND AQUEOUS MATRICES
 NIROP FRIDLEY, MINNESOTA
 PAGE 1 OF 2

Analytical Parameter	Analytical Method	Standard Operating Procedure (1)
TCL Volatile Organics - aqueous samples	SW-846 ⁽²⁾ 8260A	LTL-8260 (low-level option)
TCL Volatile Organics - soil samples	OLM03.1 ⁽³⁾	---
TCL Semivolatile Organics	OLM03.1	---
TCL Polychlorinated Biphenyls	OLM03.1, Modified	LTL-8082 plus addendum
TAL Metals and Cyanide	ILM04.0 ⁽⁴⁾	---
Total Suspended Solids	SM ⁽⁵⁾ 2540D	LTL-9202
Alkalinity (as CaCO ₃)	EPA ⁽⁶⁾ 310.1	LTL-9005
Hardness (as CaCO ₃)	EPA 130.2	LTL-9009
Sulfate	EPA 300.0	LTL-9110
Nitrate	EPA 300.0	LTL-9110
Nitrite	EPA 300.0	LTL-9110
Dissolved Chloride	EPA 300.0	LTL-9110
Dissolved Bromide	EPA 300.0	LTL-9110
Dissolved Phosphate	EPA 300.0	LTL-9110
Dissolved Methane	Chapelle ⁽⁷⁾	AM18
Total Organic Carbon	Lloyd Kahn ⁽⁸⁾	LTL-9116
Hexavalent Chromium	SW-846 3060A/7196A	LTL-7014/LTL-7401
pH	SW-846 9045C	LTL-9113
Oxidation-Reduction Potential	ASTM Method D1498-76 ⁽⁹⁾ Modified for Soil Samples	LTL-9128 plus Addendum
Ferrous Iron	Spot Test ⁽¹⁰⁾	LTL-7601
Sulfide	Spot Test ⁽¹¹⁾	LTL-9205

TABLE 7-1

**SUMMARY OF ORGANIC AND INORGANIC ANALYTICAL PROCEDURES
SOLID AND AQUEOUS MATRICES
NIROP FRIDLEY, MINNESOTA
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- 1 Laucks Testing Laboratories, Inc., SOPs for all non-CLP analyses are included in Appendix A.
- 2 U.S. EPA, 1986. Test Methods for Evaluating Soil Wastes, Physical/Chemical Methods. SW-846, 3rd Ed.
- 3 U.S. EPA (U. S. Environmental Protection Agency) CLP, 1994. Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration, OLM03.1.
- 4 U.S. EPA CLP, 1995. Statement of Work for Inorganics Analysis, Multi-Media, Multi-Concentration, ILM04.0.
- 5 M. A. H. Franson (Managing Editor). Standard Methods for the Examination of Water and Wastewater. 18th Ed.
- 6 U.S. EPA, 1983. Methods for Chemical Analysis of Water and Wastes.
- 7 Francis H. Chapelle, U.S. Geological Survey. Protocol for Assessing the Natural Attenuation of Chlorinated Ethenes in Groundwater Systems. July, 1996.
- 8 U.S. EPA, Region II, Environmental Services Division, Monitoring Management Branch. Lloyd Kahn, Determination of Total Organic Carbon in Sediment.
- 9 American Society for Testing and Materials, 1981. Standard Practice for Oxidation-Reduction Potential of Water. ASTM Designation: D1498-76.
- 10 Fritz Feigl. Spot Tests in Inorganic Analysis. 1958.
- 11 Wilfred W. Scott, Sc.D. Standard Methods of Chemical Analysis. 5th Ed., Volume 1.

8.0 INTERNAL QUALITY CONTROL CHECKS

Field-related Quality Control checks were discussed in Section 3.0 of this Quality Assurance Project Plan and in Section 8.0 of the attendant Field Sampling Plan (Volume II). This section provides additional information regarding internal quality control checks for the field and the laboratory.

8.1 FIELD QUALITY CONTROL CHECKS

Quality Control (QC) procedures for pH, specific conductance, temperature, dissolved oxygen, oxidation-reduction potential, and turbidity will include calibrating the instruments as described in Section 9.1 of the Field Sampling Plan (FSP) and in the Standard Operating Procedures provided in Appendix A of the FSP. Quality Control procedures for the field GC were discussed in Section 3.0 of this QAPP. Assessment of field sampling precision and bias will be made by collection of field duplicates and rinsate blanks for laboratory analysis. Collection of the QC samples will be in accordance with the procedures provided in Section 8.0 of the FSP at the frequencies indicated in Tables 2-3 and 2-4 of the FSP. Quality Control limits for field-related Quality Control checks were provided in Section 3.0 of this QAPP.

8.2 LABORATORY QUALITY CONTROL CHECKS

The identified subcontract laboratory (Laucks Testing Laboratories, Inc.) has a Quality Control program that ensures the reliability and validity of the analyses performed at the laboratory. The laboratory maintains a Quality Assurance Plan which describes the policies, organization, objectives, quality control activities, and specific quality assurance functions employed by the laboratory. A copy of the Table of Contents for the Laucks Testing Laboratories, Inc., Quality Assurance Plan is provided in Appendix B. In addition, several SOPs regarding laboratory Quality Assurance procedures are included in Appendix A. The Table of Contents included in Appendix A provides a list of SOP titles and associated SOP numbers.

Reagent water is produced in the laboratory by a deionizing system consisting of two mixed bed deionizers, one carbon bed, and one colloid removal bed. The water is polished by an 0.2 μm filter before being delivered to bench locations by a PVC plastic plumbing system. Reagent water is checked weekly for conductivity which must be less than 1.0 $\mu\text{mho/cm}$. Reagent water is checked monthly for the following parameters using the criteria shown:

- Total Matter - less than 2 mg/L
- Soluble Silica - less than 10 µg/L
- Ammonia - less than 100 µg/L
- Non-Purgeable Organic Carbon - less than 1.0 mg/L

The pressure drops across the filters are checked and logged weekly. The filters are changed when the pressure drop exceeds 20 psi. Tell-tale lights for conductance are checked weekly, and resin beds exchanged when the light goes out. Filter and resin bed changes, the results of all checks, and any maintenance performed by outside service engineers is recorded in the reagent water logbook.

All analytical procedures are documented in writing as SOPs. Laboratory SOPs for all non-CLP analyses are provided in Appendix A of this QAPP. Internal quality control procedures for CLP analyses (volatile and semivolatile organics, PCBs, metals, and cyanide) are specified in the Statements of Work (SOWs) for organics (OLM03.1) and inorganics (ILM04.0). Modifications to OLM03.1 for PCB analyses are provided in the Addendum to Laucks SOP LTL-8082 (Appendix A). Internal quality control procedures for all non-CLP analyses (including TCL volatile analysis for aqueous samples) are specified in the method-specific SOPs provided in Appendix A. It should be noted that the 10% frequency requirement for matrix spikes and laboratory duplicates for inorganic analyses which is specified in this QAPP exceeds the requirements stated in the CLP SOWs and laboratory SOPs. The more stringent frequency requirement, as specified in this QAPP, will override the requirements stated in the SOWs and SOPs and must be met for the OU3 RI project samples.

Several internal laboratory Quality Control checks are briefly discussed in the remainder of this section.

Laboratory method blanks are prepared and analyzed in accordance with the analytical method employed to determine whether contaminants originating from laboratory sources have been introduced and have affected environmental sample analyses. A method blank generally consists of an aliquot of analyte-free water (or purified sodium sulfate for soil/sediment samples) that is subjected to the same preparation and analysis procedures as the environmental samples undergoing analysis. With the exception of recognized VOC common laboratory contaminants (e.g., methylene chloride, acetone, 2-butanone, and phthalate esters), method blanks must not contain levels of target analytes above the reported detection limits (above 2.5X the CRQL for methylene chloride and above 5X the CRQL for acetone, 2-butanone, and phthalate esters). If method blank contamination is found to exist above allowable limits, corrective actions indicated in the CLP SOWs or laboratory SOPs must be followed.

Under no circumstances are laboratory method blank contaminant values subtracted from environmental sample analysis results.

Instrument blank analysis is performed during PCB analysis to demonstrate that PCBs are not detected at greater than 0.5 times the CRQL and that the surrogate retention times are within the retention time windows. If analytes are detected at greater than half the CRQL, or the surrogate retention times are outside the retention time windows, all data collection must be stopped and corrective action must be taken. An acceptable instrument blank must be run before additional data is collected. One instrument blank every 12 hours is the minimum contract requirement.

Matrix spike analysis for organic fraction analyses will be performed in duplicate with a frequency of one per 20 environmental samples of like matrix as a measure of laboratory precision. For inorganic analyses, matrix spike and **laboratory duplicate** analysis will be performed for every 10 environmental sample analyses of like matrix. With the exception of volatile and semivolatile MSD analyses, laboratory duplicates are prepared by thoroughly mixing and splitting a sample aliquot into two portions and analyzing each portion following the same analytical procedures that are used for the environmental sample analyses. For volatile and semivolatile MSD analyses, a second sample aliquot is used for analysis in order to avoid constituent loss through the homogenization process. The field crew provides extra volumes of sample matrices designated for laboratory quality control analyses, as required. Control limits for laboratory duplicate analyses are specified in the SOWs for CLP analyses and are established statistically by the laboratory in accordance with method-specific procedures and general protocols outlined in the laboratory SOPs for non-CLP analyses. The laboratory SOPs and CLP SOWs define under what circumstances corrective actions are warranted and how they must be performed when required.

Surrogates are organic compounds (typically brominated, fluorinated, or isotopically labeled), which are similar in nature to the compounds of concern, and which are not likely to be present in environmental media. Surrogates are spiked into each sample, standard, and method blank prior to analysis, and are used only in organic chromatographic analysis procedures as a check of method effectiveness. Surrogate recoveries are evaluated against control limits specified in the CLP SOW, where applicable, or laboratory-derived statistical control limits.

Laboratory control samples (LCS) serve to monitor the overall performance of each step during the analysis, including the sample preparation. Laboratory control sample analysis will be performed for

metals and engineering parameter analyses. Aqueous LCS results must fall within the control limits specified in the CLP SOW, where applicable, or statistically established by the laboratory. Solid LCS results must fall within the control limits established by EPA-EMSL/LV, where applicable, or the supplier of the LCS standard. Aqueous and solid Laboratory Control Samples shall be analyzed utilizing the same sample preparations, analytical methods and QA/QC procedures as employed for the samples.

Internal standard performance criteria ensure that GC/MS analysis sensitivity and response are stable during every analytical run. Internal standard area counts for samples and blanks must not vary by more than a factor of two (- 50% to + 100%) from the associated 12-hour calibration standard. The retention time of the internal standards in samples and blanks must not vary by more than ± 30 seconds from the retention time of the associated 12-hour calibration standard.

Additional internal laboratory Quality Control checks include mass tuning for GC/MS analysis and second column confirmation for GC/EC analysis.

9.0 DATA REDUCTION, VALIDATION, AND REPORTING

This section describes the procedures to be used for data reduction, validation, and reporting for the Operable Unit 3 (OU3) Remedial Investigation (RI) for the NIROP Fridley. All data generated during the course of the OU3 RI will be maintained in hardcopy form by B&R Environmental in the Naval Facilities Engineering Command Southern Division central files located in Pittsburgh, Pennsylvania.

In addition to the central files, all validation reports and electronic data will be maintained in the Chemistry/Toxicology/Risk Assessment Department database records files located in Pittsburgh. A Standard Operating Procedure (SOP CT-05) governs Database Management and Quality Assurance and is included in Appendix C. Upon completion of the contract, all files will be relinquished to the United States Navy.

9.1 DATA REDUCTION

Data reduction will be completed for both field measurements and laboratory-generated analytical data. Field data reduction will be relatively limited versus the degree of laboratory data reduction required for the project. Reduction of both field data and laboratory data are discussed in the remainder of this section.

9.1.1 Field Data Reduction

Field data will be generated as a result of real time measurement of organic vapor concentrations via a Photoionization Detectors (for health and safety monitoring and to support selection of soil samples for shipment to the analytical laboratory), through onsite water quality testing for general indicator parameters including hydronium ion concentration (pH), specific conductance, turbidity, and temperature, and through the use of field instruments or field test kits for measurement of additional groundwater parameters including dissolved oxygen, oxidation-reduction potential, dissolved ferrous iron, dissolved reduced manganese, and hydrogen sulfide (as sulfide). On-site analysis of soils for volatile organic analyses using a field GC will also be performed.

Field measurements of organic vapor concentrations (parts per million on a volume/volume basis relative to methane or benzene) will be recorded in the site logbook but will not be used once the field effort is completed. Hence, no further reduction of field PID data will be completed. The remaining field parameters will be recorded in the site logbook and on sample logsheets immediately after the

measurements are taken and later encoded in the OU3 RI data base for presentation in the RI Report. If an error is made in the logbook, the error will be legibly crossed out (single-line strikeout), initialed and dated by the field member, and corrected in a space adjacent to the original (erroneous) entry. No calculations will be necessary to reduce these data for inclusion in the RI Report.

Reduction of analytical results obtained via field GC analysis will be completed in accordance with Section 5.10.8 of the field GC SOP (Appendix C). Analytical data will be recorded in the field GC injection logbook. Individual sample results will be recorded on the raw analytical data and on summary data sheets. Figure 4 of the field GC SOP provides an example page format for the field GC injection logbook.

Field data will be entered in the electronic data base manually and the entries will be verified by an independent reviewer to make sure that no "transcription" errors occurred. Field measurements will be recorded and reported in the following units:

- Hydronium ion concentration (standard pH units)
- Temperature (degrees Celsius)
- Specific conductance (millimhos)
- Turbidity (Nephelometric turbidity units)
- Dissolved oxygen (mg/L)
- Dissolved ferrous iron (mg/L)
- Dissolved reduced manganese (mg/L)
- Hydrogen sulfide (as sulfide) (mg/L)
- Oxidation-reduction potential (mV)
- Volatile Organics by field GC analysis ($\mu\text{g/Kg}$)

Standard pH units as specified above is the negative logarithm (base 10) of the hydronium ion concentration in moles/liter. Additional aspects of field data handling are provided in Sections 9.2 and 9.3.

9.1.2 Laboratory Data Reduction

The majority of the laboratory analytical data for the OU3 RI will be generated via the U.S. EPA Contract Laboratory Program analytical methods, quality assurance requirements, and reporting procedures. Therefore, data reduction for volatile organics, semivolatile organics, polychlorinated biphenyls, metals, and cyanide will be completed in accordance with applicable laboratory SOPs and with the most current

Statements of Work for Organic and Inorganic Analysis as identified in previous sections of this Quality Assurance Project Plan. In addition to the TCL and TAL results, the contracted laboratory will also generate analytical results for several general chemistry parameters. Laboratory reduction of these analytical results will be completed in accordance with the method-specific laboratory Standard Operating Procedures included in Appendix A. Laboratory data reduction is also discussed in Section 6.2.5 of the laboratory's Quality Assurance Plan.

The laboratory's procedures for review and approval of data are presented in SOP LTL-1018 (Appendix A). These procedures are also discussed in Section 6.3 of the laboratory's QA Plan.

Laboratory analytical data will be reported using standard concentration units to ensure comparability with regulatory standards/guidelines and previous analytical results. Reporting units for solid and aqueous matrices for the various classes of chemicals under consideration are as follows.

- TCL volatiles in soil - $\mu\text{g}/\text{kg}$
- TCL semivolatiles in soil - $\mu\text{g}/\text{kg}$
- TCL polychlorinated biphenyls in soil - $\mu\text{g}/\text{kg}$
- TAL metals in soil - mg/kg
- Cyanide in soil - mg/kg
- Total organic carbon in soil - mg/kg
- Hexavalent chromium in soil - mg/kg
- pH in soil - standard pH units
- Oxidation-reduction potential in soil - mV
- Ferrous iron in soil - qualitative presence or absence
- Sulfide in soil - qualitative presence or absence
- TCL volatiles in groundwater - $\mu\text{g}/\text{L}$
- TCL semivolatiles in groundwater - $\mu\text{g}/\text{L}$
- TCL polychlorinated biphenyl in groundwater - $\mu\text{g}/\text{L}$
- TAL metals in groundwater - $\mu\text{g}/\text{L}$
- Cyanide in groundwater - mg/L
- Total suspended solids in groundwater - mg/L
- Total hardness in groundwater - mg/L
- Total alkalinity in groundwater - mg/L
- Sulfate in groundwater - mg/L

- Nitrate in groundwater - mg/L
- Nitrate in groundwater - mg/L
- Dissolved chloride in groundwater - mg/L
- Dissolved bromide in groundwater - mg/L
- Dissolved phosphate in groundwater - mg/L
- Dissolved methane in groundwater - mg/L

With the exception of pH, ORP, ferrous iron, and sulfide in soil samples (which will only be used to support the data validation of hexavalent chromium), all laboratory analytical results will be presented in summary tables in the RI Report. These results will be presented as received by the laboratory with the possible exception of the elimination of false positives as a result of data validation (as discussed in Section 9.2).

Descriptive statistics may also be performed for use in describing the nature and extent of contamination and for risk assessment. These statistics, as described in the following paragraphs, include the determination of average concentrations for duplicate samples and the determination of upper 95% confidence limits.

Determination of average concentrations for duplicate samples will be necessary because duplicate samples will be collected as a Quality Control measure. Arithmetic means will be determined for duplicate samples for reporting purposes in summary tables in the RI Report. The original duplicate sample results will be presented in an Appendix to the RI Report as discussed in Section 9.3. Averages for duplicates will be determined using distinct equations which are contingent upon the analytical results for the duplicate samples. The equations to be used are as follows:

Positive result for both the original and duplicate sample:

$$\text{Average} = (\text{Original Result} + \text{Duplicate Result})/2$$

Nondetect for both the original and duplicate sample:

$$\text{Average} = (\text{Original Quantitation Limit}/2 + \text{Duplicate Quantitation Limit}/2)/2$$

Nondetect for one sample and positive result for the other (when the quantitation limit/2 for the nondetect < positive result for the other sample):

$$\text{Average} = (\text{Quantitation Limit}/2 + \text{Positive Result})/2$$

Nondetect for one sample and positive result for the other (when the quantitation limit/2 for the nondetect \geq positive result for the other sample):

$$\text{Average} = \text{Positive Result}$$

Note that the preceding treatment of average results includes the handling of nondetects quantitatively as values equal to one-half the quantitation limit. This is a typical procedure for the handling of nondetects.

In the event that manipulation of the analytical data for evaluation of nature and extent of contamination or for risk assessment purposes is necessary, calculations to determine representative concentrations for the exposure assessment will be performed. Such procedures will only be necessary in the event that the results for various sampling locations are pooled to generate representative concentrations for an exposure unit. Based on the anticipated distance between sampling points, it is considered unlikely that data will be pooled (i.e., each individual sampling point will be treated separately). However, in the event that pooling of data is completed, representative concentrations will be determined using the following equations:

Normally distributed data

$$\text{UCL} = X_m + t(s / \sqrt{n})$$

Where: UCL = the upper 95% confidence limit
 X_m = the arithmetic mean concentration
t = the Student's t statistic
s = the sample standard deviation
n = the number of samples

Log-normally distributed data

$$UCL = \exp(X_m + 0.5s^2 + sH / \sqrt{n-1})$$

Where: UCL = the upper 95% confidence limit
X_m = the arithmetic mean concentration
s = the sample standard deviation
H = H statistic
n = the number of samples
exp = the exponential function (e)

Note that distributional assumption testing will be completed prior to use of the preceding equations. Either the Shapiro-Wilk W-Test or the Komolgorov-Smirnov test will be used to test for normality or log-normality.

Field Quality Control sample results will be included in the data base for the Fridley OU3 RI. Specifically, the analytical results for trip blanks, rinsate blanks, and ambient condition blanks will be provided. The results for field Quality Control Samples will be considered during the course of data validation (in concert with laboratory method blanks) to eliminate false positive results according to the 5- and 10-times rules specified in the Region V Standard Operating Procedures for Validation of CLP Organic and Inorganic Data and the National Functional Guidelines for Organic and Inorganic Data Review. The results for laboratory Quality Control samples such as method blanks will not be presented in the RI Report data base. In addition, only the original (unspiked) sample results for Matrix Spike/Matrix Spike Duplicate samples will be provided in the data base.

Additional aspects of laboratory data handling are provided in Sections 9.2 and 9.3. Treatment of both hardcopy and electronic data deliverables are discussed.

9.2 DATA VALIDATION

Validation of field measurements and laboratory analytical data are discussed in this section. Validation of field data will be limited to real time "reality" checks whereas laboratory analytical data will be validated in accordance with current U.S. EPA guidance. Validation of field measurements is discussed in Section 9.2.1. Validation of laboratory analytical data is discussed in Section 9.2.2.

9.2.1 Field Measurement Data Validation

Field measurements will not be subjected to a formal data validation process. However, field technicians will ensure that the equipment used for field measurement is performing accurately via compliance with the applicable Standard Operating Procedures. In addition, the field GC analyst will evaluate all QC results on a real-time basis, taking corrective actions when necessary as described in Sections 5.8 and 5.9 of field GC SOP (Appendix C). As described in Section 9.1.1, all field data entered into the electronic database will be independently reviewed for transcription errors.

9.2.2 Laboratory Data Validation

All CLP laboratory analytical data will be subjected to validation in accordance with the Region V Standard Operating Procedures for Validation of CLP Organic and Inorganic Data and the National Functional Guidelines for Organic and Inorganic Data Review. Data validation will be completed to ensure that the data are of evidentiary quality. Particular emphasis will be placed on holding time compliance, equipment calibration, spike recoveries, and blank results, although all required elements of the validation process will be considered.

Validation of analytical data will be completed by the B&R Environmental Chemistry Department located in B&R Environmental's Pittsburgh office. Final review and approval of validation deliverables will be completed by the Department's Data Validation Coordinator. The analytical results for non-CLP parameters will be validated versus the methods and SOPs included in Appendix A. Validation of these data will conform to the National Functional Guidelines to the greatest extent practicable. B&R Environmental will complete the validation process in accordance with the additional requirements outlined in Standard Operating Procedure CT-03 included in Appendix C.

9.3 DATA REPORTING

This section discusses data reporting requirements for field and laboratory analytical data. Section 9.3.1 discusses field measurement data handling and reporting. Section 9.3.2 discusses laboratory data handling and reporting.

9.3.1 Field Measurement Data Reporting

Unless difficulties arise, all samples for field GC analysis will be analyzed within three days of collection. The field GC analyst will provide verbal results within 24 hours of analysis to the FOL for use in selecting samples for fixed-base laboratory analysis. Verbal results for soil samples will be provided on a wet-weight basis. A data summary, including solid sample results on a dry-weight basis, and narrative report will be provided by the field GC analyst to the Task Order Manager within 30 days of the last sample collection. Field logs, COC reports, QC summaries (for calibration, internal standards, and matrix spikes), and individual raw data runs will also be included with the narrative report.

Field data will be reported in the units discussed in Section 9.1.1. The RI Report will include a comprehensive data base including all field measurements (specifically pH, specific conductance, temperature, turbidity, dissolved oxygen, oxidation-reduction potential, dissolved ferrous iron, dissolved reduced manganese, and field GC volatile results). Field Measurements will be transferred from the site logbook or sample logsheets to the electronic data base manually and will be reviewed for accuracy by an independent reviewer.

All records regarding field measurements (i.e., field logbooks, sampling logbooks, and sample logsheets) will be placed in the Southern Division central files upon completion of the field effort. Entry of these results in the data base will require removal of these results from the files. Outcards will be used to document the removal of any such documentation from the files (date, person, subject matter). Field measurement data will be reported in an appendix of the RI Report at a minimum and may also be reported in summary fashion if they are indicative of the presence of contamination (e.g., high specific conductance readings).

The B&R Information Management Systems Department will hold responsibility for field data reporting subject to oversight by the Department Manager. Key data handling personnel within the Department include the Department Manager and the Information Management Systems Group Leader.

9.3.2 Laboratory Data Reporting

Data reported by the laboratory for all analytical fractions will be in accordance with CLP reporting format, including all non-CLP data (to the extent practicable). SOP LTL-4201 (Appendix A) specifically identifies the information that will be included in CLP-type packages for organics and general chemistry parameters.

Note that based on the modifications described in the Addendum to SOP LTL-8082 (Appendix A) for TCL PCB analysis, certain summary forms related to pesticide analysis are not applicable for PCB analysis and will not be provided. All pertinent quality control data including raw data and summary forms for blanks, standards analysis, calibration information, etc., will be provided for the non-CLP analyses. Case narratives will be provided for each Sample Delivery Group.

Environmental and field Quality Control sample results (trip blanks, duplicates, rinsate blanks, ambient condition blanks) will be included in the RI Report as an appendix. The data base will include pertinent sampling information such as sample number, sampling date, general location, depth, and survey coordinates (if applicable). Sample-specific detection limits will be reported for nondetected analytes. Units will be clearly summarized in the data base and will conform to those identified in Section 9.1.2.

The analytical data will also be reported in summary fashion within the body of the RI Report text in tabular and graphic fashion. Tabular summaries will report the frequency of detection, mean concentrations, representative concentrations (if applicable), standard deviations, etc. in accordance with the data reporting requirements outlined in Risk Assessment Guidance for Superfund - Human Health Evaluation Manual (Part A). The tabular summaries will include only those analytes that are detected in at least one sample. In the event that graphical portrayals of data are informative, isoconcentration contours or "tag maps" including the location and concentration of specific Chemicals of Potential Concern will be provided in the RI Report. Quality assurance information, including surrogate recoveries, spike recoveries, spike duplicate RPDs, duplicate RPDs, and blank results will also be included in tabular form in the RI report.

Data will be handled electronically pursuant to the electronic deliverable requirements specified in B&R Environmental's Basic Ordering Agreement with analytical laboratories. This agreement requires the analytical laboratories to provide data in both hardcopy and electronic form (DBF files). The original electronic diskettes and data validation reports are maintained in the Southern Division central files. All other pertinent information, including field logbooks, sampling notebooks, chain-of-custody forms, etc. are also maintained in the central files. Various aspects of field documentation are discussed in detail in Section 5.1 of the Field Sampling Plan (Volume II of this deliverable). Standard Operating Procedure CT-05 discusses data base management and Quality Assurance and is included in Appendix C.

Validation will be completed using the hard copy data. Upon completion of validation of a Sample Delivery Group and review by the Data Validation Coordinator, the validation qualifiers will be entered in the electronic data base and will be subjected to independent review for accuracy. During this review

process, the electronic data base printout will also be contrasted with the hard copy data (Form Is) to ensure that the hard copy data and electronic data are consistent.

The B&R Information Management Systems Department will hold responsibility for laboratory data reporting subject to oversight by the Department Manager. Key laboratory data handling personnel include the Department Manager and the Information Management Systems Group Leader (Information Management Systems Department), and the Data Validation Coordinator (Chemistry Department). It is not currently planned that copies of the data validation deliverables will be provided to either the MPCA or U.S. EPA Region V. However, a summary of the validation results (actions taken and completeness, precision, and accuracy) will be provided in the RI Report.

10.0 PERFORMANCE AND SYSTEM AUDITS

Performance and system audits will be performed periodically to ensure that work is being implemented in accordance with the approved Project Plans and in an overall satisfactory manner. Such audits will be performed by various personnel and will include evaluation of field, laboratory, data validation, and data reporting processes. Examples of pertinent audits are as follows:

- The Field Operations Leader (FOL) will supervise and check daily that the field measurements are made accurately, equipment is thoroughly decontaminated, samples are collected and handled properly, and fieldwork is documented accurately and neatly.
- Performance and system audits for the laboratory will be performed regularly, by a U.S. Navy Contractor in accordance with the requirements of the Navy, and in accordance with the Laboratory Quality Assurance Plan.
- Data validators will review (on a timely basis) the chemical analytical data packages submitted by the laboratory. The data validators will check that the data were obtained through use of the approved methodology, that the appropriate level of QC effort and reporting was conducted, and whether or not the results are in conformance with QC criteria. On the basis of these factors, the data validator will generate a report describing data limitations, which will be reviewed internally by the Data Validation Coordinator prior to submittal to the Task Order Manager.
- The Task Order Manager will maintain contact with the FOL and Data Validation Coordinator to ensure that management of the acquired data proceeds in an organized and expeditious manner. Similarly, the Task Order Manager will interface with the Risk Assessment and Modeling Coordinators, as applicable.

Details regarding audit responsibilities, frequency, and procedures are discussed in the remainder of this section. Field performance and system audits are discussed in Section 10.1. Laboratory performance and system audits are discussed in Section 10.2.

10.1 FIELD PERFORMANCE AND SYSTEM AUDITS

This section discusses internal and external field performance and system audits.

10.1.1 Internal Field Audits

10.1.1.1 Internal Field Audit Responsibilities

An independent performance and system audit of field activities will be conducted by the B&R Environmental Quality Assurance Manager (QAM) or designee. When the formal field audit is conducted, the QAM (or designee) will be responsible for ensuring that sample collection, handling, and shipping protocols, as well as equipment decontamination and field documentation procedures, are being performed in accordance with the approved Project Plans and SOPs. An internal audit of office procedures will also be conducted by the QAM (or designee) to ensure compliance with SOPs regarding review of deliverables, verification of calculations, data handling and transcription, and recordkeeping.

10.1.1.2 Internal Field Audit Frequency

Internal field and office audits are conducted once per annum unless the complexity of the project dictates a greater audit frequency. One audit per annum is considered appropriate for the NIROP Fridley OU3 RI/FS. Based on uncertainties regarding project plan approval, mobilization cannot be pinpointed at this time. However, the field and office audits will be completed in accordance with the following milestone schedule: (1) field audit - within one month of mobilization; (2) office audit - within three months of receipt of the final analytical data package from the subcontract laboratory.

10.1.1.3 Internal Field Audit Procedures

The field and office audits will be conducted by the QAM (or designee) in accordance with the following procedures:

- Prior to the audit, the auditor will prepare a detailed checklist to be used as an auditing guide. An example audit checklist is provided in Appendix D.

- Upon arrival at the audit location, the auditor shall conduct a pre-audit meeting with the responsible management of the organization or project to be reviewed.
- Field audits will include a review of required project documentation (logbooks, sample log sheets, etc.) for completeness and agreement; and field operations (well installation, groundwater sampling, sample handling and preservation, etc.) to determine compliance with applicable SOPs.
- File audits will consist of reviewing required project records for completeness, organization, and ease of retrieval.
- Office audits will focus on compliance with Standard Operating Procedures governing deliverable review, verification of calculations, recordkeeping procedures, and data handling, transcription, and reporting.
- The audit checklist will be used to record observations including any noted nonconformances.
- A formal post-audit debriefing will be conducted; potential immediate corrective actions will be discussed.
- The auditor will generate a formal audit report which will address corrective actions. This report will be provided by the auditor to the Task Order Manager.
- The Task Order Manager will ensure that all corrective actions are addressed and will provide written verification of corrective action implementation by the auditor.
- The auditor will manage corrective action verification and audit closure providing all documentation to the QAM.
- The following audit records will be maintained by the QAM:
 - Original monitoring schedules and revisions
 - Audit checklists
 - Audit reports
 - Response evaluations

- Verification of corrective actions
- Follow-up checklists and audit reports

The results of the audit will be considered acceptable if all Standard Operating Procedures and project planning document requirements are followed to the letter. If problems are identified, corrective action is initiated in accordance with the procedures outlined in Section 13.0.

10.1.2 External Field Audits

External field audits may be conducted by the Minnesota Pollution Control Agency (MPCA), the U.S. EPA Region V, or both. Details regarding the responsibilities of these agencies, frequency, and procedures are left to the discretion of the agencies.

10.1.2.1 External Field Audit Responsibilities

At the discretion of the MPCA and U.S. EPA Region V.

10.1.2.2 External Field Audit Frequency

At the discretion of the MPCA and U.S. EPA Region V.

10.1.2.3 Overview of External Field Audit Process

At the discretion of the MPCA and U.S. EPA Region V.

10.2 LABORATORY PERFORMANCE AND SYSTEMS AUDITS

Internal and external laboratory performance and systems audits are discussed in this section.

10.2.1 Internal Laboratory Audits

Internal laboratory audit responsibilities, frequencies, and procedures are discussed in this section.

10.2.1.1 Internal Laboratory Audit Responsibilities

The subcontract laboratory's QA/QC Officer performs routine internal audits of the laboratory. Internal laboratory audits are also conducted by the U.S. Navy. B&R Environmental holds no responsibility for such audits. Performance and system audits of laboratories are coordinated through the NFESC by an independent Quality Assurance contractor. It is the responsibility of the NFESC and their contractor to ensure that the contracted laboratories comply with good laboratory practices and the general requirements of all analytical services provided by the laboratory.

10.2.1.2 Internal Laboratory Audit Frequency

The subcontract laboratory conducts internal system audits of each laboratory analytical department on an annual basis, at a minimum. Internal audits are performed biannually if no external audits are conducted. In addition, each laboratory department analyzes blind performance evaluation samples as described in SOP LTL-1009 (Appendix A). Data audits are also performed by the QA/QC Officer at a minimum frequency of once per year for each analytical area. Internal laboratory performance and system audits are completed by the U.S. Navy for each contracted laboratory on an 18-month schedule.

10.2.1.3 Internal Laboratory Audit Procedures

The laboratory QA/QC Officer conducts internal systems audits in order to detect any problems in sample flow, analytical procedures, or documentation and to ensure adherence to the good laboratory practices as described in Laucks Testing Laboratories, Inc., SOPs. Laucks Testing Laboratories, Inc., internal audit procedures are described in SOP LTL-1017 (Appendix A) and in Section 10 of the laboratory's Quality Assurance Plan.

Performance of the laboratory's internal system audits conducted while OU3 RI samples are being analyzed will be noted in the RI report. If significant problems are noted during the laboratory's internal audits, these issues, as well as any corrective actions taken, will be described.

Internal U.S. Navy laboratory audit procedures fall under the domain of the NFESC and its contractor. Procedures will be provided to the MPCA and U.S. EPA upon request.

10.2.2 External Laboratory Audits

This section discusses external laboratory audit responsibilities, frequencies, and procedures.

10.2.2.1 External Laboratory Audit Responsibilities

It is the responsibility of the MPCA and U.S. EPA Region V to conduct laboratory audits at their discretion.

10.2.2.2 External Laboratory Audit Frequency

An external laboratory audit may be conducted by U.S. EPA Region V or MPCA prior to the initiation of the sampling and analysis activities.

10.2.2.3 External Audit Procedures

External audit procedures are at the discretion of U.S. EPA Region V and the MPCA. External laboratory audits may include (but are not limited to) review of laboratory analytical procedures, laboratory onsite audits, and/or submission of performance evaluation samples to the laboratory for analysis.

11.0 PREVENTIVE MAINTENANCE PROCEDURES

Measuring equipment used in environmental monitoring or analysis for the NIROP Fridley OU3 RI shall be maintained in accordance with the manufacturer's operation and maintenance manuals. Equipment and instruments shall be calibrated in accordance with the procedures, and at the frequency, discussed in Section 6.0 (Calibration Procedures and Frequency). Preventive maintenance for field and laboratory equipment are discussed in the remainder of this section.

11.1 FIELD EQUIPMENT PREVENTIVE MAINTENANCE

Preventive maintenance of field equipment is described in Section 10.1 of the attendant Field Sampling Plan (Volume II). The B&R Environmental Equipment Manager and the instrument operator will be responsible for ensuring that equipment is operating properly prior to use and that routine maintenance is performed and documented. Any problems encountered while operating the instrument will be recorded in the field log book including a description of the symptoms and corrective actions taken. If problem equipment is detected or should require service, the equipment should be logged, tagged, and segregated from equipment in proper working order. Use of the instrument will not be resumed until the problem is resolved.

Preventive maintenance for the field GC will be the responsibility of the field GC analyst. A schedule of preventive maintenance for the field GC is provided in Section 5.7.6 of field GC SOP (Appendix C).

11.2 LABORATORY INSTRUMENT PREVENTIVE MAINTENANCE

Proper maintenance of laboratory instruments and equipment is essential to ensuring their readiness when needed. Dependent on manufacturer's recommendations, maintenance intervals are established for each instrument. All instruments must be labeled with a model number and serial number, and a maintenance logbook must be maintained for each instrument. Personnel must be alert to the maintenance status of the equipment they are using at all times.

11.2.1 Major Instruments

Table 11-1 provides a summary of preventive maintenance procedures performed by Laucks Testing Laboratories, Inc., for key analytical instruments.

TABLE 11-1
PREVENTIVE MAINTENANCE FOR ANALYTICAL INSTRUMENTS
NIROP FRIDLEY, MINNESOTA
PAGE 1 OF 2

Instrument	Preventive Maintenance	Maintenance Frequency
GC/MS - Volatiles	Change pump oil. Clean and rinse transfer lines, trim front end of column, rinse 6-port valve, clean sample lines, replace trap, replace column, clean source, replace fittings, change sample block on autosampler, replace filaments.	Yearly. As needed.
GC/MS - Semivolatiles	Change injection port liner and septum, clip 5-10 cm from front of column, ramp GC oven twice to 300 C. Vacuum computer's air filters. Clean source.	Daily or as needed. Approx. annually. As needed.
GC	Swab EC detectors for radioactivity. Change O ₂ traps on gas lines. Clean autosampler syringe. Change injection port liner and septum. Bake system, flush injection port, clip guard column, change analytical column, change carrier hydrocarbon trap.	Semi-annually. Approx. semi-annually. Approx. monthly. Approx. every 100 injections. As needed.
ICP	Clean or change air filters. Clean torch, replace nebulizer tips, replace pump tubing. Check sensitivity.	As needed. As needed. Daily.
GFAA	Replace or trim capillary tubing. Clean entrance windows.	As needed. As needed.
Spectrophotometer	Clean sample compartment and entrance windows. Check wavelength calibration.	Semiannually. Annually.

TABLE 11-1

PREVENTIVE MAINTENANCE FOR ANALYTICAL INSTRUMENTS
 NIROP FRIDLEY, MINNESOTA
 PAGE 2 OF 2

Instrument	Preventive Maintenance	Maintenance Frequency
Ion Chromatograph	Replace pump seals. Lubricate analytical pump motor. Check chromatography module and all gas lines for leaks. Clean conductivity detector cell electrodes, check cell calibration. Replace bed supports, clean columns, clean AMMS (membrane suppresser), replace autosampler pipette tip.	Annually. Semiannually. Every run. Monthly. As needed.
TOC Analyzer	Change pump tubing. Change other tubing, change furnace tubes, change LiOH tube, change tin trap, adjust optical balance, change septum, change permeation dryer tubing. Change IR filter screen, change gas tubing.	Each run. As needed. Check monthly; replace as needed.

The use of manufacturer recommended grades or better of supporting supplies and reagents is also a form of preventive maintenance. For example, gases used in the various gas chromatographs and metals instruments are of sufficient grade to minimize fouling of the instrument. The routine use of septa, chromatographic columns, ferrules, AA furnace tubes, and other supporting supplies from reputable manufacturers will assist in averting unnecessary periods of instrument downtime. An inventory of critical spare parts is also maintained by the laboratory to minimize instrument downtime.

11.2.2 Refrigerators/Ovens

The temperatures of refrigerators used for sample storage will be monitored once daily. The acceptable range for refrigerator temperatures is $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$. The temperatures will be recorded on a Cold Storage Temperature Log. (See Appendix 5 of SOP LTL-1008, included in Appendix A of this QAPP.) Maintenance of the log will be the responsibility of the sample custodian. The log will contain the following information:

- Date
- Time
- Temperature
- Initials of person performing the check

Assignment of responsibilities for temperature monitoring to specific personnel does not preclude the participation of other laboratory personnel. If unusual temperature fluctuations are noted, it is the responsibility of the observer to immediately notify the person in charge of the discrepancy before the condition of the samples is compromised.

Unstable or fluctuating temperatures may be indicative of malfunctions in the cooling system. On the other hand, the instability may be due to frequent opening of the door. Regardless of the cause, such an observation must be investigated, and modifications must be made to access procedures or repairs to equipment must be made to prevent jeopardizing the integrity of the samples.

Oven temperatures are checked prior to use. The required temperature is dependent on the method to be performed. The oven temperature is recorded with the associated analytical results in a logbook designated for the analytical method.

12.0 SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA PRECISION, ACCURACY, AND COMPLETENESS

Compliance with the Quality Control objectives outlined in Tables 3-1 through 3-9 of Section 3.0 will be monitored via two separate mechanisms. Precision and accuracy will be assessed through data validation in accordance with the National Functional Guidelines (to the extent practicable for non-CLP analyses). Compliance with the completeness objectives for field and laboratory data/measurement will be calculated by hand (field measurements) and electronically via a database subroutine (laboratory data). Information necessary to complete the precision and accuracy calculations will be provided in electronic and hardcopy form by the subcontract laboratory. Equations to be used for the precision, accuracy, and completeness assessment are outlined in the remainder of this section.

12.1 ACCURACY ASSESSMENT

To assure the accuracy of the analytical procedures, a minimum of 1 of every 20 samples for organic analysis and 1 of every 10 samples for inorganic analysis will be spiked with a known amount of the analyte or analytes to be evaluated. The spiked sample is then analyzed. The increase in concentration of the analyte observed in the spiked sample, because of the addition of a known quantity of the analyte, compared to the reported value of the same analyte in the unspiked sample determines the percent recovery. Daily control charts are plotted for each commonly analyzed compound and kept on matrix-specific and analyte-specific bases. The percent recovery for a spiked sample is calculated according to the following formula:

$$\%R = \frac{\text{Amount in Spiked Sample} - \text{Amount in Sample}}{\text{Known Amount Added}} \times 100$$

12.2 PRECISION ASSESSMENT

Duplicate samples (for inorganic analyses) will be prepared and analyzed at a minimum frequency of 1 per every 10 environmental samples. Duplicate samples are prepared by dividing an environmental sample into equal aliquots. Matrix spike duplicate samples (for organic analyses) will be prepared and analyzed at a minimum frequency of 1 per every 20 environmental samples. Matrix spike duplicate samples are prepared by dividing an environmental sample into equal aliquots and then spiking each of the aliquots with a known amount of analyte. The duplicate samples are then included in the analytical sample set. The splitting of the sample allows the analyst to determine the precision of the preparation and analytical

techniques associated with the duplicate samples. The relative percent difference (RPD) between the sample (or spike) and duplicate (or duplicate spike) is calculated and plotted. The RPD is calculated according to the following formula:

$$RPD = \frac{\text{Amount in Sample} - \text{Amount in Duplicate}}{0.5 (\text{Amount in Sample} + \text{Amount in Duplicate})} \times 100$$

12.3 COMPLETENESS ASSESSMENT

Completeness is the ratio of the number of valid sample results to the total number of samples analyzed with a specific matrix and/or analysis. Following the completion of the analytical testing, the percent completeness will be calculated by the following equation:

$$\text{Completeness} = \frac{(\text{number of valid measurements})}{(\text{number of measurements planned})} \times 100$$

The results of the data validation process and the completeness assessment will be summarized in Section 4.0 of the RI Report (Nature and Extent of Contamination). Field and laboratory completeness objectives for this project are 90 percent and 95 percent, respectively.

13.0 CORRECTIVE ACTION

Under the B&R Environmental QA/QC program, it is required that any and all personnel noting conditions adverse to quality report these conditions immediately to the Task Order Manager and Quality Assurance Manager (QAM). These parties, in turn, are charged with performing root-cause analyses and implementing appropriate corrective action in a timely manner. It is ultimately the responsibility of the QAM to document all findings and corrective actions taken and to monitor the effectiveness of the corrective measures performed.

13.1 FIELD CORRECTIVE ACTION

Field nonconformances or conditions adverse to quality must be identified and corrected as quickly as possible so that work integrity or quality of product is not compromised. The need for corrective action may arise based on deviations from Project Plans and procedures, adverse field conditions, or other unforeseen circumstances. Corrective action needs may become apparent during the performance of daily work tasks or as a consequence of internal or external field audits.

Corrective action may include resampling and may involve amending previously approved field procedures. If warranted by the severity of the problem (e.g., if a change in the approved Project Plan documents or SOPs is required), the Navy will be notified in writing via a Field Task Modification Request (FTMR), and Navy (in conjunction with U.S. EPA Region V and MPCA) approvals will be obtained. The Field Operations Leader (FOL) is responsible for initiating FTMRs; an FTMR will be initiated for all deviations from the Project Plan documents, as applicable. An example of an FTMR is provided as Figure 13-1. Copies of all FTMRs will be maintained with the onsite project planning documents and will be placed in the final evidence file.

Minor modifications to field activities such as a slight offset of a boring location will be initiated at the discretion of the FOL, subject to onsite approval by NIROP personnel and the onsite MPCA representative. Major modifications (e.g., elimination of a sampling point) must be obtained via an FTMR.

Corrective actions for out-of-control situations during field GC analysis are documented in the field GC logbook and in the final field GC report. The field GC SOP (Appendix C) defines out-of-control situations for field GC analysis and the appropriate corrective action procedures for these situations.

FIGURE 13-1

**BROWN & ROOT ENVIRONMENTAL
FIELD TASK MODIFICATION REQUEST FORM**

Client Identification _____ Project Number _____ FTMR Number _____

To _____ Location _____ Date _____

Description:

Reason for Change:

Recommended Disposition:

Field Operations Leader (Signature, if applicable) _____ Date _____

Disposition:

Task Order Manager (Signature, if required) _____ Date _____

Distribution:

Program Manager
Quality Assurance Officer
Task Order Manager
Field Operations Leader

Others as required _____

13.2 LABORATORY CORRECTIVE ACTION

In general, laboratory corrective actions are warranted whenever an out-of-control event or potential out-of-control event is noted. The specific corrective action taken depends on the specific analysis and the nature of the event. Generally, the following occurrences alert laboratory personnel that corrective action may be necessary:

- QC data are outside established warning or control limits;
- method blank analyses yield concentrations of target analytes above acceptable levels;
- undesirable trends are detected in spike recoveries or in duplicate RPDs;
- there is an unexplained change in compound detection capability;
- inquiries concerning data quality are received;
- deficiencies are detected by laboratory QA staff audits or from performance evaluation sample test results.

Any corrective action taken above the analyst level that cannot be performed immediately at the instrument will be documented. Corrective actions are typically documented for out-of-control situations on a Corrective Action form or an Out-of-Control Event form (included as Appendices 1 and 2 of SOP LTL-1008, which is in Appendix A of this QAPP).

Further detail describing the system used by Laucks Testing Laboratories, Inc., to identify, document, and resolve out-of-control events is provided in SOP LTL-1008.

13.3 CORRECTIVE ACTION DURING DATA VALIDATION AND DATA ASSESSMENT

As a means of oversight, the QAM will audit a percentage of the data validation, assessment, and evaluation deliverables generated/performed. Oversight audits may also be conducted directly by the U.S. Navy personnel, or by an independent data validation firm under contract to the U.S. Navy.

The need for corrective action may become apparent during data validation, interpretation, or presentation activities, or problems may be identified as a result of oversight findings. The performance of rework, instituting a change in work procedures, or providing additional/refresher training are possible corrective actions relevant to data evaluation activities. The Task Order Manager will be responsible for approving the implementation of corrective action.

13.4 CORRECTIVE ACTION FOR ADMINISTRATIVE ACTIVITIES

Findings identified by the conduct of office procedures and file audits may also necessitate the performance of corrective actions. Corrective actions involving file management and office procedures usually consist of correction of an isolated nonconformance or the performance of activities necessary to conform with clarified guidance.

14.0 QUALITY ASSURANCE REPORTS TO MANAGEMENT

Quality Assurance reports to management will be provided in five primary formats during the course of the NIROP Fridley OU3 Remedial Investigation. Data validation letters will be prepared on a Sample Delivery Group-specific basis and will summarize Quality Assurance issues for the subcontract laboratory data. Internal audit reports regarding compliance with Standard Operating Procedures (specifically those regarding recordkeeping and review of deliverables) and compliance with the Field Sampling Plan and Health and Safety Plan are also prepared. In addition, written weekly reports summarizing accomplishments and Quality Control/Quality Assurance issues during the field investigation will be provided by the Field Operations Leader. Finally, monthly progress reports will be provided to the Navy.

14.1 CONTENTS OF PROJECT QUALITY ASSURANCE REPORTS

The contents of the specific Quality Assurance reports are as follows. The data validation reports address all major and minor laboratory noncompliances as well as noted sample matrix effects. In the event that major problems occur with the analytical laboratory (e.g., holding time exceedances or calibration noncompliances, etc.) the Data Validation Coordinator notifies the Task Order Manager, the Technical Program Manager, and the Laboratory Services Coordinator. Such notifications (if necessary) are typically provided via internal memoranda and are placed in the project file. Such reports contain a summary of the noncompliance, a synopsis of the impact on individual projects, and recommendations regarding corrective action and compensational adjustments. Corrective actions are initiated at the program level.

Internal field and office audits are conducted on an annual basis for each active project. The Quality Assurance Manager (or designee) conducts the audits to ensure that projects are completed in accordance with applicable Standard Operating Procedures and project planning documents. The primary emphasis of internal office audits is to ensure that all calculations are checked, that recordkeeping is conducted in accordance with Standard Operating Procedure, and that all deliverables are subjected to peer review by experienced senior staff members. Field audits are conducted to ensure that sampling, sample shipment, recordkeeping, etc. are completed in accordance with the Field Sampling Plan and relevant Standard Operating Procedures. At the completion of such audits, the Task Order Manager is provided a Quality Assurance report that outlines the scope of the audit, any findings regarding nonconformance, recommendations for corrective action, and a proposed schedule for completion of corrective action and post-corrective action monitoring.

The Field Operations leader will provide the Task Order Manager with weekly reports regarding accomplishments, deviations from the Field Sampling Plan, upcoming activities, and a Quality Assurance summary during the course of the field investigation. In addition, monthly project review meetings are held for all active Navy CLEAN projects. Issues discussed at the project review meeting include all aspects of budget and schedule compliance, and Quality Assurance/Quality Control problems. The Task Order Manager provides a monthly progress report to the Navy which addresses the project budget, schedule, accomplishments, planned activities, and Quality Assurance/Quality Control issues and intended corrective action. Any changes to the QAPP and any staff changes that affect the project during the field work will be noted in the RI Report.

14.2 FREQUENCY OF QUALITY ASSURANCE REPORTS

As discussed in the preceding section, Quality Assurance reports are generated either frequently or infrequently contingent upon the type of Quality Assurance report generated. The following frequencies will apply for the NIROP Fridley OU3 RI: 1) Data validation QA Reports - Contingent upon SDG delivery data; 2) Internal Office Audit QA Reports - Once per annum; 3) Internal Field Audit Reports - once per annum; 4) Weekly field progress reports - weekly during the course of the field investigation; 5) Monthly Progress Reports - monthly.

14.3 INDIVIDUALS RECEIVING/REVIEWING QUALITY ASSURANCE REPORTS

Data validation Quality Assurance Reports are provided to the Task Order Manager for inclusion in the project files. In the event that major problems are observed for a given laboratory, the Program Manager, Deputy Program Manager, Quality Assurance Manager, Task Order Manager, and Laboratory Services Coordinator are provided with copies of the QA report. Copies of internal field and office audit QA Reports are provided to the Program Manager, Deputy Program Manager, and Task Order Manager. Weekly field progress reports are provided to the Task Order Manager. Monthly progress reports are provided to the Navy.

APPENDIX A

LABORATORY STANDARD OPERATING PROCEDURES

APPENDIX A

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• LTL-7601	Spot Test for the Presence of Ferrous Iron (Fe ²⁺) in Soil, Revision 0
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LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-7014

Title: Alkaline Digestion For Hexavalent Chromium By SW 846 Method 3060A

Revision history:

Number	Date
0	06/03/97

Written by: Bill Lundberg
Bill Lundberg, Inorganic Supervisor

Date: 6/4/97

Approved by: Harry Romberg
Harry Romberg, QA Officer

Date: 6-4-97

Approved by: Karen J. Kotz
Karen Kotz, Laboratory Director

Date: 6/5/97

1. Introduction and Scope

1.1 Method Description

1.1.1 Method 3060A is an alkaline digestion procedure for extracting hexavalent chromium, Cr(VI), from soluble, adsorbed, and precipitated forms of chromium compounds in soils, sludges, sediments, and some industrial waste materials. To quantify total Cr(VI) in a solid matrix, three criteria must be satisfied: (a) the extracting solution must solubilize all forms of Cr(VI), (b) the conditions of the extraction must not induce reduction of native Cr(VI) to Cr(III), and (c) the method must not cause oxidation of native Cr(III) contained in the sample to Cr(VI). Method 3060A meets these criteria for a wide spectrum of solid matrices. Under the alkaline conditions of the extraction, minimal reduction of Cr(VI) or oxidation of native Cr(III) occurs. The addition of Mg^{2+} in a phosphate buffer to the alkaline solution has been shown to suppress oxidation if observed. The accuracy of the extraction procedure is assessed using spike recovery data for soluble and insoluble forms of Cr(VI) (e.g., $K_2Cr_2O_7$ and $PbCrO_4$), coupled with measurement of ancillary soil properties, indicative of the potential for the soil to maintain a Cr(VI) spike during digestion, such as oxidation-reduction potential (ORP), pH, organic matter content, ferrous iron, and sulfides. Recovery of an insoluble Cr(VI) spike can be used to assess the first two criteria, and method-induced oxidation is minimal except in soils high in Mn and amended with soluble Cr(III) salts or freshly precipitated $Cr(OH)_3$. The sample is digested using 0.28M Na_2CO_3 /0.5M NaOH solution and heating at 90-95°C for 60 minutes to dissolve the Cr(VI) and stabilize it against reduction to Cr(III). After digestion the Cr(VI) is quantitated using SW 846 7196A.

1.1.2 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.2 Sample Collection, Sample Storage, Holding Times

1.2.1 Samples should be collected using devices and placed in containers that do not contain stainless steel (e.g., plastic or glass). A 16 oz glass jar will be required due to the possible need to analyze the sample for other parameters should the matrix spike (MS) exceed limits.

1.2.2 Samples should be stored field-moist at $4^{\circ}C \pm 2^{\circ}C$ until analysis.

1.2.3 Hexavalent chromium has been shown (interlaboratory studies) to be quantitatively stable in field-moist soil samples for at least one month from sample collection. In addition, Cr

(VI) has also been shown (interlaboratory studies) to be stable in the alkaline digestate for up to 96 hours after extraction from soil.

1.3 Definition of Terms

- 1.3.1 This section defines terms and acronyms as they are used in this SOP. Other terms, such as MS/MSD or method blank, are not defined here since it is assumed that the user of this SOP already understands their more general meaning.
- 1.3.2 Batch Identifier - A number given to each preparation or analysis group which uniquely identifies that batch. This number is generally the blank ID for preparation batches and an analysis number which is similar to the blank ID, only preceded by an "A" rather than a "B" for inorganic batches. The preparation batch IDs are discussed in other documentation. The batch identifier for the second run of soils for Cr(VI) analyzed on June 2, 1997 would be A060297_CR6_S02.
- 1.3.3 Blank spike - A background free matrix (clean sand for soils/sediments) to which a known amount of Cr(VI) is added each time samples are prepared. Blank spikes are required on all HAZWRAP and NFESC work. Note that an LCS or SRM will substitute as a blank spike for most inorganic analyses. At this time there is no known Cr(VI) LCS. In the context of this SOP, a blank spike is the same as a QC check standard. See also QC check standard.
- 1.3.4 DIW - Deionized water - Lab reagent water. This water should be free of virtually all analytes.
- 1.3.5 IDL - Instrument detection limit. The lowest concentration of a target analyte that will yield a signal:noise ratio of least 3x. Used as a starting point for selecting MDL study spiking levels.
- 1.3.6 MDL - Method detection limit - The lowest concentration a sample which will yield a positive result that is greater zero at a known level of confidence. MDLs are empirically determined by Laucks.
- 1.3.7 MDL standard - Method detection limit standard - A standard prepared so that the concentrations of the target analytes are no greater than 4x the empirically determined MDLs. This standard is used to verify that the instrument or system is capable of detecting the target analytes on an ongoing basis.

1.3.8 QC check standard - Quality control check standard. Referred to in this SOP as a blank spike. A QC check standard is used to determine whether the analytical system is in control if MS/MSD recoveries are out of control. See also blank spike.

2. Equipment List and Standards

2.1 Apparatus

- 2.1.1 Beakers: borosilicate glassware, 250-mL, with watch glass covers.
- 2.1.2 Graduated Cylinder: 100-mL.
- 2.1.3 Volumetric Flasks: Class A glassware, 1000-mL and 100-mL with stoppers.
- 2.1.4 Filtration Apparatus.
- 2.1.5 Filter membranes (0.45 μm). Preferably cellulosic or polycarbonate membranes.
- 2.1.6 Heating Device - capable of maintaining the digestion solution at 90 - 95°C with continuous auto stirring capability or equivalent.
- 2.1.7 Volumetric pipettes: Class A glassware, assorted sizes, as necessary.
- 2.1.8 Calibrated pH meter.
- 2.1.9 Calibrated balance.
- 2.1.10 Thermometer (NIST-Certified or equivalent) or other appropriate temperature sensing device.

2.2 Standards

- 2.2.1 Potassium Dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, spiking solution, 100 mg/L Cr (VI). Dissolve 0.2829 g of dried (105°C) $\text{K}_2\text{Cr}_2\text{O}_7$ in distilled deionized water in a 1 liter volumetric flask and dilute to the mark. Store at 20-25°C in a tightly sealed container for up to six months.
- 2.2.2 The Blank Spike, and MS are prepared by adding 1.0 mL of the 100 mg/L standard to their respective beakers.

2.2.3 Lead Chromate: PbCrO_4 , analytical reagent grade. The insoluble matrix spike is prepared by adding 10-20 mg PbCrO_4 to a separate aliquot. Store under dry conditions at 20-25°C in a tightly sealed container.

2.3 Reagents

2.3.1 Nitric acid: HNO_3 concentrated, analytical reagent grade or spectrograde quality. Store at 20-25°C in the dark. Discard if the solution has a yellow tinge; this is indicative of photoreduction of NO_3^- to NO_2^- .

2.3.2 Sodium carbonate: Na_2CO_3 , anhydrous, analytical reagent grade. Store at 20-25°C in a tightly sealed container.

2.3.3 Sodium hydroxide: NaOH , analytical reagent grade. Store at 20-25°C in tightly sealed container.

2.3.4 Magnesium Chloride: MgCl_2 (anhydrous), analytical reagent grade. 392.18 mg MgCl_2 is equivalent to 100 mg Mg^{2+} . Store at 20-25°C in a tightly sealed container.

2.3.5 Phosphate Buffer: 0.5M K_2HPO_4 /0.5M KH_2PO_4 buffer at pH 7: Dissolve 87.09 g analytical reagent grade K_2HPO_4 and 68.04 g analytical reagent grade KH_2PO_4 in 700 mL of deionized water. Transfer to a 1L volumetric flask and dilute to volume.

2.3.6 Digestion solution: Dissolve 20.0 ± 0.05 g NaOH and 30.0 ± 0.05 g Na_2CO_3 in deionized water in a one-liter volumetric flask and dilute to the mark. Store the solution in a tightly capped polyethylene bottle at 20-25°C and prepare fresh monthly. The pH of the digestion solution must be checked before using. The pH must be 11.5 or greater; if not, discard.

3. Safety precautions and Waste Disposal

3.1 Safety Precautions

3.1.1 All standards, samples and sample solutions should be handled as if they are hazardous substances.

3.1.2 Routine precautions include an awareness of the moving parts on the instrument you're using. These parts are often charged with power from an electrical component and have the potential to do harm if not used properly.

3.1.3 Electrical shock - All instruments present the possibility of electrical shock. The operator should take all precautions including ensuring that all instruments are operated with fully

grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.

3.2 Waste Disposal

- 3.2.1 The waste generated by this digestion are not hazardous and may discarded down the sink, while diluting with tap water. Waste segregation and disposal from the point of collection is further covered in the Laucks SOP on Waste Segregation and Disposal.

4. Calibration and Quality Control

4.1 Method Detection Limit Study

- 4.1.1 Prior to the analysis of any samples, it is necessary to establish method detection limits. This procedure is fully described in Laucks on MDL studies. Briefly, it involves the analysis of 7 replicate samples spiked at a concentration near the anticipated method detection limit. A Student's T-test is then applied to these measured values to calculate the MDL.

4.2 Method Blanks

- 4.2.1 Method blanks are used to verify contamination free reagents and apparatus. They are prepared with every set of samples prepared at the same time or at least one blank every 20 samples which ever is more frequent. Any analyte response above the detection limit is reported. Method blank control limits are that contamination should not exceed the Reporting Limit or 10% of the concentration of the lowest sample, whichever is greater.

4.2.2 Corrective action

- 4.2.2.1 Corrective action may necessitate re-preparation and re-analysis of the sample set. For example if an analyte were found in the blank but not in any of the associated samples then sample group may not require re-analysis. In addition, if sample levels exceed 10 times the blank, the level of contamination may be considered insignificant. In any case, if re-preparation and re-analysis is not being undertaken, the analyst must first discuss the issue with the Quality Assurance Officer. It is the laboratory's responsibility to ensure that method interferences caused by contaminants in acids, solvents, reagents, glassware, and other sample processing hardware leading to discrete artifacts and/or elevated baselines in the analytical run be minimized. In the extreme case of chronic contamination, blanks may have to be analyzed from each stage of the sample processing to determine the contamination source so it can be

eliminated. In all cases where blank contamination exceeds the control limit, a narrative comment must be made which documents the corrective actions taken.

4.3 Method Blank Spikes

4.3.1 A method blank spike follows the same protocol as with the matrix spike analysis except that the spiking solution is added to a method blank solution instead of an actual sample. A method blank with added analytes is a method blank spike. A method blank spike is the same as a QC check standard. A blank spike OR a standard reference material (SRM) must be analyzed. The SRM is the preferred material and the blank spike should only be analyzed where an SRM does not exist or is not practical for routine use.

4.3.1.1 Corrective action

4.3.1.2 Recovery must be within the certified acceptance range or a recovery range of 80 to 120% or the sample batch must be reanalyzed.

4.4 Pre digestion Matrix Spike

Both soluble and insoluble pre-digestion matrix spikes must be analyzed at a frequency of one per batch of ≤ 20 field samples. The soluble matrix spike should be spiked with 1.0 mL of the spiking solution prepared in 2.2.1 (equivalent to 40 mg/kg Cr(VI)) or at twice the sample concentration, whichever is greater. The insoluble matrix spike is prepared by adding 10-20 mg of $PbCrO_4$ (2.2.3) to a separate sample aliquot. It is used to evaluate the dissolution during the digestion process. Both matrix spikes are then carried through the digestion process. More frequent matrix spikes must be analyzed if the soil characteristics within the analytical batch appear to have significant variability based on visual observation.

4.4.1 A sample is chosen at random from the samples to be analyzed, and an aliquot of spiking solution is added to this sample prior to preparation. The analyst should attempt to avoid selecting samples which are identified by the client as blanks. As the purpose of the matrix spike is to test the system under "typical" conditions, the analyst may also avoid selecting the most difficult sample of the batch for spiking. It is not always required that a matrix spike analysis be performed with each preparation/analysis batch, however, the minimum frequency for MS analysis is 1 each per 20 samples per matrix. This will be best accomplished by running one with every batch for many analyses. This matrix spike sample is used to evaluate the matrix effect of the sample upon recovery of the analytes. The recovery of spike analytes is calculated as follows:

$$\text{recovery} = \frac{(\text{SS} - \text{S}) * 100}{\text{SA}}$$

where:

SS = concentration in spiked sample

S = native concentration in unspiked sample

SA = spiked added, the amount of spiking material actually added to the sample calculated on the sample basis

4.4.2 The recovery criteria are defined by SW 846 as 75% - 125%.

4.4.3 Corrective action

4.4.3.1 If the matrix spike recoveries are not within these recovery limits, the entire batch must be redigested/reanalyzed. If upon reanalysis the matrix spike is not within the recovery limits, but the LCS is within criteria specified in 4.3.1.2, information such as pH, Fe^{+2} , ORP, S_2 and TOC should be carefully evaluated, as the Cr(VI) data may be valid for use despite the perceived "QC failure." The information discussed below is provided to interpret ancillary parameter data in conjunction with data on spike recoveries.

When pre-digestion matrix spike recoveries for Cr(VI) are less than acceptance range minimum criterion (75%), this is indicative of highly reducing samples (e.g., anoxic sediments) with no measurable native Cr(VI) in the unspiked sample (assuming the criteria in 4.3.1.2 are met). Such a result indicates that the combined and interacting influences of ORP, pH and reducing agents (e.g., organic acids, Fe^{+2} and sulfides) caused reduction of Cr(VI) spikes. Oxidation-reduction potentials below the bold diagonal line on Fig. 2 of SW 846 Method 3060A (Eh/pH Phase Diagram, located in Appendix 2 of this SOP) indicates a reducing soil for Cr(VI). The downward slope to the right indicates that the Eh value, at which Cr(VI) is expected to be reduced, decreases with increasing pH. The solubility and quantity of organic constituents will influence reduction of Cr(VI). The presence of H_2S or other strong odors indicate a reducing environment for Cr(VI). In general, acidic conditions accelerate reduction of Cr(VI) in soils, and alkaline conditions tend to stabilize Cr(VI) against reduction. If spike recoveries are not within the recovery limits, the reductive nature of the sample must be documented.

4.5 Post Digestion Spike

4.5.1.1 One post-digestion Cr(VI) matrix spike must be analyzed per batch. The post-digestion matrix spike concentration should be equivalent to 40 mg/kg or twice the

sample concentration observed in the unspiked aliquot of the test sample, whichever is greater. Dilute the sample aliquot to a minimum extent, if necessary, so that the absorbance reading for both the unspiked sample aliquot and spiked aliquot are within the initial calibration curve. A guideline for the post-digestion matrix spike recovery is 85-115% recovery. If not achieved, consider the corrective actions/guidance on data use specified in 4.4.3.1. These digestates may contain soluble reducing agents for Cr(VI), such as fulvic acids.

4.6 Sample Duplicate

4.6.1 Criteria

4.6.1.1 Sample duplicates are required. At least one duplicate sample per 20 samples per matrix is required when matrix spikes are being performed. RPD values are calculated in a manner similar to MS/MSD RPDs:

$$\text{RPD} = \frac{|S1 - S2| * 100}{(S1 + S2)/2}$$

where:

S1 = measured concentration in the initial analysis

S2 = measured concentration in the duplicate analysis

4.6.1.2 Duplicate samples must have a Relative Percent Difference (RPD) of $\leq 20\%$, if both the original and the duplicate are \geq four times the laboratory reporting limit. A control limit of \pm the laboratory reporting limit is used when either the original or the duplicate sample is $<$ four times the laboratory reporting limit.

4.6.2 Corrective action

4.6.2.1 In general, reanalysis of the samples should occur if duplicate values fail to meet these criteria. Extenuating circumstances or special considerations should be discussed with the Quality Assurance Officer.

4.6.2.2 If a trend in out of control RPD values is observed, the methods used must be examined to determine the source of variance. Once this source is identified, the method must be changed so that samples can be analyzed with a predictable reproducibility. Generally, if recoveries are in control and no analyte of interest was detected in any of the samples, no immediate action will be taken on that sample set.

If integrity of reported sample values is in doubt, re-analysis may be called for. Corrective actions should be discussed with the Quality Assurance Officer.

5. Operation procedures

5.1 Sample Analysis

5.1.1 Analysis sequence

5.1.1.1 A typical batch will consist of:

- Prep Blank
- Blank Spike
- Sample
- Sample Duplicate
- Sample Spike-Soluble
- Sample Spike-Insoluble
- Sample Spike Soluble post digestion
- Up to 19 more samples

5.2 Analytical Operation

5.2.1 Adjust the temperature setting of each heating device used in the alkaline digestion by preparing and monitoring a temperature blank (a 250 mL beaker filled with 50 mL digestion solution (2.3.6)). Maintain a solution temperature of 90 - 95°C as measured with a NIST-calibrated thermometer or equivalent.

5.2.2 Place 2.5 ± 0.10 g of the as received sample into a clean and labeled 250 mL beaker. The sample should be mixed thoroughly before the aliquot is removed.

5.2.3 Add 50 mL of digestion solution (2.3.6) to each sample. Add $\cong 400$ mg of $MgCl_2$ (2.3.4) and 0.5 mL of 1.0 M phosphate buffer (2.3.5). Cover all samples with watch glasses. The Mg^{+2} is used to suppress oxidation of certain forms of Cr(III) (such as soluble forms) that can be oxidized to Cr(VI) during the procedure.

5.2.4 Stir the samples continuously (unheated) for at least five minutes using a stirring bar.

5.2.5 Heat the samples and maintain a temperature range of 90-95°C with constant stirring for 60 minutes at temperature.

- 5.2.6 Gradually cool each solution to room temperature and transfer it quantitatively to the filtration apparatus with distilled deionized water rinses and filter through a 0.45 μm membrane filter. Rinse the inside of the filter flask and filter pad with deionized water and transfer the filtrate and the rinses to a clean 250-mL beaker. NOTE: The remaining solid after filtration of the matrix spike should be saved for possible use in assessing low Cr(VI) matrix spike recoveries. Store the filtered solid at $4 \pm 2^\circ\text{C}$.
- 5.2.7 Place a magnetic stirring bar into the sample digest beaker, place the vessel on a stirrer, and, with constant stirring, slowly add concentrated nitric acid solution to the beaker dropwise. Adjust the pH of the solution to 7.5 ± 0.5 and monitor the pH with a pH meter. If the pH of the digest should drop below 7.0, discard the solution and redigest. If overshooting pH 7.5 ± 0.5 occurs repeatedly, prepare a diluted nitric acid solution and repeat digestion procedure. CAUTION: CO_2 will be evolved. This step should be performed in a fume hood.
- 5.2.8 Remove the stirring bar and rinse, collecting the rinsate in the beaker. Transfer quantitatively the contents of the beaker to a 100 mL volumetric flask and adjust the sample volume to 100 mL (to the mark on the volumetric flask) with deionized water. Mix well.
- 5.2.9 The sample digestates are now ready to be analyzed. Determine the Cr(VI) concentration in mg/kg by SW-846 Method 7196A (colorimetrically by UV-Vis spectrometry)

5.3 Compound Quantification

- 5.3.1 The quantitation of Cr(VI) follows LTL-7401 with the following exceptions:

The calibration curve is prepared to go from 0.05-0.50 mg/L.

A 1 cm cell is used

- 5.3.2 The output from the UV-Vis is calculated in mg/L in 100 mL of solution. To calculate the concentration in the soil:

$$\text{Cr(VI), mg/Kg db} = \frac{A * 100 * \text{dilution}}{\text{Sa wt.g} * \frac{\text{TS}}{100}}$$

where A= concentration in mg/L in the digest

5.3.3 Any sample exceeding the linear range of the calibration curve should be diluted and reanalyzed.

5.3.4 If a sample displays a reading at the instrument that is at odds with the analyst's observation of the color of the sample, an aliquot of the sample should be prepared at the same dilution as the sample and analyzed just like a sample, except that instead of the color reagent, an aliquot of acetone only should be used. This is the turbidity correction for that sample and its value should be subtracted from that of the colorized sample in order to compute the final result.

6. Reports

6.1 Data Packet Organization

6.1.1 The bench sheet generated during the digestion should list the sample ID, analyst, test, date, temperatures, weights, ID of the standard, and any other pertinent information.

6.2 Quality Control Reports

6.2.1 All results for quality control tests are entered into the lab data base using the QC_DB program. Printouts of all data entered must be included in the data packet. The routine minimum is a method blank report, and an MS/MSD or MS/duplicate report. Many analyses will also require an SRM, blank spike or other report.

6.3 Sample Result Reports

6.3.1 Data Qualifying Flags

6.3.1.1 Sample report results are qualified with data qualifying flags. These flags have the following definitions:

CODE	Definition
-------------	-------------------

U	: The analyte of interest was not detected, to the limit of detection indicated.
---	--

Appendix I

QC Summary Table

**Laucks Testing Laboratories
Method 3060A/7196A QA Requirements and Corrective Actions**

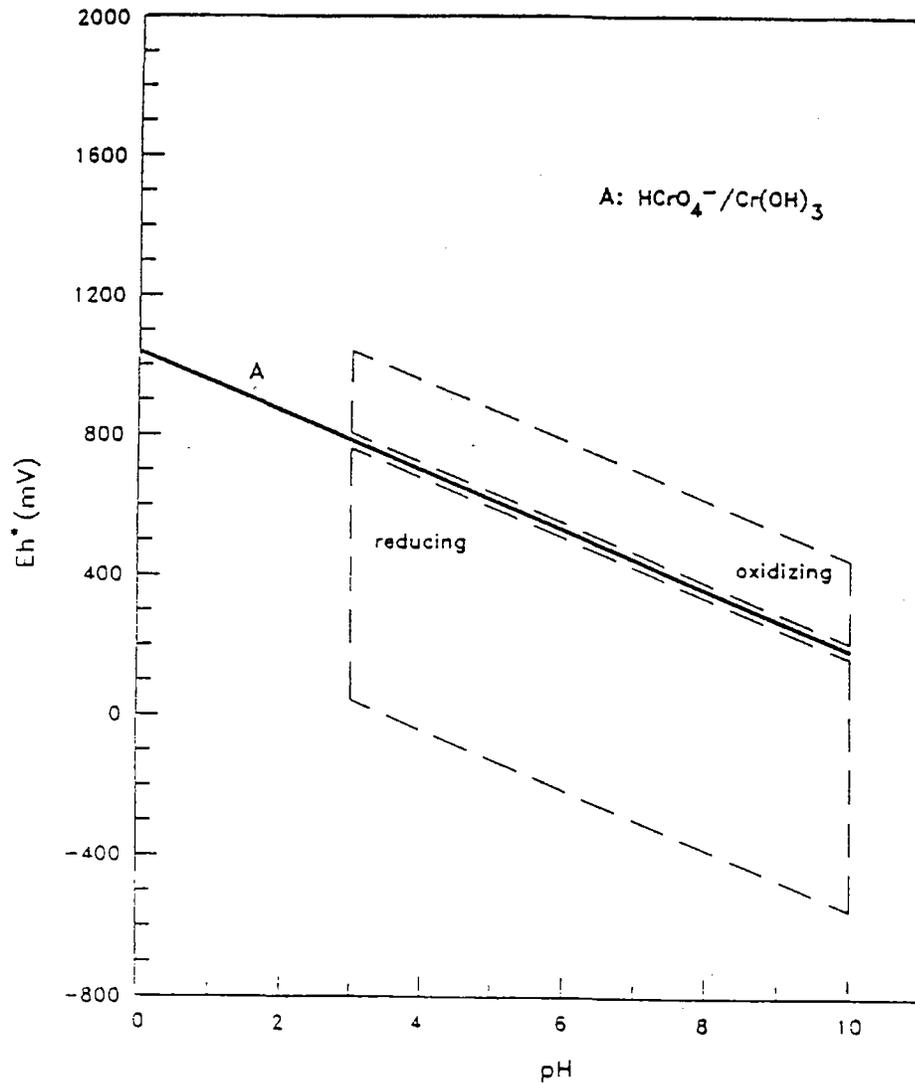
QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Method Blank	<MDL, or 10% of lowest sample	<RL, or 10% of lowest sample	1/20, minimum	Redigest	QC_DB report
Matrix Spike Recovery	75-125	75-125	1/20, minimum	Redigest	QC_DB report
Duplicate % Difference	≤20%, or ± RL	≤20%, or ± RL	1/20, minimum	Redigest	QC_DB repc
Blank Spike Recovery	80-120%	80-120%	1/20, minimum	Redigest	QC_DB report
Post digestion Matrix Spike recovery	85-115%	85-115%	1/20, minimum	Redigest	QC_DB report

See text for more specifics on the corrective actions. Results may be reported if the samples are determined to cause matrix effects. However, this entails additional determinations of pH, oxidation-reduction potential and reducing agents (TOC, sulfides, ferrous iron).

Appendix II Eh/pH Phase Diagram

FIGURE 2
Eh/pH Phase Diagram

The dashed lines define Eh-pH boundaries commonly encountered in soils and sediments.



Note the Eh values plotted on this diagram are corrected for the reference electrode voltage: 244 mV units must be added to the measured value when a separate calomel electrode is used, or 199 mV units must be added if a combination platinum electrode is used.

3060A-12

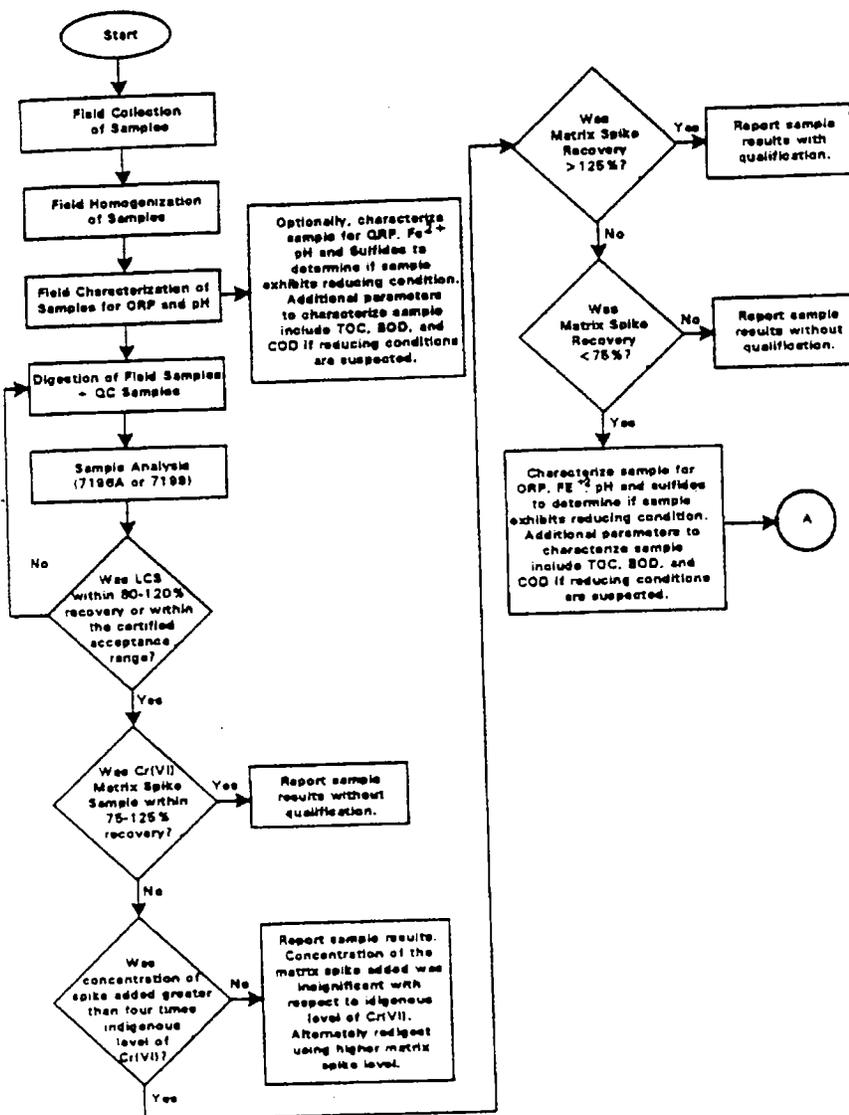
Revision 1
January 1995

SOP No: LTL-7014
Revision: 0
Date: 06/03/97
Page: 16 of 19
Replaces: none

Appendix III

Flow Charts

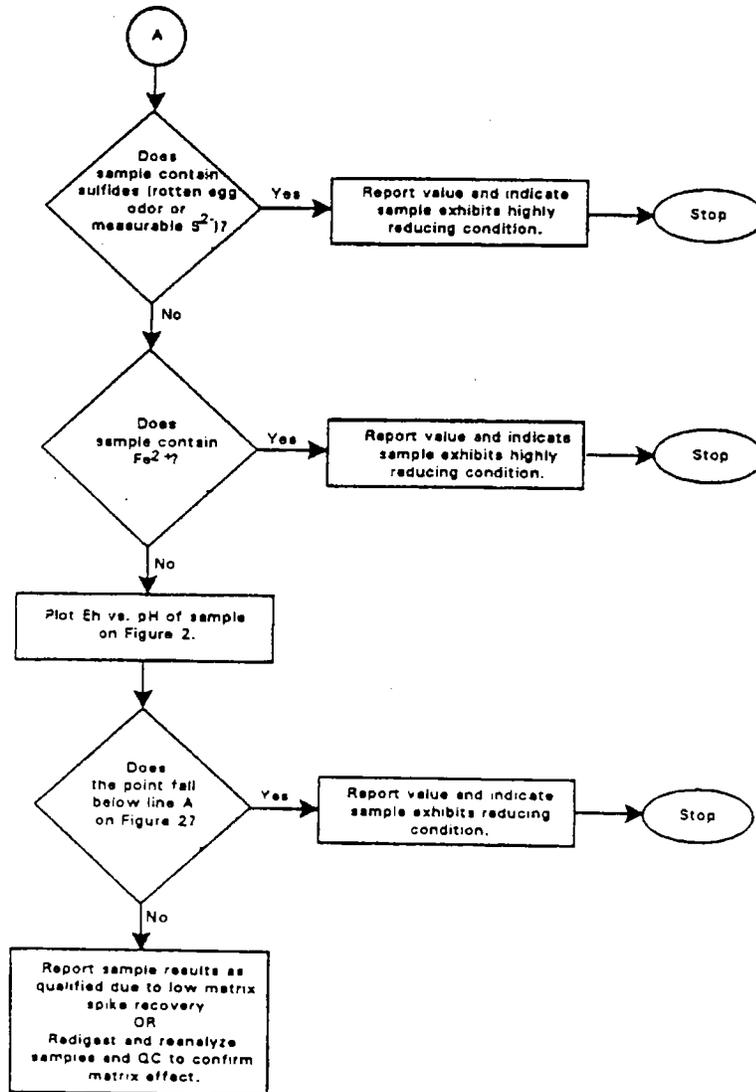
FIGURE 1
 QUALITY CONTROL FLOW CHART



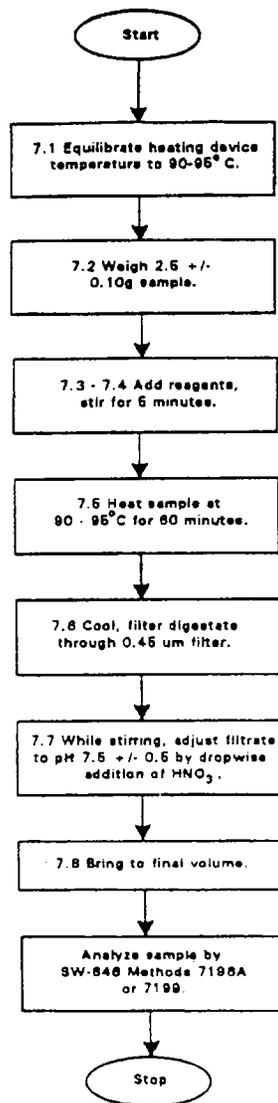
3060A-10

Revision 1
 January 1995

FIGURE 1
QUALITY CONTROL FLOW CHART (Continued)



METHOD 3060
ALKALINE DIGESTION FOR HEXAVALENT CHROMIUM



3060A-13

Revision 1
January 1995

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-7401

Title: **The Colorimetric Determination of Hexavalent Chromium by SW-846 7196A**

Revision history:

<u>Number</u>	<u>Date</u>
0	02/01/96

UNCONTROLLED

Written by: Bill Lundberg Date: 2/6/96
Bill Lundberg, Inorganics Division Manager

Approved by: Harry Romberg Date: 2-6-96
Harry Romberg, QC Officer

Approved by: Karen J Kotz Date: 2/6/96
Karen Kotz, Laboratory Director

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1. Introduction and Scope

1.1. Method Description

1.1.1. Method 7196 is used to determine the concentration of dissolved hexavalent chromium in TCLP extracts, ground waters, domestic and industrial wastes. Highly turbid or colored samples will present the possibility of positive interference, and will need to be corrected for spectrophotometrically. This method is used to measure Cr⁺⁶ in samples from 5-100 µg/L. Higher concentrations will require either dilution or the use of a shorter cell path.

1.1.2. This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.2. Sample Collection, Sample Storage, Holding Times

1.2.1. Water samples should be collected in a 500 ml unpreserved bottle. Glass and plastic are acceptable. Soil samples should be collected in a 4 or 8 oz glass soil container. Samples should be stored at 4°C ± 2°C until extraction or analysis. Water samples should be analyzed within 24 hrs of collection. Soil samples should be extracted within 7 days of collection and the extract analyzed within 24 hrs.

1.3. Definition of Terms

1.3.1. This section defines terms and acronyms as they are used in this SOP. Other terms, such as MS/MSD or method blank, are not defined here since it is assumed that the user of this SOP already understands their more general meaning.

1.3.2. **Batch Identifier** - A number given to each preparation or analysis group which uniquely identifies that batch. This number is an analysis number which is similar to the blank ID, only preceded by an "A" rather than a "B" for inorganic batches. The preparation batch IDs are discussed in other documentation. The second analysis for a water sample performed on Jan 2, 1996 would have the identifier A010296CR6W02.

1.3.3. **Blank spike** - A background free matrix (DIW for water, clean sand for soils/sediments) to which known amounts of target analytes are added each time samples are prepared. Blank spikes are required on all HAZWRAP and NFESC work. Note that an LCS or SRM (see below) will substitute as a blank spike for most inorganic analyses. In the context of this SOP, a blank spike is the same as a QC check standard. See also QC check standard.

- 1.3.4. **CCB** - Continuing Calibration Blank - This is the same acronym used in the CLP program. This is a blank which is analyzed immediately after the CCV (almost always after every 10 samples and at the end of the analytical run) during the analysis sequence to determine whether the instrument or system has maintained a stable baseline.
- 1.3.5. **CCV** - Continuing Calibration Verification - This is the same acronym used in the CLP program. This is a standard analyzed at some prescribed frequency (almost always after every 10 samples and at the end of the analytical run) during the analysis sequence to determine whether the instrument or system has remained in calibration.
- 1.3.6. **CLP** - Contract Laboratory Program - The USEPA program that contracts with laboratories to provide laboratory services. The term has come to mean a much broader set of methods and deliverables. In context of this SOP, CLP means procedures or operations which are detailed in the CLP contract and which are extended to a broader working definition.
- 1.3.7. **Corr Coef, CC** - Correlation coefficient - A measure of the "goodness of fit" of a set of data to a regression model. The closer the value is to 1, the higher the degree of confidence in the correlation
- 1.3.8. **DIW** - Deionized Water - Lab reagent water. This water should be free of virtually all analytes.
- 1.3.9. **ICB** - Initial Calibration Blank - This term is borrowed from CLP. An instrument blank is made up in the same way as calibration standards, without target analytes.
- 1.3.10. **ICV** - Initial Calibration Verification - This term is borrowed from the CLP protocol. It is a standard which is analyzed at the start of each analytical run that is compared to the initial multi-point calibration to determine whether the instrument calibration is accurate. For most inorganic methods, this verification standard is from a source different from that used to make the calibration standards.
- 1.3.11. **IDL** - Instrument Detection Limit. The lowest concentration of a target analyte that will yield a signal:noise ratio of least 3x. Used as a starting point for selecting MDL study spiking levels.
- 1.3.12. **MDL** - Method Detection Limit - The lowest concentration a sample which will yield a positive result that is greater zero at a known level of confidence. MDLs are empirically determined by Laucks.

- 1.3.13. **MDL standard** - Method detection limit standard - A standard prepared so that the concentrations of the target analytes are no greater than 4x the empirically determined MDLs. This standard is used to verify that the instrument or system is capable of detecting the target analytes on an ongoing basis.
- 1.3.14. **QC check standard** - Quality control check standard. Referred to in this SOP as a blank spike. A QC check standard is used to determine whether the analytical system is in control if MS/MSD recoveries are out of control. See also blank spike.
- 1.3.15. **SRM or LCS** - Standard Reference Material or Laboratory Control Sample. This is a material of approximately the same matrix as the samples, containing a known and usually certified amount of target analyte and which is prepared and analyzed in the same manner as a typical sample. This sample is used to demonstrate that the analytical system is in control. It may be considered to be a blank spike for most inorganic analyses and is preferred over artificially spiking blank materials.
- 1.3.16. **RSD or %RSD** - Relative Standard Deviation or percent relative standard deviation - The ratio of the standard deviation of a set of values to the mean of the set of values. A measure of the similarity of the values one to another.

2. Equipment List and Standards

2.1. Instrument

- 2.1.1. This analysis uses a Perkin-Elmer Lambda 4A spectrophotometer or equivalent instrumentation. Instrumental conditions are 540 nm, slit 1, integration 2, and a 5 cm path length cell.

2.2. Standards and Reagents

- 2.2.1. Potassium dichromate standard solution 1, 100 µg/ml
Dissolve 0.2829 g of Primary Standard Reagent $K_2Cr_2O_7$ in DIW and dilute to 1000 ml.

This solution should be prepared annually.

- 2.2.2. Potassium dichromate standard solution 2, 0.10 µg/ml
Dilute 250 µl of Standard 1 to 250 mls with DIW.

This solution should be prepared fresh daily.

- 2.2.3. Diphenylcarbazide Solution: Dissolve 250 mg of 1,5-diphenylcarbazide in 50 mls of Reagent grade Acetone. Store this solution in an amber bottle. Discard when it becomes discolored.
- 2.2.4. Sulfuric Acid Solution, 10% (v/v): Dilute 10 mls of metals grade H₂SO₄ to 100 mls with DIW

3. Safety precautions and Waste Disposal

3.1. Safety Precautions

- 3.1.1. All standards, samples and sample solutions should be handled as if they are hazardous substances.
- 3.1.2. Refer to the instrument manufacturer's manual for routine instrument precautions.
- 3.1.3. Routine precautions include an awareness of the moving parts on the instrument you're using. These parts are often charged with power from an electrical component or with high pressure gas and have the potential to do harm if not used properly.
- 3.1.4. Electrical shock - All instruments present the possibility of electrical shock. The operator should take all precautions including ensuring that all instruments are operated with fully grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.
- 3.1.5. Hexavalent chromium is highly toxic. Care should be taken to avoid ingestion.

3.2. Waste Disposal

- 3.2.1. All wastes from this analysis are disposed of in a laboratory sink. They should be flushed with copious amounts of water.
- 3.2.2. Waste segregation and disposal from the point of collection is further covered in the Laucks SOP on Waste Segregation and Disposal.

4. Calibration and Quality Control

4.1. Method Detection Limit Study

4.1.1. Prior to the analysis of any samples, it is necessary to establish method detection limits. This procedure is fully described in the Laucks on MDL studies. Briefly, it involves the analysis of 7 replicate samples spiked at a concentration near the anticipated method detection limit. A Student's T-test is then applied to these measured values to calculate the MDL.

4.2. Initial Multi-Point Calibration

4.2.1. A calibration curve is prepared by measuring 0, 5, 10, 20, and 50 mls of solution 2 into 100 ml volumetric flasks. The volume is adjusted to approximately 90 mls, and then treated like the samples. The concentration of Cr^{+6} in the flasks is 0, 5, 10, 20, and 50 $\mu\text{g/L}$. The 5 $\mu\text{g/L}$ standard is the reporting limit. Any samples above 50 $\mu\text{g/L}$ should be diluted and reanalyzed.

The instrument is calibrated from the lowest to the highest concentration.

Due to the inherent instability of Cr^{+6} , solution 2 should be prepared fresh daily.

4.2.2. Criteria

4.2.3. Initial calibration data is evaluated using the correlation coefficient of a linear regression analysis. The correlation coefficient must be 0.995 or greater for a 5-point calibration. All CCVs and sample extract concentrations must be computed using the regression equation.

4.2.4. Corrective action

4.2.5. If the criteria are not met, the instrument must be recalibrated.

4.3. Initial Calibration Verification

4.3.1. Immediately after the calibration curve, analyze a standard from a source other than that from which the calibration material was obtained.

4.3.2. Criteria

- 4.3.3. The calculated concentration of the ICV must be within the limits supplied by the manufacturer. Cr^{+6} is an inherently unstable analyte. Thus, the ICV solutions and their corresponding limits will change frequently.
- 4.3.4. Corrective action
- 4.3.5. If the ICV criteria are not met, no samples can be analyzed. Perform system maintenance and re-check the ICV. If the criteria still cannot be met, the system must be recalibrated.
- 4.4. Initial Calibration Blank
- 4.4.1. After the analysis of the ICV standard an instrument blank (ICB) is analyzed. The levels of target analytes in the ICB should not exceed the reporting limit.
- 4.4.2. Corrective action
- 4.4.3. If the initial ICB contains target analyte levels above the reporting limit, the system is out of control. The source of contamination must be identified and corrected before proceeding with the analysis.
- 4.5. Method Detection Limit Standard
- 4.5.1. After the calibration is performed, but before the analysis of any sample extracts, an MDL standard is to be analyzed. The MDL standard is used to provide on-going verification of the ability of the system to detect analytes at a concentration near the method detection limit.. It must be detected for the system to be considered in control.
- 4.5.2. Corrective Action
- 4.5.3. If target analytes are not detected, the analysis must be terminated until the problem has been solved. Alternatively, if the affected samples are well above the detection limit (ie bracketed by appropriate standards), they may be reported. No undetected values should be reported if the MDL standard for that analyte(s) is undetected.
- 4.6. Continuing Calibration Verification (CCV) and Blank (CCB)
- 4.6.1. A mid-range calibration standard is analyzed after every 10 samples. Immediately following the CCV, a blank solution is analyzed. In addition, this standard and blank must be the last samples analyzed in the run.

- 4.6.2. The CCV must fall within $\pm 10\%$ of the true value.
- 4.6.3. The levels of target analytes in the CCB should not exceed the reporting limit.
- 4.6.4. Corrective action
- 4.6.5. If CCV limits are exceeded, check calculations or perform instrument maintenance. Recalibrate and reanalyze. No sample results may be reported that are not bracketed by a successful calibration and a CCV which is in control or by preceding and following CCVs which are within limits.
- 4.6.6. If the initial CCB contains target analyte levels above the reporting limit, the system is out of control. The source of contamination must be identified and corrected and the affected samples re-analyzed. As with the CCVs, no sample results may be reported that are not bracketed by a successful initial and continuing calibration blank which are in control or by preceding and following CCBs which are within limits.
- 4.7. Method Blanks
- 4.7.1. Method blanks are used to verify contamination free reagents and apparatus. They are prepared with every set of samples prepared at the same time or at least one blank for every 20 samples, whichever is more frequent. Any analyte response above the detection limit is reported. Method blank control limits are that contamination should not exceed the reporting limit.
- 4.7.2. Corrective action
- 4.7.3. Corrective action may necessitate re-preparation and re-analysis of the sample set. For example if an analyte were found in the blank but not in any of the associated samples then sample group may not require re-analysis. In addition, if sample levels exceed 20 times the blank, the level of contamination may be considered insignificant. In any case, if re-preparation and re-analysis is not being undertaken, the analyst must first discuss the issue with the Quality Control Officer. It is the laboratory's responsibility to ensure that method interferences caused by contaminants in acids, solvents, reagents, glassware, and other sample processing hardware leading to discrete artifacts and/or elevated baselines in the analytical run be minimized. In the extreme case of chronic contamination, blanks may have to be analyzed from each stage of the sample processing to determine the contamination source so it can be eliminated. In all cases where blank contamination exceeds the control limit, a narrative comment must be made which documents the corrective actions taken.

4.8. Method Blank Spikes

- 4.8.1. A method blank spike follows the same protocol as with the matrix spike analysis except that the spiking solution is added to a method blank solution instead of an actual sample. A method blank with added analytes is a method blank spike. A method blank spike is the same as a QC check standard. A blank spike or a standard reference material (SRM) should be analyzed. The SRM is the preferred material. The blank spike should only be analyzed when an SRM is not available. We currently use a material from APG.
- 4.8.2. Corrective action
- 4.8.3. If the MS/MSD recoveries are out of control, the blank spike recoveries are examined to assess whether the method was in control during sample preparation and analysis. Re-prepare and reanalyze any samples for which both the matrix spike recoveries are low and out of control and for which the associated blank spike demonstrates out of control and low recoveries.

4.9. Matrix Spike

- 4.9.1. The method requires a spike be run on every sample matrix to verify that neither a reducing condition nor a chemical interference is affecting color development. The amount of spike added should double the concentration found in the sample, and should be at least 30 ug/L. A sample is chosen at random from the samples to be analyzed, and an aliquot of spiking solution is added to this sample prior to preparation. The analyst should attempt to avoid selecting samples which are identified by the client as blanks. As the purpose of the matrix spike is to test the system under "typical" conditions, the analyst may also avoid selecting the most difficult sample of the batch for spiking. The minimum frequency for MS analysis is 1 each per 20 samples per matrix. This will be best accomplished by running one with every batch for many analyses. This matrix spike sample is used to evaluate the matrix effect of the sample upon recovery of the analytes. The recovery of spike analytes is calculated as follows:

$$\% \text{ recovery} = \frac{(SS - S) * 100}{SA}$$

where:

SS = concentration in spiked sample

S = native concentration in unspiked sample

SA = spiked added, the amount of spiking material actually added to the sample calculated on the sample basis

4.9.2. The recovery criteria are detailed in the current Control Limits Catalog and in the Quality Control Database and will change from time to time.

4.9.3. Corrective action

4.9.4. Samples with spike recoveries outside control limits will be reviewed for possible corrective action. Corrective action will first involve recalculation, followed by possible re-preparation, and/or reanalysis of a diluted aliquot of the sample. This process should also look at the recovery of matrix spiking compounds from the SRM and/or blank spike analysis. In all cases a narrative explanation of the condition is required to detail the corrective actions taken.

4.10. Matrix Spike Duplicate

4.10.1. The compound recovery criteria are identical to those for the matrix spike sample. In addition, the matrix spike duplicate is used measure method precision. This is done by computing the relative percent difference (RPD) between the matrix spike and matrix spike duplicate recovery values. This calculation is as follows:

$$\text{RPD} = \frac{|S1 - S2|}{(S1 + S2)/2} * 100$$

where:

S1 = measured concentration for MS sample

S2 = measured concentration for MSD sample

4.10.2. RPD control limits are detailed in the current Control Limits Catalog and in the Quality Control Database and will change from time to time.

4.11. Sample Duplicate

4.11.1. Criteria

4.11.2. Sample duplicates are required only when the client requests, when CLP practices are employed, or when the method specifically calls for duplicates. At least one duplicate

sample per 20 samples per matrix is required when matrix spikes are being performed. RPD values are calculated in a manner similar to MS/MSD RPDs:

$$\text{RPD} = \frac{|S1 - S2|}{(S1 + S2)/2} * 100$$

where:

S1 = measured concentration in the initial analysis

S2 = measured concentration in the duplicate analysis

4.11.3. The RPD control limits are detailed in the current Control Limits Catalog and in the Quality Control Database and will change from time to time.

4.11.4. Corrective action

4.11.5. If a trend in out of control RPD values is observed, the methods used must be examined to determine the source of variance. Once this source is identified, the method must be changed so that samples can be analyzed with a predictable reproducibility. Generally, if recoveries are in control and no analyte of interest was detected in any of the samples, no immediate action will be taken on that sample set. If integrity of reported sample values is in doubt, re-analysis may be called for. Corrective actions should be discussed with the Quality Control Officer.

5. Operation procedures

5.1. Sample Analysis Sequence

S0
S10
S20
S50
S5
ICV
ICB/PB
Sample 1
Sample 1D (or S, depending upon client needs)
Sample 1S (or MSD, depending upon client needs)
Sample 2
Sample 3
etc
after 10 samples
CCV 1
CCB 1
Sample 11
etc
CCV 2
CCB 2

5.1. Instrumental Conditions

5.1.1. The samples are measured with a Perkin-Elmer UV-VIS spectrophotometer.

- The slit is set at 1 nm
- The integration is set for 2 secs
- The wavelength is 540 nm.
- For low level calibration use the 5 cm cells. The analytical curve may be moved up by using the 1 cm cells.
- The zero standard is used to auto-zero the instrument.

5.2. Analytical Operation

5.2.1. If Cr⁺⁶ in soil is requested, the sample is extracted using the TCLP extraction, SW 846 1311. This is detailed in the applicable Laucks SOP.

5.2.2. Starting with a water sample or aqueous extract:

1. Transfer 95 mls to a 100 ml volumetric flask.
2. Add 2.0 mls of the diphenylcarbazide solution and mix.
3. Adjust the pH to 2.0 ± 0.5 with 10% H_2SO_4 . Use the Corning 155 pH meter, and the epoxy, gel filled electrode.
4. Dilute to 100 mls with DIW.
5. Let the solution stand for 5-10 mins for maximum color development
6. Measure the absorbance at 540 nm using the zero standard as a reference.

5.2.3. If the sample appears to be turbid, it will have to be corrected for. This is done by preparing a second aliquot. This is treated like the sample, except that the diphenylcarbazide is not added. This solution is read and the adsorbance is subtracted from the reading of the sample.

5.2.4. In some instances, the adsorbance reading will be due largely to turbidity. If the reading is greater than the high standard, the sample needs to be diluted and reanalyzed. If the client needs lower reporting limits than this can achieve:

1. Filter an aliquot of the sample, and spike an aliquot of sample and then filter. If the recovery is 85-115%, the method is in control.
2. Analyze the sample by SW 846 7197. This method is not affected by sample turbidity.

5.2.5. Compound Quantification

$$Cr^{+6}, \text{ mg/L} = \text{ Measured concentration at instrument} * \text{ dilution}$$

If a soil sample was analyzed, the mg/L value is divided by the %Total Solids/100.

6. Reports

6.1. Data Packet Organization

6.1.1. Each data package will contain a bench sheet showing all volumes, weights, dilutions, dates and analyst's initials, a copy of the instrumental output, and a copy of the Quality Control report.

6.2. Quality Control Reports

6.2.1. All results for quality control tests are entered into the lab data base using the quality control database. A summary of all data entered must be included in the data packet. The routine minimum is a method blank report, and an MS/MSD or MS/duplicate report. Many analyses will also require an SRM, blank spike or other report.

6.3. Sample Result Reports

6.3.1. Data Qualifying Flags

Sample report results are qualified with data qualifying flags. These flags have the following definitions:

CODE	Definition
-------------	-------------------

U	: The analyte of interest was not detected, to the limit of detection indicated.
---	--

SOP No: LTL-7401
Revision: 0
Date: 02/01/96
Page: 16 of 17
Replaces: none

Appendix II

QC Summary Table

Laucks Testing Laboratories
Method 7196A QA Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Initial Calibration	Multi-point	Multi-point R>.995	One per run	Recalibrate	Printout of calibration
Initial Calibration Verification	Required One per 15 samples	Manufacturer supplied	One per run	Recalibrate or Reanalyze	Printout of result
Initial Calibration Blank	One per batch	< Reporting limit	One per run	Reanalyze	Printout of result
Continuing Calibration Verification	Not required	90-110 % recovery	One after every 10 samples, and at the end of the run.	Recalibrate	Printout of result
Continuing Calibration Blank	Not required	< Reporting limit	One after every 10 samples, and at the end of the run.	Recalibrate	Printout of result
MDL standard recovery	Not required	Detectable	One per run	Recalibrate	Printout of result
Matrix Spike Recovery	85-115 % One per matrix	See QC database	One MS/MSD or one MS/DUP per 20	Dilute and Reanalyze	Printout of result
*MS/MSD RPD	Not Required	See QC database	One MS/MSD or one MS/DUP per 20	Dilute and Reanalyze	Printout of result
*Duplicate % Difference	Not Required	See QC database	One MS/MSD or one MS/DUP per 20	Dilute and Reanalyze	Printout of result

* Either an MSD or a Duplicate will be analyzed

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-7601

Title: **Spot Test for the Presence of Ferrous Iron (Fe⁺²) in Soil.**

Revision history:

<u>Number</u>	<u>Date</u>
0	04/09/97

Written by: Jim Owens Date: 4-9-97
Jim Owens, Principal

Reviewed by: Harry Romberg Date: 4-9-97
Harry Romberg, QA Officer

Approved by: Karen J. Kotz Date: 4/9/97
Karen Kotz, Laboratory Director

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 4.2 Corrective Action3
5. Operation procedures3
6. Data Reporting4
7. References4

1. Introduction and Scope

1.1 Method Description

- 1.1.1 This method covers the procedure for the qualitative determination of Ferrous (reduced) iron in soil.

2. Equipment List and Standards

2.1 Equipment

- 2.1.1 Test tube, 10 or 20 ml.
2.1.2 Spot plate
2.1.3 Eye dropper

2.2 Reagents

- 2.2.1 *a,a'*-dipyridyl solution - prepared by adding 0.1 gram of *a,a'*-dipyridyl in 10 mls of ethanol and bring to 100 ml. final volume with Type II water.

3. Safety precautions

3.1 Safety Precautions

- 3.1.1 All standards, samples and sample solutions should be handled as if they are hazardous substances.

4. Quality Control

4.1 Laboratory Duplicate

- 4.1.1 At least one sample duplicate per 10 samples is required.

4.2 Corrective Action

- 4.2.1 The duplicate portion of the sample should reproduce the same qualitative results as the initial aliquot. If the duplicate results do not confirm the first analysis the sample should be mixed thoroughly and two new aliquots taken for confirmation

5. Operation procedures

- 5.1.1 Add approximately 5 grams of representative soil to a test tube or other appropriate container. If the soil is lumpy, gently break up the sample using a mortar and pestle, if necessary.
- 5.1.2 Add approximately 20 mls. of deionized water and shake or mix for about one minute. Let settle until the supernatant is relatively clear, approximately 10 minutes.

- 5.1.3 With an eye dropper transfer approximately 1 ml. of supernatant to a spot plate. Alternately, approximately one to two grams of soil may be placed directly on the spot plate. Add several drops of the dipyrityl solution to the spot plate.
- 5.1.4 If ferrous iron is present a definite reddish-pink color change will develop within two to three minutes. The intensity of the color is indicative of the ferrous iron concentration.

6. Data Reporting

- 6.1.1 All reagent preparation must be documented in the Inorganics logbooks. All reagents must be traceable to the original stock or neat material.
- 6.1.2 The analyst must record the following information on the analytical benchsheet: date, analyst initials, Laucks sample identification number, sample and quality control results. Indicate the intensity of the color development, if any.
- 6.1.3 Copies of the above documentation must be placed in each applicable workorder file for long term document storage.

7. References

- 7.1.1 Spot Test in Inorganic Analysis, by Fritz Feigl, 1958.

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-8082

Title: Analysis of Organochlorine Pesticides/PCBs by USEPA CLP SOW, Including Revisions Through OLM03.1

Revision history:

Number	Date
1	01/28/93
2	08/15/94
3	03/10/97

UNCONTROLLED

Revised by: *Cheryl DeBoer*
Cheryl DeBoer, GC Chemist

Date: 3-10-97

Approved by: *Karen J. Kotz*
Karen Kotz, Laboratory Director

Date: 3/10/97

Approved by: *Harry Romberg*
Harry Romberg, QC Officer

Date: 3-10-97

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1. Introduction and Scope

1.1. Method Description

1.1.1. This document describes procedures and specifications for the instrumental analysis of chlorinated pesticides and Aroclors. The analysis is accomplished by gas chromatography utilizing a two-column electron capture detector technique. The intent of this document is to supplement the USEPA Contract Laboratory Protocol - Statement Of Work rev. OLM03.1. and as such, will mainly address optional instructions from the SOW.

1.1.2. This method is restricted to use by, or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of chromatograms. Each analyst performing this method must have demonstrated the ability to perform the described chromatographic analysis and/or data interpretation.

1.2. Sample Collection, Sample Storage, Holding Times

1.2.1. Samples are normally collected in glass containers with Teflon-lined caps. All samples and sample extracts are stored at 4°C. Water samples must be extracted within 5 days of sample receipt, soil samples within 10 days of sample receipt for USEPA (for all other in-house assignments, the holding times are 7 days for water samples and 14 days for soil samples - from sample collection date). All extracts must be analyzed within 40 days of sample preparation.

1.3. Definition of Terms

1.3.1. This section defines terms and acronyms as they are used in this SOP. Other terms, such as MS/MSD or method blank, are not defined here since it is assumed that the user of this SOP already understands their more general meaning.

1.3.2. Batch Identifier A number given to each sample delivery group which uniquely identifies that batch. This number is generally six or seven digits and is unique to the client/project.

1.3.3. Blank spike A background free matrix (DIW for water, clean sand for soils/sediments) to which known amounts of target analytes and surrogates are added each time sample extracts are prepared. Blank spikes are required on all HAZWRAP and NEESA work. In the context of this SOP, a blank spike is the same as a QC check standard. See also QC check standard.

- 1.3.4. CCV Continuing calibration verification. This is a standard analyzed at some prescribed frequency during the analysis sequence to verify that the instrument has remained in calibration.
- 1.3.5. CF Calibration factor. The ratio of analyte instrument response to nanograms injected. This term is defined in the same way in both the CLP contract and SW 846.
- 1.3.6. CLP Contract Laboratory Program. The USEPA program that contracts with laboratories to provide laboratory services. The term has come to mean a much broader set of methods and deliverables. In the context of this SOP, CLP means procedures or operations which are detailed in the CLP contract and which are extended to a broader working definition.
- 1.3.7. Corr Coef, CC Correlation coefficient. A measure of the "goodness of fit" of a set of data to a regression model. The closer the value is to 1, the higher the degree of confidence in the correlation.
- 1.3.8. CRQL Contract Required Quantitation Limit - The value used when reporting a non-detect. This is contractually set.
- 1.3.9. DIW Deionized water. Lab reagent water. Organic-free water. Since the systems used to provide DIW at Laucks all contain carbon polishing filters, they are capable of providing organic-free water for use in method blanks and method blank spikes.
- 1.3.10. %D Percent Difference - The difference between two concentrations, expressed as a percent. Mathematically: the lower concentration is subtracted from the higher concentration, the difference is then divided by the lower concentration and that value is multiplied by 100. A %D of greater than 25% between two concentrations on different columns causes the result chosen (the lower concentration) to be flagged with a "P".
- 1.3.11. PIBLK Instrument blank. Blank solvent containing the method surrogates is injected into the instrument to monitor for carry over between sample extract injections.

- 1.3.12. QC period Quality control period. An analysis sequence initiated by the analysis of one or more standards, followed by sample extracts/digests, and terminated with a standard analysis. A QC period can be open-ended chronologically, but calibration verification must be documented using the procedures in this SOP.
- 1.3.13. RSD or %RSD Relative standard deviation or percent relative standard deviation. The ratio of the standard deviation of a set of values to the mean of the set of values expressed as a percentage. A measure of the similarity of the values one to another.
- 1.3.14. RT, Retention time The time (in minutes) at which a target analyte elutes from a chromatography column.
- 1.3.15. RT window Retention time window. The +/- value which is applied to the ICV to establish the time range used to make tentative compound identifications.
- 1.3.16. Sequence A set of sample extracts/digests and standard solutions introduced into an instrument in a chronologically continuous group. See also QC period.

2. Equipment List and Standards

2.1. Chromatographic System

2.1.1. A gas chromatograph with a fully programmable oven, heated injection port, autosampler, and an electronic data acquisition system capable of raw data storage.

GC system including an HP5890 GC, 7673 autosampler, 18652A or 35900A analog to digital converter, EZChrom acquisition software, and Target software, which is used for data processing.

Two each - Electron Capture Detectors (HP model 19233).

Two each - Dissimilar chromatographic columns, 0.53mm ID or 0.45mm ID, fused silica.

The lab currently has different combinations in use:

5890A: DET A; DB-608,	DET B; DB-5	0.53mmx30m
5890B: DET A; DB-5,	DET B; DB-608	0.53mmx30m
5890M: DET A; DB-5,	DET B; DB-608	0.53mmx30m

Note: Equivalent or better equipment may be substituted for the above at any time.

2.1.2. Consult maintenance logs found directly next to each instrument for details on programs and flow settings.

2.1.3. Gasses used are Helium carrier gas, Argon-5% Methane makeup gas, both high purity grades. The column carrier gas used is high purity helium with a high capacity heated water and oxygen scrubber followed with an indicator water and oxygen trap. Make-up gas is 5% Methane/Argon with high capacity water and oxygen scrubbers followed with an indicator water and oxygen trap.

2.1.4. Column flows are set at about 8.0 mls per minute. Consult individual maintenance logs for exact settings. These flows are set with an electronic bubble meter connected down stream of the detector with the make-up gas shut off at its source. Make-up gas flow is approximately 70 mls/minute.

2.1.5. All GC instruments in use are configured with an HP split/splitless injection port in the splitless injection mode. The liner is a straight through type (HP PN 19251-60540) with a small amount of silanized glass wool place just above the column end. The column is positioned 2 to 3 mm above a thick, gold plated end washer in the GC inlet.

2.2. Standards

2.2.1. Individual Standard Solution Concentrations(ng/mL) in Hexane

The standards listed below are prepared from certified materials. All working level standards are prepared in hexane (solvent), every six months, unless otherwise specified.

Pesticide Standard Mix A: Compound	INDAL STD1	INDAM STD2	INDAH STD3
1. Tetrachloro-m-xylene	5.0	20.0	80.0
2. alpha-BHC	5.0	20.0	80.0
3. gamma-BHC (Lindane)	5.0	20.0	80.0
4. Heptachlor	5.0	20.0	80.0
5. Endosulfan I	5.0	20.0	80.0
6. Dieldrin	10.0	40.0	160.0
7. Endrin	10.0	40.0	160.0
8. 4,4'-DDD	10.0	40.0	160.0
9. 4,4'-DDT	10.0	40.0	160.0
10.Methoxychlor	50.0	200.0	800.0
11.Decachlorobiphenyl	10.0	40.0	160.0
12.Isodrin	12.5	50.0	200.0

Pesticide Standard Mix B: Compound	INDBL STD1	INDBM STD2	INDBH STD3
1. Tetrachloro-m-xylene	5.0	20.0	80.0
2. beta-BHC	5.0	20.0	80.0
3. delta-BHC	5.0	20.0	80.0
4. Aldrin	5.0	20.0	80.0
5. Heptachlor epoxide	5.0	20.0	80.0
6. gamma-Chlordane	5.0	20.0	80.0
7. alpha-Chlordane	5.0	20.0	80.0
8. 4,4'-DDE	10.0	40.0	160.0
9. Endosulfan II	10.0	40.0	160.0
10. Endrin aldehyde	10.0	40.0	160.0
11. Endosulfan sulfate	10.0	40.0	160.0
12. Endrin ketone	10.0	40.0	160.0
13. Decachlorobiphenyl	10.0	40.0	160.0
14. Isodrin	12.5	50.0	200.0

2.2.2. Resolution Check Mix (ng/mL) in Hexane

<u>Compound</u>	<u>Conc.</u>
1. gamma-Chlordane	10.0
2. Endosulfan I	10.0
3. 4,4'-DDE	20.0
4. Dieldrin	20.0
5. Endosulfan sulfate	20.0
6. Endrin ketone	20.0
7. Methoxychlor	100.0
8. Tetrachloro-m-xylene	20.0
9. Decachlorobiphenyl	20.0
10. Isodrin	50.0

2.2.3. Performance Evaluation Mix (PEM) (ng/mL) in Hexane
(PEM mixture is prepared weekly in Hexane.)

<u>Compound</u>	<u>Conc.</u>
1.alpha-BHC	10.0
2.beta-BHC	10.0
3.gamma-BHC(Lindane)	10.0
4.Endrin	50.0
5.4,4'-DDT	100.0
6.Methoxychlor	250.0
7.Tetrachloro-m-xylene	20.0
8.Decachlorobiphenyl	20.0
9.Isodrin	50.0

2.2.4. Pest Spike Mix solution (ug/mL) in Acetone

<u>Compound</u>	<u>Conc.</u>
1. gamma-BHC (Lindane)	0.5
2. Heptachlor	0.5
3. Aldrin	0.5
4. Dieldrin	1.0
5. Endrin	1.0
6. 4.4'-DDT	1.0

2.2.5. Surrogate Solution (ug/mL) in acetone.

<u>Compound</u>	<u>Conc.</u>
1. Tetrachloro-m-xylene	0.2
2. Decachlorobiphenyl	0.2
3. Isodrin	0.5

2.2.6. Multicomponent standard solutions (ng/mL) in Hexane

<u>Compound</u>	<u>Conc.</u>
Aroclor 1016/1260	100.0
Aroclor 1221	200.0
Aroclor 1232	100.0
Aroclor 1242	100.0
Aroclor 1248	100.0
Aroclor 1254	100.0
Toxaphene	500.0

These multi-component standards contain the following surrogates at the levels listed:

<u>Surrogate</u>	<u>Conc.</u>
Tetrachloro-m-xylene	20.0
Decachlorobiphenyl	20.0
Isodrin	50.0

2.2.7. PIBLK solution (ng/mL) in Hexane

<u>Compound</u>	<u>Conc.</u>
Tetrachloro-m-xylene	20.0
Decachlorobiphenyl	20.0
Isodrin	50.0

2.2.8. Please Refer to Appendix I for detailed listing of all stock standard mixtures.

3. Safety precautions and Waste Disposal

3.1. Routine Safety Precautions

3.1.1. All standards and sample extracts should be handled as if they contain hazardous substances.

3.1.2. Refer to the instrument manufacturer's manual for routine instrument precautions.

3.1.3. Routine precautions include an awareness of the moving parts on the instrument you're using. These parts are often charged with power from an electrical component or with high pressure gas and have the potential to do harm if not used properly.

3.1.4. Electrical shock - All instruments present the possibility of electrical shock. The operator should take all precautions including ensuring that all instruments are operated with fully

3.1.5. Grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.

3.1.6. The electron capture detectors contain a radioactive source and caution should be used when working with the detectors.

3.2. Waste disposal

3.2.1. The sample extracts, standards, and solvent rinses are disposed of by depositing them in the hazardous waste container located in the GC area sample preparation area - Fume hood.

3.2.2. Waste segregation and disposal from the point of collection is further covered in Laucks SOP on Waste Disposal.

4. Calibration and Quality Control

4.1. Contract Required Detection Limits

4.1.1. The CLP SOW states the following Contract Required Detection Limits for Pesticides and PCBs.

<u>Analyte</u>	<u>Water (ug/L)</u>	<u>Soil (ug/Kg)</u>
alpha-BHC	0.050	1.7
beta-BHC	0.050	1.7
delta-BHC	0.050	1.7
gamma-BHC (Lindane)	0.050	1.7
Heptachlor	0.050	1.7
Aldrin	0.05	1.7
Heptachlor Epoxide	0.050	1.7
Endosulfan I	0.050	1.7
Dieldrin	0.10	3.3
4,4'-DDE	0.10	3.3
Endrin	0.10	3.3
Endosulfan II	0.10	3.3
4,4'-DDD	0.10	3.3
Endosulfan sulfate	0.10	3.3
4,4'-DDT	0.10	3.3
Methoxychlor	0.50	17.
Endrin ketone	0.10	3.3
Endrin aldehyde	0.10	3.3
alpha-Chlordane	0.050	1.7
gamma-Chlordane	0.050	1.7
Toxaphene	5.0	170.
Aroclor-1016	1.0	33.
Aroclor-1221	2.0	67.
Aroclor-1232	1.0	33.
Aroclor-1242	1.0	33.
Aroclor-1248	1.0	33.
Aroclor-1254	1.0	33.
Aroclor-1260	1.0	33.

4.2. Retention Time Windows

4.2.1. Refer to the detailed discussion in Appendix V on the determination of absolute retention times as required by the CLP SOW.

4.3. Initial Multi-Point Calibration

4.3.1. Inject the standard solutions in the order specified in appendix II using evaluation criteria and corrective action specified in that appendix.

4.4. External Standard Calibration

4.4.1. External standard initial calibration data is evaluated by the %RSD.

4.4.2. CFs are calculated using the equation:

$$CF = \frac{\text{response}}{\text{ng injected}}$$

4.4.3. The calculated CFs are tabulated and the %RSD calculated.

4.4.1. Corrective action

4.4.1.1. If the criteria are not met, the instrument must be re calibrated.

4.5. Instrument Blank

4.5.1. After the analysis of the Initial calibration and prior to any continuing calibration verification standards, an instrument blank (PIBLK) is analyzed. This is to verify that there is no carryover between sample injections. Evaluation criteria are detailed in Appendix VII.

4.5.2. Any sample that is suspected of containing high concentrations of target analytes should be followed by a PIBLK. This PIBLK analysis is used only to make a judgment as to the possibility of carry-over into the sample extract immediately following the PIBLK.

4.6. Continuing Calibration Verification

4.6.1. The mid-range calibration standards (INDAM and INDBM) or a PEM is analyzed at the frequency detailed in the sample analysis section. In addition, these standards must be the last injection made in the analysis sequence. Evaluation criteria are detailed in Appendix IV.

4.6.2. Corrective action

4.6.2.1. The CF for each compound is calculated and the percent difference is calculated. The %D results cannot exceed the detailed CCV criteria listed in Appendix IV.

4.7. Chromatographic Resolution

4.7.1. A resolution check must be performed with every initial calibration. This check uses a separate solution, the resolution check mix (RESCHK). The resolution measured must meet the criteria detailed below.

4.7.2. Criteria

4.7.2.1. The resolution criterion is that the height of the valley between two adjacent peaks in the Resolution Check Mixture must not be greater than 60% of the height of the shorter peak. The poorest resolution on the DB-608 column probably will be between DDE and Dieldrin, between Methoxychlor and Endrin ketone and between Endosulfan I and gamma-Chlordane. On the DB-1701 column, resolution difficulties most frequently occur between Endosulfan I and gamma-Chlordane, and between Methoxychlor and Endosulfan sulfate.

4.7.3. Corrective action

4.7.3.1. Perform system maintenance and re-analyze the resolution check standard. If satisfactory resolution cannot be demonstrated, no sample extracts can be analyzed.

4.8. Updating Retention Time Windows

4.8.1. The retention times for all target analytes must fall within the RT windows established by the Initial Calibration.

4.9. Instrument Blank

4.9.1. Criteria

4.9.1.1. There must be no detectable levels of target analytes in the initial PIBLK. Other PIBLKS cannot exhibit a concentration exceeding 1/2 of the CRQL.

4.9.2. Corrective action

4.9.2.1. If the initial PIBLK contains measurable levels of target analytes the system is out of control. The source of contamination must be identified and corrected. Please refer to Appendix VII for more detailed information.

4.10. Continuing Calibration Verification/Performance Evaluation Mix

4.10.1. A set of INDAM and INDBM standards or a PEM is analyzed every 12 hours.

4.10.1. Criteria

4.10.1.1. After every 12 hours a set of INDAM and INDBM standards or a PEM is analyzed.
The CF for each compound is calculated and the percent difference is calculated as follows.

$$\%D = \frac{CF_i - CF_c}{CF_i} \times 100 \quad \text{or} \quad \%D = \frac{C_i - C_c}{C_i} \times 100$$

where:

CF_i = CF from ICV standard

CF_c = CF from CCV standard

4.10.1.2. The %D results cannot exceed the detailed CCV criteria.

4.10.1.3. The retention times for all target analytes must fall within the RT windows established by the ICV.

4.10.2. Corrective action

4.10.2.1. Check calculations or perform instrument maintenance. To validate the quantification of target analytes in analytical samples, the samples must be bracketed by in-control CCVs. However, CCV CFs can be outside the control limits as long as the corresponding samples contain no detectable levels of the target analyte for which the CF is out of control, the CF value exceeds the upper control limit (i.e., there is increased sensitivity). Algebraically, this means a greater negative percent difference than the control limit.

4.11. Method Blanks

4.11.1. Criteria

4.11.1.1. Method blanks are used to verify contamination free reagents and apparatus. They are prepared with every set of samples extracted at the same time at least one blank every 20 samples which ever is more frequent. Any analyte response above the detection limit is reported. Method blank cannot contain any analyte at greater than the CRQL. The surrogate retention times must be within the retention time windows calculated from the initial calibration sequence, and surrogate recoveries must fall within the 30-150% recovery limits. These limits are not advisory for method blanks.

4.11.2. Corrective action

4.11.2.1. If surrogate recoveries are out of control, check all calculations. If no calculation errors are detected, reanalyze the method blank. If surrogates are still out of control, all samples associated with the method blank must be re-extracted.

4.11.2.2. If analytes are present in the blank above the CRQL, first reanalyze the method blank. If the method blank criteria are still not met, all samples associated with the method blank must be re-extracted and reanalyzed.

4.12. Matrix Spike

4.12.1. Criteria

4.12.1.1. A sample is either chosen at random or designated by the client. An aliquot of spiking solution is added to this sample prior to extraction. It is not required that a matrix spike analysis be performed with each extraction batch, however, the minimum frequency for MS analysis is 1 each per 20 samples per matrix. This matrix spike sample is used to evaluate the matrix effect of the sample upon recovery of the analytes. The recovery of spike analytes is calculated as follows:

$$\% \text{ recovery} = \frac{SS - S}{SS} \times 100$$

where:

SS = concentration in spiked sample

S = native concentration in unspiked sample

4.12.1.2. Recovery control limits are detailed in Appendix VIII.

4.12.2. Corrective action

4.12.2.1. Samples with spike recoveries outside control limits will be reviewed for possible corrective action. This process should look at the recovery of surrogate compounds in the MS sample and at the recovery of matrix spiking compounds from the extraction batch blank spike analysis. In all cases a narrative explanation of the condition is required to detail the corrective actions taken.

4.13. Matrix Spike Duplicate

4.13.1. Criteria

4.13.1.1. The compound recovery criteria are identical to those for the matrix spike sample. In addition, the matrix spike duplicate is used measure method precision. This is done by computing the relative percent difference (RPD) between the matrix spike and matrix spike duplicate recovery values. This calculation is as follows:

$$\% RPD = \frac{|S_1 - S_2|}{(S_1 + S_2)/2} \times 100$$

where:

S_1 = measured concentration for MS sample
 S_2 = measured concentration for MSD sample

4.13.1.2. RPD control limits are detailed in Appendix VIII.

4.13.2. Corrective action

4.13.2.1. Samples with spike recoveries or RPDs outside control limits will be reviewed for possible corrective action. This process should look at the recovery of surrogate compounds in the MS sample and at the recovery of matrix spiking compounds from the extraction batch blank spike analysis. In all cases a narrative explanation of the condition is required to detail the corrective actions taken.

4.14. Surrogate Recovery

4.14.1. Criteria

4.14.1.1. Surrogates are chemically similar compounds added to every sample, method blank, and QC sample prior to sample processing. They are used to monitor for potential sample processing errors and matrix effects. Surrogate compound recoveries are calculated as follows:

$$\% \text{ recovery} = \frac{S_m \times 100}{S_a}$$

where:

S_m = concentration of surrogate measured in extract
 S_a = concentration of surrogate added

4.14.1.2. Detailed surrogate recovery control limits are tabulated in Appendix VII.

4.14.2. Corrective Action

- 4.14.2.1. Check calculations for possible error. Low surrogate recoveries are greater potential indicators of poor method performance than high surrogate recovery since non-GC/MS methods cannot separate co-eluting interferences. Hence corrective action is not required for high surrogate recoveries.
- 4.14.2.2. Low surrogate recoveries in the method blank may require that all the samples in the associated batch be re-extracted and re-analyzed. In any case, it is imperative to identify the problem associated with low recovery so that it can be corrected. It is a requirement that all out of control surrogate recoveries and the corrective action taken be discussed in the narrative.

5. Operation procedures

5.1. Chromatographic Conditions

- 5.1.1. Consult the individual maintenance log books for specific conditions. The following are general operating parameters used on gas chromatographs that are used for CLP pesticides. These conditions are maintained on 5890A, 5890B, and 5890M Gas Chromatographs.

Carrier Gas:	Helium
Column Flow:	8 mL/min
Make-up Gas:	Argon/Methane-5% (high purity)
Make-up Flow:	70 mls/min.
Injector Temperature:	205 °C
Injection:	On-column
Injection Volume:	1 µL
Injector:	Grob-type, splitless
Initial Temperature:	150 °C
Initial Hold Time:	0.5 min.
Temperature Ramp:	4 °C/min.
Final Temperature:	275 °C
Final Hold Time:	11.0 min.
ECD Temperature:	350 °C

The above conditions must be used for the analysis of all standards, samples, blanks, and MS/MSDs.

5.2. Sample Analysis

5.2.1. Analysis sequence

- 5.2.1.1. See Appendix II for a detailed analysis injection sequence.

5.2.2. Compound Identification

- 5.2.2.1. Compounds are tentatively identified if a peak elutes in the retention time window characteristic of that compound on the primary column. To confirm the presence of that compound in the sample extract, the peak must also elute in its characteristic retention time window on a second column. Retention time windows are established as previously described and are updated each QC period. Compounds can only be identified if the ICV and CCV criteria previously detailed are strictly adhered to.

5.2.2.2. The experienced analyst's judgment weighs heavily in evaluating chromatograms for compound identification. For instance, the retention times of surrogate compounds may be outside their expected windows due to sample matrix effects. The analyst may decide to re-adjust the target analyte's retention time windows on an ad hoc basis based on such an observed shift. The data processing software allows the operator to increase the retention time window half-width beyond the method- specified width. This can occur only on a sample-specific basis and is used when the analyst examining the data suspects that a retention time shift has occurred. If this is done, it must be fully documented in the case narrative notes.

5.2.3. Compound Quantitation

Target compound concentrations are calculated using the following equations:

5.2.3.1. Aqueous samples

5.2.3.2. The external standard equation, as expressed in CLP SOW is:

$$\text{Concentration } \mu\text{g/L} = \frac{(A_x) (V_t) (Df) (GPC)}{(CF) (V_o) (V_i)}$$

Where:

A_x = Response (area or height) of the peak for the compound to be measured.

CF = Calibration factor for the midpoint concentration external standard (area per ng).

V_o = Volume of water extracted in milliliters (mL).

V_i = Volume of extract injected in microliters (μL). (If a single injection is made onto two columns, use one half the volume in the syringe as the volume injected onto each column.)

V_t = Volume of the concentrated extract in microliters (μL).

GPC = GPC factor. $GPC = 1$ if no GPC clean-up was performed or $GPC = 2$ if GPC clean-up was performed.

Df = Dilution factor. The dilution factor for analysis of water samples by this method is defined as follows.

$$\frac{\mu\text{L most conc. extract used to make dilution} + \mu\text{L clean solvent}}{\mu\text{L most conc. extract used to make dilution}}$$

If no dilution is performed, $Df = 1.0$.

5.2.3.3. Non-aqueous samples

5.2.3.4. The results calculation for non-aqueous samples is very similar to that for aqueous samples. The only difference is the inclusion of a total solids term to calculate the dry weight equivalent of the initial sample size.

$$\text{Concentration (Dry weight basis) ug/Kg} = \frac{(A_x) (V_t) (Df) (GPC)}{(CF) (V_i) (W_s) (D)}$$

Where:

A_x and CF are as given for aqueous samples above.

V_t = Volume of the concentrated extract in microliters (μL). (This volume must be 5000 μL .)

V_i = Volume of extract injected in microliters (μL). (If a single injection is made onto two columns, use one half the volume in the syringe as the volume injected onto each column.)

D = $[100 \times (\% \text{ Moisture})] / 100$

W_s = Weight of sample extracted in grams (g).

GPC = A factor used to account for the amount of extract that is lost as a result of GPC clean-up. If GPC clean-up is performed, the factor = 2. If GPC was not performed, the factor = 1. Note that GPC clean-up is required for all soil sample extracts.

Df = Dilution factor. The dilution factor for analysis of water samples by this method is defined as follows.

$$\frac{\mu\text{L most conc. extract used to make dilution} + \mu\text{L clean solvent}}{\mu\text{L most conc. extract used to make dilution}}$$

If no dilution is performed, $Df = 1.0$.

6. Reports

6.1. Data Packet Organization

6.1.1. See Appendix III for a check list detailing data packet organization.

6.2. Quality Control Reports

6.2.1. All results for quality control tests are entered into the lab data base. Printouts of all data entered must be included in the data packet. The routine minimum is a method blank report, a method blank spike report, and an MS/MSD report.

6.3. Sample Result Reports

6.3.1. Data Qualifying Flags

Sample report results are qualified with data qualifying flags. These flags have the following definitions:

<u>Code</u>	<u>Definition</u>
U	The analyte of interest was not detected, to the reporting limit indicated.
B	The analyte of interest was detected in the method blank associated with the sample, as well as in the sample itself. The B flag is applied without regard to the relative concentrations detected in the blank and sample.
J	The analyte of interest was detected below the Contract Required Quantitation Limit (CRQL) but above 1/2 of the CRQL. This value should be regarded as an estimate.
D	The value reported is derived from the analysis of a diluted sample or sample extract.
P	When a dual column /dual detector GC technique is employed, this flag indicates that calculated results from the two determinations differ by more than 25%. Generally, we report the lower value.
E	The value reported is based on a sample or sample extract in which the target analyte concentration exceeded the calibration range. The value reported should be considered an estimate.
C	The target analyte's presence was confirmed by GC/MS.

6.4. Control Chart(s)

6.4.1. The recovery values for gamma-BHC (Lindane), Heptachlor, Aldrin, Aroclor 1260, Tetrachloro-m-xylene, Decachlorobiphenyl, and Isodrin in the LCS are plotted on control charts. Corrective action should be employed for instances where the recovery exceeds control limits even once, where recovery exceeds the same warning limit on 3 consecutive occasions, where recovery is on the same side of the mean for more than 8 consecutive points, or where there is any obvious cyclical occurrence or obvious pattern.

7. References

- 7.1. USEPA CLP Statement Of Work, Revision OLM03.1, August 1994
- 7.2. Method for Instrumental Analysis of Organochlorine Pesticides and PCBs, Laucks Testing Labs SOP, September 1989

APPENDIX I

Standard Solution Concentrations, units

-Pesticide Matrix Spike Mix, Supelco Cat.#4-8449
-Pesticide Standard Mix A, Restek Cat.#32003
-Pesticide Standard Mix B, Restek Cat.#32004

- 1.1 High level A and B mixtures are made at 16 times the prescribed level of the low level standard. These standards are made in hexane every 6 months, or more frequently if the condition of the standard warrants it. Isodrin is present as an optional third surrogate at 50 ppb in the midpoint concentration levels.
- 1.2 Aroclors are dilutions of EPA stocks.
- 1.3 PEM - This standard is made from a dilution of a certified Restek stock standard; Cat.#32002.
- 1.4 All performance evaluation mixtures stock dilutions are made weekly in hexane. Isodrin is present as an optional third surrogate at 50 ppb. This standard is made fresh weekly.
- 1.5 Resolution Check Mixture - This standard is made from a dilution of a certified Restek stock standard; Cat.#32001.
- 1.6 All resolution check mixture stock dilutions are made in hexane. Isodrin is present as an optional third surrogate at 50 ppb. This standard is made fresh every six months.
- 1.7 Surrogates are made from neat materials: DCB source is Chem Service. TCMX source is Aldrich. Isodrin source is Aldrich.
- 1.8 These standards are made in hexane. Isodrin is present as an optional third surrogate at 50 ppb in the midpoint concentration levels.
- 1.9 The supplier names and catalog numbers listed are for reference only. Certified standards from different manufacturers may be substituted at any time.

APPENDIX II

Analysis Sequence

This section is referenced to section III D (6.1 to 6.2) of USEPA CLP SOW OLM03.1 contract.

6. Initial Calibration

6.1 Initial Calibration Sequence

6.1.1 Before any samples are analyzed, it is necessary to complete the initial calibration sequence given below.

NOTE: Steps 16 and 17 are used as part of the calibration verification as well (see appendix IV).

INITIAL CALIBRATION SEQUENCE

1. Resolution Check
2. Performance Evaluation Mixture
3. Aroclor 1016/1260
4. Aroclor 1221
5. Aroclor 1232
6. Aroclor 1242
7. Aroclor 1248
8. Aroclor 1254
9. Toxaphene
10. Low Point Standard A
11. Low Point Standard B
12. Midpoint Standard A
13. Midpoint Standard B
14. High Point Standard A
15. High Point Standard B
16. Instrument Blank
17. Performance Evaluation Mixture

6.1.2 Samples may be analyzed only after the initial calibration acceptance criteria (6.2) are met. Otherwise, the analytical system is not functioning adequately for use with this protocol.

6.1.3 The initial calibration may continue to be used as long as the analytical system remains under control. The proof that the analytical system is under control is provided by the analyses of the Performance Evaluation Mixtures. If those analyses do not meet the criteria described in

appendix IV, appropriate corrective action must be taken, and the initial calibration sequence must be repeated. The calibration sequence must also be repeated if any major change in instrument hardware or instrument parameters is made (e.g., if a new column is installed or if the detector temperature is changed).

6.2 Initial Calibration Acceptance Criteria

6.2.1 The initial calibration sequence must be analyzed in the order listed in paragraph 6.1 using the GC/ECD operating conditions described in paragraph 5.1.1. The standards must be prepared according to Section 2.2 of this SOP. Calculate the calibration factors and retention times according to paragraph 9.2.2 of Appendix VI.

6.2.2 The resolution criterion is that the height of the valley between two adjacent peaks in the Resolution Check Mixture must not be greater than 60% of the height of the shorter peak. The poorest resolution on the DB-608 column probably will be between DDE and Dieldrin, between Methoxychlor and Endrin ketone and between Endosulfan I and gamma-Chlordane. On the DB-1701 column, resolution difficulties most frequently occur between Endosulfan I and gamma-Chlordane, and between Methoxychlor and Endosulfan sulfate.

6.2.3 The breakdown of DDT and Endrin in both of the Performance Evaluation Mixtures must be less than 20.0 percent, and the combined breakdown of DDT and Endrin must be less than 30.0 percent where

$$\% \text{ Breakdown DDT} = \frac{\text{Amount found in ng (DDD+DDE)} * 100}{\text{Amount in ng of DDT injected}} \quad \text{EQ.1}$$

$$\% \text{ Breakdown Endrin} = \frac{\text{Amount found in ng (Endrin Aldehyde + Endrin ketone)} * 100}{\text{Amount of Endrin injected in ng}} \quad \text{EQ.2}$$

$$\text{Combined \% Breakdown} = \% \text{ Breakdown DDT} + \% \text{ Breakdown Endrin} \quad \text{EQ.3}$$

- 6.2.4 All single component pesticide and surrogate peaks in both runs of the Performance Evaluation Mixtures must be greater than or equal to 90.0 percent resolved on each column.
- 6.2.5 The relative percent difference of the calculated amount and the true amount from each of the single component pesticides and surrogates in both of the PEMs must be less than or equivalent to 25.0 percent, using equation 4 of Appendix IV paragraph 7.1.
- 6.2.6 At least one chromatogram from each of the two Individual Standard Mixtures A and B, run during the initial calibration, must yield peaks that give recorder deflections of 50 to 100 percent of full scale.
- 6.2.7 The resolution between any two adjacent peaks in the midpoint concentrations of Individual Standard Mixtures A and B in the initial calibration must be greater than or equal to 90.0 percent.
- 6.2.8 The % RSD of the calibration factors for each single component analyte and surrogate must be less than or equal to 20.0 percent, except alpha-BHC and delta-BHC. The %RSD of the calibration factors for alpha-BHC and delta-BHC must be less than or equal to 25.0 percent. The %RSD of the calibration factors for the two surrogates must be less than or equal to 30.0 percent. Up to two single component target compounds (but not surrogates) per column may exceed the 20.0 percent limit for % RSD (25.0 % for alpha-BHC and delta-BHC), but those compounds must have a % RSD of less than or equal to 30.0 percent.
- 6.2.9 The absolute retention times of each of the single component pesticides and surrogates in both runs of the PEM must be within the retention time windows determined from the three-point initial calibration.
- 6.3 Corrective Action.
- 6.3.1 If the technical acceptance criteria for the initial calibration are not met, inspect the system for problems. It may be necessary to change the column, bake out the detector, clean the injection port, or take other corrective actions to achieve the acceptance criteria.
- 6.3.2 Contamination should be suspected as a cause if the detector cannot achieve acceptable linearity using this method. In the case of light contamination, baking out the detector at an elevated temperature (350 °C) should be sufficient to achieve acceptable performance. In the case of heavy contamination, passing hydrogen through the detector 1-2 hours at an elevated temperature may correct the problem. In the case of severe contamination, the detector may require servicing by the ECD manufacturer. **DO NOT OPEN THE DETECTOR. THE ECD CONTAINS RADIOCHEMICAL SOURCES.**

6.3.3 If the laboratory cleans out a detector using an elevated temperature, the ECD electronics must be turned off during the bake out procedure.

6.3.4 After bake out or hydrogen reduction, the detector must be recalibrated using the initial calibration sequence.

6.3.5 Initial calibration technical acceptance criteria **MUST** be met before any samples or required blanks are analyzed. Any samples or required blanks analyzed after the initial calibration criteria have not been met will require reanalysis.

APPENDIX III

Data Packet Check List

Organics Complete SDG FILE (CSF) Inventory Sheet (FORM DC-2-2) for PEST/PCB Data:

6. Pesticides

REQUIREMENT	DESCRIPTION	(notes, form no.)	Check
a.) <u>QC SUMMARY</u>			
Form II PEST	surrogate % recovery	water (2E)	_____
		soil (2F)	_____
Form III PEST	MS/MSD	water (3E)	_____
		soil (3F)	_____
Form IV PEST	method blank summary	(4C)	_____

b.) SAMPLE DATA

In order by sample number & chromatograph column.
For each sample:

Form I PEST	OAD	(ID)	_____
Chromatograms:	(if no hit @ low std scale)		
first column:			
second column:			
Integration reports:	(annotated <CRQL, RT out, manual integration, etc.)		
first column,			_____
second column			_____
Manual worksheets	confirmation, etc.		_____

c.) STANDARDS DATA

Form VI	PEST-1	init. calib. single component	(6D)	_____
	PEST-2	init. calib. single component	(6E)	_____
	PEST-3	init. calib. multi component	(6F)	_____
	PEST-4	analyte resolution (form only)	(6G)	_____
	PEST-5	performance evaluation mixture	(6H)	_____
	PEST-6	individual std mixture A	(6I)	_____
	PEST-7	individual std mixture B	(6J)	_____
Form VII	PEST-1	CCVs using PEMS, PIBLKs	(7D)	_____
	PEST-2	CCVs using INDA, INDB	(7E)	_____
Form VIII	PEST	analytical sequence	(8D)	_____
Form IX	PEST-1	florisil (form only)	(9A)	_____
	PEST-2	GPC (form only, data follows)	(9B)	_____
Form X	PEST-1	ID single component	(10A)	_____
	PEST-2	ID multi-component	(10B)	_____

Chromatograms (first column, second column)
over Reports (first column, second column)
for all standards:

Resolution check data _____
PEM, _____
INDA (L,M,H), _____
INDB (L,M,H), _____
Multicomponent analytes _____
(Toxaphene, PCBS), _____
Midpoint INDA & INDB used as CCVs _____
Florisil data _____
GPC calibration data _____
All multicomponent standards analyzed for confirmation _____
(high level PCBS, etc.) _____
Integration methods for each sequence _____

d.) RAW OC DATA

In chronological order:

BLANKS:

method

Form I PEST	OAD	(1D)	_____
Chromatograms			_____
Integration reports			_____

instrument

Form I PEST	OAD	(ID)	_____
Chromatograms			_____
Integration reports	(annotated <1/2 CRQL)		_____
Sulfur cleanup	(soils)		_____
Form I PEST	OAD	(ID)	_____
Chromatograms			_____
Integration reports			_____

MATRIX SPIKE

Form I PEST	OAD	(ID)	_____
Chromatograms			_____
Integration reports			_____

MATRIX SPIKE DUPLICATE

Form I PEST	OAD	(ID)	_____
Chromatograms			_____
Integration reports			_____

MISCELLANEOUS

Analysis sequence: both channels	_____
Data reduction methods	_____
Extraction bench sheets	_____
% total solids, pH, bench sheets	_____
Logbook sheets for surrogates, spikes	_____
standards log package	_____
GPC chromatogram traces	_____

APPENDIX IV

Continuing Calibration Verification Criteria

This Appendix references section III D 9.3 of USEPA of CLP OLM03.1 SOW.

7. Calibration Verification

- 7.1 Three types of analyses are used to verify the calibration and evaluate instrument performance. The analyses of instrument blanks, Performance Evaluation Mixtures (PEM), and the mid point concentration of Individual Standard Mixtures A and B constitute the continuing calibration. Sample data are not acceptable unless bracketed by acceptable analyses of instrument blanks, PEMs, and both Individual Standard Mixtures A and B.
- 7.2 An instrument blank and the PEM must bracket one end of a 12-hour period during which sample data are collected, and a second instrument blank and the mid point concentration of Individual Standard Mixtures A and B must bracket the other end of the 12-hour period.
- 7.3 For the 12-hour period immediately following the initial calibration sequence, the instrument blank and the PEM that are the last two steps in the initial calibration sequence bracket the front end of that 12-hour period. The injection of the instrument blank starts the beginning of that 12-hour period. Samples may be injected for 12 hours from the injection of the instrument blank. The three injections immediately after that 12-hour period must be an instrument blank, Individual Standard Mixture A, and Individual Standard Mixture B. The instrument blank must be analyzed first, before either standard. The Individual Standard Mixtures may be analyzed in either order (A,B or B,A).
- 7.4 The analyses of the instrument blank and Individual Standard Mixtures A and B immediately following on 12-hour period may be used to begin the subsequent 12-hour period, provided that they meet the acceptance criteria in paragraphs 7.8-7.14. In that instance, the subsequent 12-hour period must be bracketed by the acceptable analyses of an instrument blank and a PEM, in that order. Those two analyses may in turn be used to bracket the front end of yet another 12-hour period. This progression may continue every 12 hours until such time as any of the instrument blanks, PEMs, or Individual Standard Mixtures fails to meet the acceptance criteria in paragraphs 7.8-7.14. The 12-hour time period begins with the injection of the instrument blank. Standards (PEM or Individual Standard Mixtures), samples and required blanks may be injected for 12:00 hours from the time of injection of the instrument blank.
- 7.5 If more than 12 hours have elapsed since the injection of the instrument blank that bracketed as previous 12-hour period, an acceptable instrument blank, and PEM must be analyzed in

order to start a new sequence. This requirement applies even if no analyses were performed since the last standard was injected.

- 7.6 After a break in sample analyses, the laboratory may only resume the analysis of samples using the current initial calibration for quantitation by analyzing an acceptable instrument blank and a PEM.
- 7.7 If the entire 12-hour period is not required for the analyses of all samples to be reported and all data collection is to be stopped, the incomplete sequence must be ended with either the instrument blank/PEM combination or the instrument blank/Individual Standard Mixtures A and B combination, whichever was due to be performed at the end of the 12-hour period.
- 7.8 All single component pesticides and surrogates in the Performance Evaluation Mixtures used to demonstrate continuing calibration must be greater than or equal to 90.0 percent resolved. The resolution between any two adjacent peaks in the midpoint concentrations of Individual Standard Mixtures A and B in the initial calibration must be greater than or equal to 90.0 percent.
- 7.9 The absolute retention time for each of the single component pesticides and surrogates in the PEMs and mid point concentration of the Individual Standard Mixtures used to demonstrate continuing calibration must be within the retention time window determined from the three-point initial calibration described.
- 7.10 The percent difference between the calculated amount and the true amount for each of the single component pesticides and surrogates in the PEM and mid point concentration of the Individual Standard Mixtures used to demonstrate continuing calibration must be less than or equal to 25.0 percent and greater than -25.0 percent, using Equation 4.

EQ. 4

$$RPD = \frac{|C_{nom} - C_{calc}|}{(C_{nom} + C_{calc})/2} \times 100$$

C_{nom} nominal concentration of each analyte

C_{calc} calculated concentration of each analyte from the analyses of the standard

- 7.11 The percent breakdown of DDT and Endrin in the PEM must be less than or equal to 20.0 percent on each column. The combined breakdown of DDT and Endrin must be less than or equal to 30.0 percent on each column.
- 7.12 All instrument blanks must demonstrate that no analyte may be detected at greater than $\frac{1}{2}$ the CRQL for that analyte.
- 7.13 Analysts are cautioned that running an instrument blank and a performance evaluation mixture once every 12 hours is the minimum contract requirement. Late eluting peaks may carry over from one injection to the next if highly complex samples are analyzed or if the GC conditions are unstable. Such carryover is unacceptable. Therefore, it may be necessary to run instrument blanks and performance evaluation mixtures more often to avoid discarding data.
- 7.14 The requirements for running the instrument blanks, Performance Evaluation Mixture, and Individual Standard Mixtures A and B are waived when no samples, method blanks, or matrix spikes are run during that 12-hour period. After a break in sample analysis, a laboratory may resume the analysis of samples, method blanks, and matrix spikes and may use the current initial calibration for quantitation only after an acceptable PEM is run (paragraphs 7.2 - 7.6). If a successful PEM cannot be run after an interruption, an acceptable initial calibration must be run before sample data may be collected. All acceptable sample analyses must be bracketed by acceptable performance evaluation mixtures and instrument blanks.

APPENDIX V

Determination of Absolute Retention Times

This Appendix references Section III D 9.2.4 of USEPA CLP OLM03.1 SOW.

- 8.1 During the initial calibration sequence, absolute retention times (RT) are determined for all single response pesticides, the surrogates, and at least three major peaks of each multi-component analyte.
- 8.2 For single component pesticides, an RT is measured in each of three calibration standards and the mean RT is calculated as the average of the three values. An RT is measured for the surrogates in each of the three analytes of Individual Mixture A during the initial calibration and the mean RT is calculated as the average of the three values.
- 8.3 A retention time window is calculated for each single component analyte and surrogate by using the list in paragraph 8.4. Windows are centered around the mean absolute retention time for the analyte established during the initial calibrations.
- 8.4 Retention time windows for single and multicomponent analytes and surrogates.

Compound	Retention Time Window in Minutes
alpha-BHC	± 0.05
beta-BHC	± 0.05
gamma-BHC	± 0.05
delta-BHC	± 0.05
Heptachlor	± 0.05
alpha-Chlordane	± 0.07
gamma-Chlordane	± 0.07
Aldrin	± 0.05
Heptachlor epoxide	± 0.07
Dieldrin	± 0.07
Endrin	± 0.07
Endrin aldehyde	± 0.07
Endrin ketone	± 0.07
DDD	± 0.07
DDE	± 0.07
DDT	± 0.07
Endosulfan I	± 0.07
Endosulfan II	± 0.07

Endosulfan sulfate	±	0.07
Methoxychlor	±	0.07
Aroclors	±	0.07
Toxaphene	±	0.07
Tetrachloro-m-xylene	±	0.05
Decachlorobiphenyl	±	0.10

- 8.5 For each multicomponent analyte, the RTs for three to five peaks are calculated from the initial calibration standard analysis. An RT window of +0.07 minutes is used for all multicomponent analyte peaks.
- 8.6 Analytes are identified when peaks are observed in the RT window for the compound on both GC columns.

APPENDIX VI

Calibration Factors and Criteria

This Appendix references Section III D 9.2.4 of USEPA CLP OLM03.1 SOW.

9. Calibration Factors for Single Pesticides

9.1 During the initial calibration sequence, the Contractor must establish the magnitude of the linear ECD response range for each single component pesticide and surrogate on each column and for each GC system. This is accomplished by analyzing the Individual Standard Mixtures A and B at three concentrations during the initial calibration sequence.

9.2 The linearity of the instrument is determined by calculating a percent relative standard deviation (%RSD) of the calibration factors from a three-point calibration curve for each single component pesticide and surrogate. Either peak area or peak height may be used to calculate calibration factors used in the %RSD equation. For example, it is permitted to calculate linearity for Endrin based on peak area and to calculate linearity for Aldrin based on peak height. It is not permitted within a %RSD calculation for an analyte to use calibration factors calculated from both peak area and peak height. For example, it is not permitted to calculate the calibration factor for the low point standard for endrin using peak height and calculate the midpoint and high point standard calibration factors for endrin using peak area.

9.2.1 Calculate the calibration factor for each single component pesticide and surrogate over the initial calibration range using Equation 5.

9.2.2 Calculate the mean and the %RSD of the calibration factors for each single component pesticide and surrogate over the initial calibration range using Equations 6 and 7.

$$CF = \frac{\text{Peak Area (or Height) of the Standard}}{\text{Mass Injected (ng)}} \quad \text{EQ. 5}$$

$$\overline{CF} = \sum_{i=1}^n \frac{CF_i}{n} \quad \text{EQ. 6}$$

$$\%RSD = \frac{SD}{\overline{CF}} \times 100 \quad \text{EQ. 7}$$

Where: $SD = \frac{\sum_{i=1}^n (CF_i - \overline{CF})^2}{n - 1}$ and n=3

9.2.3 The linearity of the calibration is considered acceptable when the %RSD of the three point calibration is less than 20.0 percent (alpha-BHC and delta-BHC less than 25.0 percent) except noted in the following.

The % RSD of the two surrogates must be less than or equal to 30.0 percent. Up to two single compound target compounds (but not surrogates) per column may be exceed the 20.0 percent limit for % RSD. (25.0 percent for alpha-BHC and delta-BHC), but those compounds must have a % RSD of less than or equal to 30.0 percent.

9.2.4 If the linearity requirements listed above are met, the calibration factor from the mid point concentration standard is used for quantitation of each single component pesticide.

9.3 Sample analysis may not proceed until a satisfactory calibration has been demonstrated.

10. Calibration Factors for Toxaphene and Aroclors

10.1 Toxaphene and Aroclors require only a single-point calibration and they present special analytical difficulties. Because of the alteration of these materials in the environment, it is probable that samples which contain multicomponent analytes will give patterns similar to, but not identical with, those of the standards.

10.2 A set of three to five major peaks is selected for each multicomponent analyte. Retention times and calibration factors are determined from the initial calibration analysis for each peak.

11. Acceptance Criteria for Chromatograms of Calibration Standards

The identification of single component pesticides by gas chromatographic methods is based primarily on retention time data. The retention time of the apex of a peak can be verified only from an on-scale chromatogram. The identification of multicomponent analytes is based primarily on recognition of patterns of retention times displayed on a chromatogram. Therefore, the following requirements apply to all data presented for single component and multicomponent analytes.

11.1 The chromatograms that result from the analyses of the Resolution Check Mixture, the Performance Evaluation Mixture, and Individual Standard Mixtures A and B during the

initial calibration sequence must display the single component analytes present in each standard at greater than 10 percent of full scale but less than 100 percent of full scale.

- 11.2 The chromatograms, for at least one of the three analyses each of Individual Standard Mixtures A and B from the initial calibration sequence, must display the single component analytes at greater than 50 percent and less than 100 percent of full scale.
- 11.3 The chromatograms of the standards for the multicomponent analytes analyzed during the initial calibration sequence must display the peaks chosen for identification of each analyte at greater than 25 percent and less than 100 percent of full scale.
- 11.4 For any standard containing alpha-BHC, the baseline of the chromatogram must return to below 50 percent of full scale before the elution time of alpha-BHC, and return to below 25 percent of full scale after the elution time of alpha-BHC and before the elution time of decachlorobiphenyl.
- 11.5 If a chromatogram is replotted electronically to meet requirements, the scaling factor used must be displayed on the chromatogram.
- 11.6 If the chromatogram of any standard needs to be replotted electronically to meet these requirements, both the initial chromatogram and the replotted chromatogram must be submitted in the data package.

APPENDIX VII

Sample Analysis

This Appendix references to Section III D 10.2 of USEPA CLP OLM03.1 SOW.

1. Sample Analysis

- 1.1 Unless ambient temperature on-column injection is used (see paragraph 4.2), the injector must be heated to at least 200°C. The gas chromatographic conditions from paragraph 4 must be used.
- 1.2 The injection must be made on-column by using either automatic or manual injection. If autoinjectors are used, 1.0 µL injection volumes may be used. Manual injections shall use at least 2.0 µL injection volumes. The same injection volume must be used for all standards, samples, and blanks associated with the same initial calibration. If a single injection is used for two GC columns attached to a single injection port, it may be necessary to use an injection volume greater than 2 µL. However, the same injection volume must be used for all analyses.
- 1.3 Analysis of a sample on both GC columns is required for all samples, blanks, matrix spikes, and matrix spike duplicates.
- 1.4 The requirements for the analysis sequence apply to both GC columns and to all instruments used for these analyses.
- 1.5 The laboratory will identify and quantitate analyte peaks based on RT and calibration factor established during the initial calibration sequence, as long as an acceptable calibration verification (see Appendix IV) is performed every 12 hours.
- 1.6 The protocol is intended to achieve the quantitation limits shown in Exhibit C whenever possible. If sample chromatograms have interfering peaks, a high baseline, or off-scale peaks, then those samples must be reanalyzed following dilution, further cleanup, or re-extraction. Samples which cannot be made to meet the given specifications after one re-extraction and three-step cleanup (GPC, Florisil, and sulfur removal) are reported in the SDG Narrative and do not require further analysis. No limit is placed on the number of re-extractions of samples that may be required because of contaminated method blanks.
- 1.7 The sample must be analyzed at the most concentrated level that is consistent with achieving satisfactory chromatography (defined below). If dilution is employed solely to bring a peak within the calibration range or to get a multicomponent pattern on scale, the results for both

the more and the less concentrated extract must be reported. The resulting changes in quantitation limits and surrogate recovery must be reported also for the diluted samples.

- 1.8 If the Contractor has reason to believe that diluting the final extracts will be necessary, an undiluted run may not be required. If an acceptable chromatogram (as defined below) is achieved with the diluted extract, an additional extract 10 times the concentration of the dilute sample must be injected and reported with the sample data.
 - 1.9 No target analyte concentrations may exceed the upper limit of the initial calibration.
 - 1.10 A standard for any identified multicomponent analyte must be analyzed on the same instrument within 72 hours of its detection in a sample.
 - 1.11 The identification of single component pesticides by gas chromatographic methods is based primarily on retention time data. The retention time of the apex of a peak can be verified only from an on-scale chromatogram. The identification of multicomponent analytes is based primarily on recognition of patterns of retention times displayed on a chromatogram. Therefore, the following requirements apply to all data presented for single component and multicomponent analytes.
 - 1.11.1 When no analytes are identified in a sample, the chromatograms from the analyses of the sample extract must use the same scaling factor as was used for the low point standard of the initial calibration associated with those analyses.
 - 1.11.2 Chromatograms must display single component pesticides detected in the sample at less than full scale.
 - 1.11.3 Chromatograms must display the largest peak of any multicomponent analyte detected in the sample at less than full scale.
 - 1.11.4 If an extract must be diluted, chromatograms must display single component pesticides between 10 and 100 percent of full scale.
 - 1.11.5 If an extract must be diluted, chromatograms must display the peaks chosen for quantitation of multicomponent analytes between 25 and 100 percent of full scale.
 - 1.11.6 For any sample, the baseline of the chromatogram must return to below 50 percent of full scale before the elution time of alpha-BHC, and return to below 25 percent of full scale after the elution time of alpha-BHC and before the elution time of decachlorobiphenyl.
 - 1.11.7 If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram.
-

1.11.8 If the chromatogram of any sample needs to be replotted electronically to meet these requirements, both the initial chromatogram and the replotted chromatogram must be submitted in the data package.

2. Quantitation of Analytes

2.1 Quantitation must be performed and reported on both columns.

2.2 Analytes must be quantitated with an electronic integrator or with a laboratory data system. The analyst can use either peak height or peak area as the basis for quantitation. The use of an electronic integrator or a laboratory data system is required.

2.3 The chromatograms of all samples must be reviewed by a qualified pesticide analyst before they are reported.

2.4 In order to be quantitated, the detector response (peak area or peak height) of all of the single component analytes must lie between the response of the low and high concentrations in the initial calibration. If the analytes are detected below the CRQL, they are reported as present below the CRQL, and flagged according to the instructions in exhibit B. If they are detected at a level greater than the high calibration point, the sample must be diluted either to a maximum of 1:100,000 or until the response is within the linear range established during calibration. Guidance in performing dilutions and exceptions to this requirement are given below.

2.4.1 If the response is still above the high calibration point after the dilution of 1:100,000, contact the client immediately.

2.4.2 Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

2.4.3 The dilution factor chosen should keep the response of the largest peak for a target compound in the upper half of the initial calibration range of the instrument.

2.4.4 Do not submit data for more than two analyses, i.e., the original sample extract and one dilution, or, if a screening procedure was employed, from the most concentrated dilution analyzed and one further dilution.

2.4.5 Do not dilute MS/MSD samples to get either spiked or non-spiked analytes within the calibration range. If the sample from which the MS/MSD aliquots were taken contains high levels of the spiked analytes, calculate the concentration and recovery of the analytes from the undiluted analysis and note the problem in the SDG Narrative.

2.5 The concentrations of the single component pesticides are calculated by using the following equations:

2.5.1 Water

$$\text{Concentration ug/L} = \frac{(A_x)(V_t)(D_f)(G_P C)}{(C_F)(V_o)(V_i)} \quad \text{EQ. 8}$$

Where

A_x = Area of the peak for the compound to be measured

C_F = Calibration factor for the mid point concentration external standard (area per ng)

V_o = Volume of water extracted in milliliters (mL)

V_i = Volume of extract injected in microliters (uL)

V_t = Volume of the concentrated extract in microliters (uL)

G_PC = GPC factor. (If no GPC is performed, GPC = 1. If GPC is performed, then GPC = 2).

D_f = Dilution Factor. The dilution factor for analysis of water samples by this method is defined as follows:

$$\frac{\text{uL most conc. extract used to make dilution} + \text{uL clean solvent}}{\text{uL most conc. extract used to make dilution}}$$

If no dilution is performed, D_f = 1.0.

2.5.2 Soil/Sediment (assuming GPC Clean-up is used)

$$\begin{array}{l} \text{Concentration} \\ \text{(Dry weight basis)} \end{array} \quad \text{ug/Kg} = \frac{(A_x) (V_t) (D_f) (GPC)}{(CF) (V_i) (W_s) (D)} \quad \text{EQ. 9}$$

Where:

Ax and CF are as given for water, above.

Vt = Volume of the concentrated extract in microliters (μL) (*This volume must be 5000 μL*)

Vi = Volume of extract injected in microliters (μL)

D = $\frac{100 - \% \text{ moisture}}{100}$

Ws = Weight of sample extracted in grams (g)

GPC = GPC factor. (If no GPC is performed, GPC = 1. If GPC is performed, then GPC = 2).
Note that GPC clean-up is required for all soil sample extracts.

Df = Dilution Factor. The dilution factor for analysis of soil samples by this method is defined as follows:

$$\frac{\text{uL most conc. extract used to make dilution} + \text{uL clean solvent}}{\text{uL most conc. extract used to make dilution}}$$

If no dilution is performed, Df = 1.0.

The factor of 2.0 in the numerator is used to account for the amount of extract that is not recovered from the mandatory use of GPC cleanup. Concentrating the extract collected after GPC to 5.0 mL rather than 10.0 mL for water samples not subjected to GPC, maintains the sensitivity of the soil method comparable to that of the water method, but correction of the numerical result is still required.

2.5.3 Note that the calibration factors used for the quantitation of the single component pesticides are the calibration factors from the mid point concentration standard for each analyte.

2.5.4 Because of the likelihood that compounds co-eluting with the target compounds will cause positive interferences and increase the concentration determined by the method, the lower of the two concentrations calculated for each single component pesticide is reported on Form I.

In addition, the concentrations calculated for both the GC columns are reported on Form X, along with a percent difference comparing the two concentrations. The percent difference is calculated according to Equation 10 below.

$$\% D = \frac{\text{Conc.H} - \text{Conc.L}}{\text{Conc.L}} \times 100 \quad \text{EQ. 10}$$

Where:

Conc.H = The higher of the two concentrations for the target compound in question

Conc.L = The lower of the two concentrations for the target compound in question

Note that using this equation will result in percent difference values that are always positive. The value will also be greater than a value calculated using the higher concentration in the denominator. However, given the likelihood of a positive interference raising the concentration determined on one GC column, this is a conservative approach to comparing the two concentrations.

- 2.6 The concentrations of the surrogates are calculated in a similar manner as the other analytes, using Equation 8. and 9. The recoveries of the surrogates are calculated according to Equation 11.

$$\text{Surrogate Percent Recovery} = \frac{Qd}{Qa} \times 100$$

EQ. 11

Qd = Quantity determined by analysis

Qa = Quantity added to sample/blank

The limits for the recovery of the surrogates are 30-150 percent for both surrogate compounds. As these limits are only advisory, no further action is required by the laboratory. However, frequent failures to meet the limits for surrogate recovery warrant investigation by the laboratory.

- 2.7 The quantitative determination of Toxaphene or Aroclors is somewhat different from that of single component analytes. Quantitation of peaks within the detector linear range CRQL to > 16 times CRQL is based on a single calibration point assuming linear detector response.

Alternatively, a linear calibration range may be established during a run sequence by a three-point calibration curve for any multicomponent analyte.

- 2.8 The reporting requirements for multicomponent analytes are similar to those for single component analytes. If the concentration is calculated to be 10^6 times the CRQL, contact the client immediately.
- 2.9 The quantitation of toxaphene or Aroclors must be accomplished by comparing the heights or the areas of each of the three to five major peaks of the multicomponent analyte in the sample with the calibration factor for the same peaks established during the initial calibration sequence. The concentration of multicomponent analytes is calculated by using Equations 8 and 9, where A_x is the area for each of the major peaks of the multicomponent analyte. The concentration of each peak is determined and then an average concentration for three to five major peaks is determined and reported on Form I (Exhibit B). The following table lists the number of potential quantitation peaks for each Aroclor and Toxaphene.

<u>Analyte</u>	<u>No. of Potential Quantitation Peaks</u>
Aroclor 1016/1260	5
Aroclor 1221	3
Aroclor 1232	4
Aroclor 1242	5
Aroclor 1248	5
Aroclor 1254	5
Toxaphene	4

- 2.10 The choice of the peaks used for multicomponent quantitation and the recognition of those peaks may be complicated by the environmental alteration of the Toxaphene or Aroclors, and by the presence of coeluting analytes or matrix interferences, or both.
- 2.11 If more than one multicomponent analyte is observed in a sample, the Contractor must choose separate peaks to quantitate the different multicomponent analytes. A peak common to both analytes present in the sample must not be used to quantitate either compound.
- 2.12 The reporting requirements for Toxaphene and the Aroclors are similar to those for the single component analytes, except that the lower mean concentration (from the three to five peaks) is reported on the Form I, and the two mean concentrations reported on the Form X. The two mean concentrations are compared by calculating the percent difference using equation 10.

3. Sample Data Acceptance Criteria

- 3.1 The requirements above apply to both columns, and quantitation must be performed on both GC columns and reported.
- 3.2 All samples must be analyzed as part of a valid analysis sequence (paragraph 5). They must be bracketed by acceptable instrument blanks (paragraph 15.3), acceptable Performance Evaluation Mixtures, and acceptable Individual Standard Mixtures A and B (appendix IV) that were analyzed at the required frequency.
- 3.3 The retention times for both of the surrogates must be within the retention time windows as calculated in paragraph 8.
- 3.4 Reportable data for a sample must include a chromatogram in which a baseline returns to below 50 percent of full scale before the elution time of alpha-BHC, and to below 25 percent of full scale after alpha-BHC and before decachlorobiphenyl.
- 3.5 If dilution has been applied and if no peaks are detected above 25 percent of full scale, analysis of a more concentrated sample is required.
- 3.6 Reportable sample data must include chromatogram(s) which meet the criteria in paragraph 12.11.

4. Blanks

There are two types of blanks required by this method: the method blank and the instrument blank. A separate sulfur cleanup blank may be required if all samples associated with a given method blank are not subjected to sulfur cleanup. Samples that are associated with a sulfur cleanup blank are also associated with the method blank with which they were extracted. Both the method and sulfur cleanup blanks must meet the respective acceptance criteria for the sample analysis acceptance criteria to be met.

4.1 Method blank

- 4.1.1 Method blanks are spiked with the surrogate solution, extracted, cleaned up, and analyzed by following the same procedure that is used with the samples. A water method blank is one liter of reagent water treated as the water sample aliquot. A soil method blank is 30 g of sodium sulfate treated as the soil sample aliquot.

Method blank analysis must be performed once for the following, whichever is most frequent, and analyzed on each GC/EC system used to analyze samples:

- Each SDG (not to exceed 20 field samples), or
- Each matrix within an SDG, or
- Each extraction procedure within an SDG, or
- Whenever samples are extracted.

4.1.2 In order to be acceptable, a method blank analysis cannot contain any of the analytes listed in Exhibit C at greater than the CRQL. The surrogate retention times must be within the retention time windows calculated from the initial calibration sequence mean retention time for both tetrachloro-m-xylene and decachlorobiphenyl. The surrogate recoveries must fall within the acceptance windows of 30-150%. In the case of a method blank, these limits are not advisory.

4.1.3 All samples associated with an unacceptable method blank (see Form IV) must be re-extracted and reanalyzed.

4.2 Sulfur Cleanup Blank.

4.2.1 The sulfur cleanup blank is a modified form of the method blank. The sulfur cleanup blank is hexane spiked with the surrogates and passed through the sulfur cleanup procedure (see Section II, paragraph 7.4).

4.2.2 The sulfur cleanup blank is prepared when only part of a set of samples extracted together requires sulfur removal. A method blank is associated with the entire set of samples. The sulfur cleanup blank is associated with the part of the set which required sulfur cleanup. If all the samples associated with a given method blank are subjected to sulfur cleanup, then the method blank must be subjected to sulfur cleanup, and no separate sulfur cleanup blank is required.

4.2.3 In order to be acceptable, a sulfur blank analysis cannot contain any of the analytes listed in Exhibit C at greater than the CRQL. The surrogate retention times must be within the retention time windows calculated from the initial calibration sequence mean retention time for both tetrachloro-m-xylene and decachlorobiphenyl and surrogate recoveries must be within the acceptance windows of 30-150%. In the case of a sulfur clean-up blank, the limits are not advisory.

4.2.4 All samples associated with an unacceptable sulfur blank (see Form IV) must be re-extracted and reanalyzed.

4.3 Instrument blank

- 4.3.1 An instrument blank is a hexane or iso-octane solution containing 20.0 ng/mL of tetrachloro-m-xylene and decachlorobiphenyl and 50.0 ng/mL of isodrin.
- 4.3.2 The first analysis in a 12-hour analysis sequence must be an instrument blank. All acceptable samples analyses are to be bracketed by acceptable instrument blanks, as described in paragraph 5.1.
- 4.3.3 An acceptable instrument blank must be analyzed within a 12-hour analysis sequence and must demonstrate that no analyte in Exhibit C is detected at greater than 0.5 times the CRQL and that the surrogate retention times are within the retention time windows.
- 4.3.4 If analytes are detected at greater than half the CRQL or the surrogate RTs are outside the RT windows, all data collection must be stopped, and corrective action must be taken. Data for samples which were run between the last acceptable instrument blank and the unacceptable blank are considered suspect. An acceptable instrument blank must be run before additional data are collected. After an acceptable instrument blank is run, all samples which were run after the last unacceptable instrument blank must be reinjected during a valid run sequence and must be reported.
- 4.3.5 Analysts are cautioned that running an instrument blank once every 12 hours is the minimum contract requirement. Late eluting peaks may carry over from one injection to the next if highly complex samples are analyzed or if the GC conditions are unstable. Such carryover is unacceptable. Therefore, it may be necessary to run instrument blanks more often to avoid discarding data.

APPENDIX VIII

MS/MSD

This Section references Section III D 12.2 of USEPA CLP OLM03.1 SOW.

1. Matrix Spike/Matrix Spike Duplicate

- 1.1 A matrix spike and matrix spike duplicate must be extracted and analyzed at least once with every 20 samples of each matrix. NOTE: There is no differentiation between "low" and "medium" soil samples in this method. Therefore only one soil MS/MSD is to be submitted.
- 1.2 The surrogate retention times must be within the retention time windows specified.
- 1.3 The percent recoveries and the relative percent difference between the recoveries of each of the 6 compounds in the matrix spike samples will be calculated and reported by using the following equations:

$$\text{Matrix Spike Recovery} = \frac{\text{SSR} - \text{SR}}{\text{SA}} \times 100 \quad \text{EQ. 12}$$

Where

SSR = Spike sample result
SR = Sample result
SA = Spike added

$$\text{RPD} = \frac{|\text{MSR} - \text{MSDR}|}{\frac{1}{2}(\text{MSR} + \text{MSDR})} \times 100 \quad \text{EQ. 13}$$

Where

RPD = Relative percent difference
MSR = Matrix spike recovery
MSDR = Matrix spike duplicate recovery

The vertical bars in the formula above indicate the absolute value of the difference, hence RPD is always expressed as a positive value.

1.4 The Contractor shall report matrix spike and matrix spike duplicate recoveries and percent difference values with the analytical results (see Exhibit B). The limits for matrix spike compound recovery and RPD are given below. As these limits are only advisory, no further action by the laboratory is required, however, frequent failures to meet the limits for recovery or RPD warrant investigation by the laboratory.

MATRIX SPIKE RECOVERY AND
RELATIVE PERCENT DIFFERENCE LIMITS

Compound	% R		RPD	
	Water	Water	Soil	Soil
gamma-BHC (Lindane)	56-123	15	46-127	50
Heptachlor	40-131	20	35-130	31
Aldrin	40-120	22	34-132	43
Dieldrin	52-126	18	31-134	38
Endrin	56-121	21	42-139	45
4,4'-DDT	38-127	27	23-134	50

APPENDIX IX

Form Instructions

This Appendix references Section III B of the USEPA CLP OLM03.1 SOW.

SECTION III B

FORM INSTRUCTION GUIDE

This section includes specific instructions for the completion of all required forms. Each of the forms is specific to a given fraction (volatile, semivolatile, pesticide/Aroclor), and in some instances specific to a given matrix (water or soil) within each fraction. The contractor shall submit only those forms pertaining to the fractions analyzed for a given sample or samples. For instance, if a sample is scheduled for volatile analysis only, provide only VOA forms. There are two pages relating to the semivolatile fraction for Forms I, VI, VII, and VIII. whenever semivolatiles are analyzed and one of the above-named forms is required, both pages (SV-1 and SV-2) must be submitted. These instructions are arranged in the following order:

- A. General Information and Header Information
- B. Organic Analysis Data Sheets (Form I)
- C. Surrogate Recovery (Form II PEST)
- D. Matrix Spike/Matrix Spike Duplicate Recovery (Form III)
- E. Method Blank Summary (Form IV)
- F. GC Initial Calibration Data (From VI PEST-1, PEST-2, PEST-3, PEST-4)
- G. GC/EC Continuing Calibration (Form VII PEST)
- H. Pesticide Analytical Sequence (Form VIII PEST)
- I. Pesticide Cleanup Procedures (Form IX PEST-1, PEST-2)
- J. Pesticide/Aroclor Identification (Form X PEST-1, PEST-2)
- K. Sample Log-In Sheet (Form DC-1)

L. Document Inventory Sheet (Form DC-2)

A. General Information and Header Information

- A.1. The data reporting forms presented in Section IV have been designed in conjunction with the computer-readable data format specified in Exhibit H, Data Dictionary and Format for Data Deliverables in Computer-Readable Format. The specific length of each variable for computer-readable data transmission purposes is given in the Data Dictionary (Exhibit H). Information entered on these forms must not exceed the size of the field given on the form, including such laboratory-generated items as Lab Name and Lab Sample ID.
- A.2. Note that on the hard copy forms (Section IV), the space provided for entries is greater in some instances than the length prescribed for the variable as written to diskette (see Exhibit H). Greater space is provided on the hard copy forms for the sake of visual clarity.
- A.3. Values must be reported on the hard copy forms according to the individual form instructions in this Section. For example, results for concentrations of VOA target compounds must be reported to two significant figures if the value is greater than or equal to 10. Values can be written to the diskette file in any format that does not exceed the field specification as given in the record specifications and discussed in "Record Structure", paragraph 5 of Exhibit H.
- A.4. All characters which appear on the data reporting forms presented in the contract (Exhibit B, Section IV) must be reproduced by the Contractor when submitting data, and the format of the forms submitted must be identical to that shown in the contract. No information may be added, deleted, or moved from its specified position without prior written approval of the EPA Administrative Project Officer. The names of the various fields and compounds (i.e., "Lab Code," "Chloromethane") must appear as they do on the forms in the contract, including the options specified in the form (i.e., "Matrix: (soil/water)" must appear, not just "Matrix"). For items appearing on the uncompleted forms (Section IV), the use of uppercase and lowercase letters is optional.
- A.5. Alphabetic entries made onto the forms by the Contractor shall be in ALL UPPERCASE letters (i.e., "LOW", not "Low" or "low"). If an entry does not fill the entire blank space provided on the form, null characters shall be used to remove the remaining underscores that comprise the blank line. See Exhibit H for more detailed instructions. However, do not remove the underscores or vertical bar characters that delineate "boxes" on the forms. The only exception would be those underscores at the bottom of a "box" that are intended as a data entry line (for instance, on Form 2A, line 30, if data must be entered on line 30, it will replace the underscores).

- A.6. Six pieces of information are common to the header sections of each data reporting form. They are Lab Name, Contract, Lab Code, Case No., SAS No., and SDG No. Except as noted below for SAS No., this information must be entered on every form and must match on every form.
- A.7. The "Lab Name,, shall be the name chosen by the Contractor to identify the laboratory. It may not exceed 25 characters.
- A.8. The "Lab Code" is an alphabetical abbreviation of up to 6 letters, assigned by the EPA, to identify the laboratory and aid in data processing. This lab code shall be assigned by the EPA at the time a contract is awarded, and shall not be modified by the Contractor, except at the direction of the EPA. If a change of name or ownership occurs at the laboratory, the lab code will remain the same until the contractor is directed by the EPA to use another lab code assigned by the EPA.
- A.9. The "Case No." is the EPA-assigned Case number associated with the sample, and reported on the Traffic Report.
- A.10. The "Contract" is the number of the EPA contract under which the analyses were performed. In the case of multiple laboratories operating under a corporate-wide contract, the contract number entered shall be that of the corporate contract, regardless of the facility performing the analyses (see Lab Code, above).
- A.11. The "SDG No." is the Sample Delivery Group number. The Sample Delivery Group (SDG) number is the EPA Sample Number of the first sample received in the SDG. When several samples are received together in the first SDG shipment, the SDG number shall be the lowest sample number (considering both alpha and numeric designations) in the first group of samples received under the SDG.
- A.12. The "SAS No." is the EPA-assigned number for analyses performed under Special Analytical Services. If samples are to be analyzed under SAS only and reported on these forms, then enter SAS No. and leave Case No. blank. If samples are analyzed according to the "Routine Analytical Services" (IFB) protocols and have additional "SAS" requirements, list both Case No. and SAS No. on all forms. If the analyses have no SAS requirements, leave "SAS No." blank. NOTE: Some samples in an SDG may have a SAS No. while others do not.
- A.13. The other information common to most of the forms is the "EPA Sample No.". This number appears either in the upper right-hand corner of the form, or as the left column of a table summarizing data from a number of samples. When the "EPA Sample No." is entered into the triple-spaced box in the upper right-hand corner of Form I, Form IV, or Form X, it should be entered on the middle line of the three lines that comprise the box.

A.14. All samples, matrix spikes, matrix spike duplicates, blanks, and standards shall be identified with an EPA Sample Number. For field samples, matrix spikes and matrix spike duplicates, the EPA Sample Number is the unique identifying number given in the Traffic Report that accompanied that sample.

A.15. In order to facilitate data assessment, the following sample suffixes must be used:

XXXXXX = EPA sample number
XXXXXXMS = Matrix spike sample
XXXXXXMSD = Matrix spike duplicate sample
XXXXXXRE = Re-extracted and re-analyzed sample
XXXXXXDL = Sample analyzed at a secondary dilution

A.16. Form VIII Pest requires that all samples analyzed in a given analytical sequence be listed, regardless of whether or not they are part of the SDG being reported. Therefore, use "ZZZZZ" as the EPA Sample No. for any sample analysis not associated with the SDG being reported.

A.17. For blanks and standards, the following identification scheme must be used as the "EPA Sample No."

1. Volatile blanks shall be identified as VBLK##.
2. Semivolatile blanks shall be identified as SBLK##.
3. Pesticide/Aroclor method blanks shall be identified as PBLK##.
4. Pesticide/Aroclor instrument blanks shall be identified as PIBLK##.

A.18. The "EPA Sample No." must be unique for each blank within an SDG. Within a fraction, a laboratory must achieve this by replacing the two-character "##" terminator of the identifier with one or two characters or numbers, or a combination of both. For example, possible identifiers for volatile blanks would be VBLK1, VBLK2, VBLKA1, VBLKB2, VBLK10, VELKAB, etc.

A.19. Volatile and semivolatile standards shall be identified as SFTD###, where

F = Fraction (V for volatiles; S for semivolatiles).

STD = Indicates a standard.

= The concentration in ug/L of volatile standards (i.e., 010, 020, 050, 100, and 200) or the amount injected in ng for semivolatile standards (i.e., 020, 050, 080, 120, and 160).

A.20. As for the blank identifiers, these designations will have to be concatenated with other information to uniquely identify each standard.

A.21. For pesticide/Aroclor standards, the following scheme shall be used to enter "EPA Sample Number".

<u>Name</u>	<u>EPA Sample Number</u>
Individual Mix A (low point)	INDAL##
Individual Mix A (mid point)	INDAM##
individual Mix A (high point)	INDAH##
Individual Mix B (low point)	INDBL##
Individual Mix B (mid point)	INDBM##
Individual Mix B (high point)	INDBH##
Resolution Check	RESC##
Performance Evaluation Mixture	PEM##
Toxaphene	TOXAPH##
Aroclor 1016	AR1016##
Aroclor 1221	AR1221##
Aroclor 1232	AR1232##
Aroclor 1242	AR1242##
Aroclor 1248	AR1248##
Aroclor 1254	AR1254##
Aroclor 1260	AR1260##

A.22. The permitted mixture of Aroclor 1016 and Aroclor 1260 shall be entered as AR1660##.

A.23. If the standards are injected onto both GC columns on the same instrument simultaneously, the same EPA Sample Number may be used for reporting data for the standards for both columns. If simultaneous injections are not made, then the same number may not be used.

A.24. Several other pieces of information are common to many of the Data Reporting Forms. These include Matrix, Sample wt/vol., Level, Lab Sample ID, and Lab File ID.

A.25. For "Matrix", enter "SOIL" for soil/sediment samples, and enter "WATER" for water samples. NOTE: The matrix must be spelled out. Abbreviations such as "S" or "W" shall not be used.

- A.26. For "Sample wt/vol." enter the number of grams (for soil) or milliliters (for water) of sample used in the first blank line, and the units, either "G" or "ML", in the second blank.
- A.27. For Pesticide/Aroclor forms, there is no differentiation between low and medium soil samples and no level is entered on any of these forms.
- A.28. "Lab Sample ID" is an optional laboratory-generated internal identifier. Up to 12 alphanumeric characters may be reported here. If the contractor does not have a Lab Sample ID, this field may be left blank.
- A.29. "Lab File ID" is the laboratory-generated name of the GC/MS data system file containing information pertaining to a particular analysis. Up to 14 alpha-numeric characters may be used here.
- A.30. "Instrument ID" is common to many of the forms, particularly those containing calibration data. The identifier used by the laboratory must include some indication of the manufacturer and/or model of the instrument, and contain additional characters that differentiate between all instrument of the same type in the laboratory.
- A.31. "GC Column" and "ID (mm)" are common to various other forms. These two fields are to be used to identify the stationary phase of the GC column (previously called GC Column ID), and the internal diameter of the GC column in millimeters (mm). For packed columns, convert the ID from inches to millimeters as necessary, and enter in the "ID" field.
- A.32. Forms II, IV, V, VIII, IX, and X contain a field labeled "page _ of _" in the bottom left-hand corner. If the number of entries required on any of these forms exceeds the available space, continue entries on another copy of the same fraction-specific form duplicating all header information. If a second page is required, number the pages consecutively, as "page 1 of 2" and "page 2 of 2." If a second page is not required, number the page "page 1 of 1." NOTE: These forms are fraction-specific, and often matrix-specific within fraction. For example, Form II VOA-1 and Form II VOA-2 are for different data. Therefore, do not number the pages of all six versions of Form II as "1 of 6, 2 of 6, etc." Number only pages within a fraction-specific and matrix specific form.
- A.33. For rounding off numbers to the appropriate level of precision, observe the following common rules. If the figure following those to be retained is less than 5, drop it (round down). If the figure is greater than 5, drop it and increase the last digit to be retained by 1 (round up). If the figure following the last digit to be retained equals 5, round up if the digit to be retained is odd, and round down if that digit is even.

B. Organic Analysis Data Sheet (Form I)

B.1. Form I PEST

- B.1.1. This form is used for tabulating and reporting sample analysis results for target compounds. If all fractions are not requested to be analyzed, only the pages specifically required must be submitted. If the pesticide/Aroclor analysis is the only analysis requested, only Form I Pest must be submitted for that sample.
- B.1.2. Complete the header information on each page of Form I required, according to the instructions in Part A and as follows:
- B.1.3. For pesticides/Aroclors, enter the values for the percent moisture determined during the analysis. In the field "decanted (Y/N)", enter "Y" if the sample had standing water above the soil/sediment that was decanted, or "N" if no water was decanted off the surface of the sample. Report percent moisture (decanted or not decanted) to the nearest whole percentage point (i.e., 5%, not 5.3%). Leave these fields blank for Form I for method blanks and instrument blanks.
- B.1.4. For pesticides/Aroclors, enter the method of extraction as "SEPF" for separatory funnel, "CONT" for continuous liquid-liquid extraction, or "SONC" for sonication (soils only).
- B.1.5. If gel permeation chromatography, "GPC Cleanup", was performed, enter "Y" for yes. Otherwise, enter "N" for no, if GPC was not performed. NOTE: GPC is required for all soil samples analyzed for semivolatiles and pesticides/Aroclors, therefore all soil sample forms will contain "Y" in this field.
- B.1.6. For soil samples only, enter pH for semivolatiles and pesticides/Aroclors, reported to 0.1 pH units.
- B.1.7. "Date Received" is the date of sample receipt at the laboratory, as noted on the Traffic Report (i.e., the VTSR). It should be entered as MM/DD/YY.
- B.1.8. "Date Extracted" and "Date Analyzed" should be entered in a similar fashion. If continuous liquid-liquid extraction procedures are used, enter the date on which the procedure was started for "Date Extracted". If separatory funnel or sonication procedures are used, enter the data on which the procedure was completed. For pesticide/Aroclor samples, the date of analysis should be the date of the first GC analysis performed. The date of sample receipt will be compared with the extraction and analysis dates of each fraction to ensure that contract holding times were not exceeded.

- B.1.9. For pesticides/Aroclors, enter the actual volume of the most concentrated sample extract, in microliters, under "Concentrated Extract Volume". This volume typically will be 1000 μL , or 500 μL when GPC was performed. If a dilution of the sample extract is made in a subsequent analysis, this volume will remain the same, but the dilution factor will change.
- B.1.10. For pesticides/Aroclors, enter the volume of the sample extract injected into the GC under "Injection Volume". Report this volume in microliters to one decimal place, i.e., 1.0 μL . Note: A 2.0 microliter injection is required for semivolatile analyses.
- B.1.11. If a sample or sample extract has been diluted for analysis, enter the "Dilution Factor" as a single number, not a fraction, such as "100.0," for a 1 to 100 dilution of the sample. Enter 0.1 for a concentration of 10 to 1. If a sample was not diluted, enter "1.0." Reported dilution factors to one decimal place.
- B.1.12. For positively identified target compounds, the Contractor shall report the concentrations detected as uncorrected for blank contaminants.
- B.1.13. Report all pesticide/Aroclor results to two significant figures.
- B.1.14. The appropriate concentration units, $\mu\text{g/L}$ or $\mu\text{g/kg}$, must be entered.
- B.1.15. If the result is a value greater than or equal to the quantitation limit, report the value.
- B.1.16. Under the column labeled "Q" for qualifier, flag each result with the specific Data Reporting Qualifiers listed below. The Contractor is encouraged to use additional flags or footnotes. The definition of such flags must be explicit and must be included in the SDG Narrative.
- B.1.17. For reporting results, the following contract specific qualifiers are to be used. The seven qualifiers defined below are not subject to modification by the laboratory. Up to five qualifiers may be reported on Form I for each compound.
- B.1.18. The seven EPA-defined qualifiers to be used are as follows:
- U - Indicates compound was analyzed for but not detected. the sample quantitation limit must be corrected for dilution and for percent moisture. For example, 10 U for phenol in water if the sample final volume is the protocol-specified final volume. If a 1 to 10 dilution of extract is necessary, the reported limit is 100 U. For a soil sample, the value must also be adjusted for percent moisture. For example, if the sample had 24% moisture and a 1 to 10 dilution factor, the sample quantitation limit for phenol (330 U) would be corrected to

$$\frac{(330 U) \times df}{D}$$

Where

$$D = \frac{100 - \% \text{ moisture}}{100}$$

and Df = dilution factor

For example, at 24% moisture, $D = \frac{100 - 24}{100} = 0.76$

$(330 U) \times 10 = 4300. U$ (rounded to the correct number of significant figures).

For soil samples subjected to GPC clean-up procedures, the extract must be concentrated to 0.5 mL, and the sensitivity of the analysis is not compromised by the cleanup procedures. Therefore, the CRQL values in Exhibit C will apply to all samples, regardless of cleanup. However, if a sample extract cannot be concentrated to the protocol-specified volume (see Exhibit C), this fact must be accounted for in reporting the sample quantitation limit.

- J - Indicates an estimated value. This flag is used either when estimating a concentration for tentatively identified compounds where a 1:1 response is assumed, or when the mass spectral data indicate the presence of a compound that meets the identification criteria but the result is less than the sample quantitation limit but greater than zero. For example, if the sample quantitation limit of 10 µg/L, but a concentration of 3 µg/L is calculated, report it as 3J. The sample quantitation limit must be adjusted for dilution as discussed for the U flag.
- N - Indicates presumptive evidence of a compound. This flag is only used for tentatively identified compounds, where the identification is based on a mass spectral library search. It is applied to all TIC results.
- P - This flag is used for a pesticide/Aroclor target analyte when there is greater than 25% difference for detected concentrations between the two GC columns (see Form X). The lower of the two values is reported on Form I and flagged with an "P".
- C - This flag applies to pesticide results where the identification has been confirmed by GC/MS. If GC/MS confirmation was attempted but was unsuccessful, do not apply this flag, instead use a laboratory-define flag, discussed below.
- B - This flag is used when the analyte is found in the associated blank as well as in the sample. It indicates possible/probable blank contamination and warns the data user to take appropriate

action. This flag must be used for a TIC as well as for a positively identified target compound.

E - This flag identifies compounds whose concentrations exceed the calibration range of the GC/MS instrument for that specific analysis. If one or more compounds have a response greater than full scale, except as noted in Exhibit D, the sample or extract must be diluted and re-analyzed according to the specifications in Exhibit D. All such compounds with a response greater than full scale should have the concentration flagged with an "E" on the Form I for the original analysis. If the dilution of the extract causes any compounds identified in the first analysis to be below the calibration range in the second analysis, then the results of both analyses shall be reported on separate copies of Form I. The Form I for the diluted sample shall have the "DL" suffix appended to the sample number. NOTE: For total xylenes, where three isomers are quantified as two peaks, the calibration range of each peak should be considered separately, e.g., a diluted analysis is not required for total xylenes unless the concentration of either peak separately exceeds 200 µg/L.

D - This flag identifies all compounds identified in an analysis at a secondary dilution factor. If a sample or extract is re-analyzed at a higher dilution factor, as in the "E" flag above, the "DL" suffix is appended to the sample number on the Form I for the diluted sample, and all concentration values reported on that Form I are flagged with the "D" flag. This flag alerts data users that any discrepancies between the concentrations reported may be due to dilution of the sample or extract.

A - This flag indicates that a TIC is a suspected aldol-condensation product.

X - Other specific flags may be required to properly define the results. If used, they must be fully described, and such description attached to the Sample Data Summary Package and the SDG Narrative. Begin by using "X". If more than one flag is required, use "Y" and "Z" as needed. If more than five qualifiers are required for a sample result, use the "X" flag to combine several flags, as needed. For instance, the "X" flag might combine the "A", "B", and "D" flags for some sample. The laboratory-defined flags are limited to the letters "X", "Y", and "Z".

The combination of flags "BU" or "UB" is expressly prohibited. Blank contaminants are flagged "B" only when they are detected in the sample.

C. Surrogate Recovery (Form II and PEST)

C.1. Form II is used to report the recoveries of the surrogate compounds added to each pesticide/Aroclor sample, blank, matrix spike, and matrix spike duplicate.

- C.2. Complete the header information and enter EPA Sample Numbers as described in part A. For semivolatile soil samples only, specify the "level" as "LOW" or "MED", as on Form I. Do not mix low and medium level samples on one form. Complete one for each level. For each surrogate, report the percent recovery to the nearest whole percentage point, and to the number of significant figures given by the QC limits at the bottom of the form.
- C.3. Flag each surrogate recovery outside the QC limits with an asterisk (*). The asterisk must be placed in the last space in each appropriate column, under the "#" symbol. In the far right-hand column, total the number of surrogate recoveries outside the QC limits for each sample. If no surrogates were outside the limits, enter "O".
- C.4. If the surrogates are diluted out in any analysis, enter the calculated recovery, or "O" (zero) if the surrogate is not detected, and flag the surrogate recoveries with a "D" in the column under the "#" symbol. Do not include results flagged "D" in the total number of recoveries for each sample outside the QC limits.
- C.5. The pesticide surrogate recoveries must be reported from both GC columns used for the analyses. Therefore, identify each GC column in the header, entering the stationary phase under "GC Column" (previously called GC Column ID), and the internal diameter (ID) of the column in millimeters under "ID". The assignment of columns as "1" and "2", is left to the discretion of the laboratory if the analyses are performed by simultaneous injection into a GC containing two columns. If so analyzed, the assignment of "GC Column 1" and "GC Column 2" must be consistent across all the reporting forms. If the analysis is not performed by simultaneous injection, then the assignment of GC Column number should be based on the chronological order of the two analyses.
- C.6. The pesticide surrogate recovery limits are only advisory, but the Contractor must flag those recoveries outside the advisory QC limits or diluted out, nonetheless.
- C.7. Number all pages as described in part A.
- D. Matrix Spike/Matrix Spike Duplicate Recovery (Form III)
- D.1. This form is used to report the results of the analyses of a matrix spike and matrix spike duplicate. The form is matrix-specific for volatiles and semivolatiles.
- D.2. Complete the header information as instructed in Part A, including the EPA Sample Number for the matrix spike, without the suffixes MS or MSD.
- D.3. All water samples are "LOW". Therefore, there is no MS/MSD for "medium level waters", and none shall be reported.

- D.4. In the upper box in Form III, under "SPIKE ADDED", enter the calculated concentration in $\mu\text{g/L}$ or $\mu\text{g/Kg}$ (according to the matrix) that results from adding each spiked compound to the aliquot chosen for the matrix spike (MS). For instance, for base/neutral compounds in medium level soils, if 50 μg of spike are added to 1 g of soil, the resulting concentration is 50,000 $\mu\text{g/Kg}$. Enter the "SAMPLE CONCENTRATION", in 50,000 similar units, of each spike compound detected in the original sample. If a spike compound was not detected during the analysis of the original sample, enter the sample result as "O" (zero). Under "MS CONCENTRATION", enter the actual concentration of each spike compound detected in the matrix spike aliquot. Calculate the percent recovery of each spike compound in the matrix spike aliquot to the nearest whole percent, according to Exhibit E, and enter under "MS % REC". Flag all percent recoveries outside the QC limits with an asterisk (*). The asterisk must be placed in the last space of the percent recovery column, under the "#" symbol.
- D.5. For pesticide/Aroclor matrix spikes and matrix spike duplicates, the concentration used for "MS CONCENTRATION" AND "MSD CONCENTRATION" must be the concentration of the spiked analyte reported on Form I that those analyses. Of the two concentrations calculated for each pesticide/Aroclor target compound, one on each GC column, the lower concentration is reported on Form I, and both concentrations are reported on Form X. The lower concentration is reported on Form III and used in the calculation of spike recovery, even if that concentration yields a recovery value that is outside the advisory QC limits.
- D.6. Complete the lower box on Form III in a similar fashion, using the results of the analysis of the matrix spike duplicate (MSD) aliquot. Calculate the relative percent difference (RPD) between the matrix spike recovery and the matrix spike duplicate recovery, and enter this value in the lower box under "% RPD". Report the relative percent difference to the nearest whole percent. Compare the RPDs to the QC limits given on the form, and flag each RPD outside the QC limits with an asterisk (*) in the last space of the "% RPD" column, under the "#" symbol.
- D.7. Summarize the values outside the QC limits at the bottom of the page. No further action is required by the laboratory. Performance-based QC limits will be generated and updated from recovery and RPD data.
- E. Method Blank Summary (Form IV)
- E.1. This form summarizes the samples associated with each method blank analysis. A copy of the appropriate Form IV is required for each blank.

- E.2. Complete the header information on Form IV as described in Part A. The "EPA Sample No." entered in the box at the top of Form IV shall be the same number entered on the Form I for the blank itself.
- E.3. For pesticide/Aroclor blanks, enter the method of extraction as "SEPF" for separator-y funnel, "SONC" for sonication, or "CONT" for continuous liquid-liquid extraction.
- E.4. For pesticide/Aroclor blanks, there is no differentiation between medium and low level soil samples, so no "Level" is entered on this form.
- E.5. For pesticide/Aroclor method blanks, enter the date of extraction of the blank.
- E.6. If the samples associated with pesticide/Aroclor blank are subjected to sulfur cleanup, then the blank must also be subjected to sulfur cleanup. If sulfur cleanup is employed, enter "Y" in the "Sulfur Cleanup" field, else, enter "N". If only some of the samples associated with the method blank are subjected to sulfur cleanup, a separate sulfur cleanup blank is required (see Exhibit D PEST). If a separate sulfur cleanup blank is prepared, complete one version of Form IV associating all the samples with the method blank, and a second version of Form IV listing only those samples associated with the separate sulfur cleanup blank. Note: Subjecting all samples associated with a method blank to sulfur cleanup avoids the need for two forms.
- E.7. Pesticide/Aroclor contaminants must meet the identification criteria in Exhibit D PEST, which requires analysis of the blank on two different GC Columns. Therefore, enter the date, time and instrument ID of both analyses of the blank on the pesticide method blank summary. The information on the two analyses is differentiated as Date Analyzed (1), Date Analyzed (2), etc. If the analyses were run simultaneously, the order of reporting is not important, but must be consistent with the information reported on all other pesticide forms. Otherwise, (1) shall be the first analysis, and (2) the second. Identify the GC Column and internal diameter as described previously.
- E.8. Enter "Lab File ID" only if GC/MS confirmation was attempted. otherwise, leave blank.
- E.9. For all three fractions, as appropriate, summarize the samples associated with a given method blank in the table below the header, entering EPA Sample Number and Lab Sample ID. For volatiles, enter the Lab File ID and time of analysis of each sample. For semivolatile, enter the Lab File ID and Date Analyzed. For pesticides/Aroclors, enter the dates of both analyses as Date Analyzed (1) and Date Analyzed (2), as discussed above.
- E.10. Number all pages as described in part A.
- F. GC/EC Initial Calibration Data (Form VI PEST-1, PEST-2, PEST-3, PEST-4)
-

- F.1. The initial calibration of pesticides and Aroclors involves the determination of retention times, retention time window, and calibration factors. For single component pesticide target compounds, these data are calculated from the analyses of the Individual Standard Mixtures A and B at three different concentration levels. For the multicomponent target compounds, these data are calculated from a single point calibration.
- F.2. For each set of three analyses of Individual Standard Mixture A (low point, mid point, and high point), and set of three analyses of Individual Standard Mixture B, during an initial calibration, complete one copy of Form VI for each GC column used. Thus, each initial calibration will require at least two forms for the Individual Mixture A analyses, and two for Individual Mixture B analyses. However, for each of the forms, half of the compounds will have no entries, as they are not in that mixture.
- F.3. Complete the header information as above. Enter the Instrument ID, GC Column, and ID as described previously. Enter the dates of analysis of the first and last of the three standards on each form under "Date(s) Analyzed". Under "Level (x low)", enter the concentration of the low point, mid point, and high point calibration standards as a multiplier of the low point. Therefore, for the low point, enter "1.0". The concentration of the mid point standard is specified in Exhibit D as ten times the low point, therefore, enter "4.0" for "mid". The high point standard must be at least 16 times the low point, but may be higher, if that value lies within the linear range of the instrument, as specified in Exhibit D. Therefore, enter the appropriate multiplier to the high point standard concentration to one decimal place.
- F.4. For each standard analyzed, enter the retention time of each applicable analyte in minutes and decimal minutes, under the appropriate concentration level. Calculate the mean retention time of each analyte from the three individual mixtures, and report it under "Mean RT". Calculate the retention time window for each analyte, using these specifications in Exhibit D, and enter the lower limit of the window under RT Window "From", and the upper limit of the window under "To". The retention times of the surrogates are reported for both Individual mixtures, but the windows are only required to be calculated for individual Mixture A.
- F.5. For each three analyses of the same Individual Standard Mixture (A or B), the laboratory must also complete the calibration factor data on Form VI PEST-2. In a similar fashion as for the retention time data on Form VI PEST-1, prepare one form for each group of three standards, for each instrument and GC column used. Enter the concentration level of the standards in the same fashion as on Form VI PEST-1.
- F.6. Enter the calibration factor for each compound in each of the standards, and calculate a mean calibration and a percent relative standard deviation (%RSD), and enter on the form.

As with surrogate retention times, the calibration factors are only required from Individual Mixture A analyses.

- F.7. In order to be used for sample analyses, the %RSD of the initial calibration factors must be less than or equal to 20.0 percent, (25.0 % for alpha-BHC and delta-BHC), except as noted in the following. The %RSD of the calibration factors for the two surrogates must be less than or equal to 30.0 percent. Up to two single component target compounds (but not surrogates) may exceed the 20.0 percent limit for %RSD, (25.0% for alpha-BHC and delta-BHC) but these compounds must have a %RSD of less than or equal to 30.0 percent. These criteria apply to both GC columns.
- F.8. For the multicomponent target compounds, the retention times, retention time windows, and calibration factor must be reported in a similar fashion for each single point calibration standard. For each multi-component compound, the laboratory must select at least three peaks from each analyte, according to the specifications in Exhibit D. The retention and calibration factor data apply to each peak. Complete one version of Form VI PEST-3 for each GC column, for each initial calibration that applies to samples in the data package.
- F.9. Form VI is used also to report the results of analysis of the Resolution Check Solution that must begin each pesticide/Aroclor initial calibration sequence. The purpose of the Resolution Check Solution is to demonstrate for each initial calibration that the GC columns employed are capable of satisfactorily resolving the most difficult of the target analytes. One copy of Form VI PEST-4 is completed that covers both GC columns.
- F.10. Complete the header information as described in Instruction A. Using the same assignment of first and second GC columns made for Form IV, enter the GC Column, ID, Instrument ID, and Data and Time Analyzed. Enter the "EPA Sample No." for the Resolution Check Standard. If simultaneous injections on a single GC are used, the EPA Sample No. may be the same for both Resolution Check Standards. If simultaneous injections were not used, use different suffixes to identify the standards.
- F.11. In the boxes on the form, list each analyte, in retention time order, including both surrogate compounds. Thus, the order of analytes in the two boxes on a copy of this form will be different, due to the dissimilarity of the stationary phases of the two GC columns used. Enter the name of each target analyte in the Resolution Check Mixture as it appears on Form I PEST. Spell out the names of the surrogates as they appear on Form VI PEST-2.
- F.12. Enter the retention time of each analyte from the analysis under "RT". Calculate the resolution between each pair of analytes according to the formulae in Exhibit D. The resolution is calculated as percentage of the height of the smaller of each pair of adjacent peaks. Enter the resolution between the first and second peaks on the line for the first analyte listed in the box. Enter the resolution between the second and third peaks on the line

for the second analyte, and so on, until the resolutions of all possible pairs of adjacent analytes have been entered. NOTE: Only eight of the nine resolution fields will be filled. In order for these GC columns to be used for pesticide/Aroclor analyses, the resolution of all pairs of peaks listed on this form must be greater than or equal to 60.0%.

G. GC/EC Continuing Calibration (Form VII PEST)

- G.1. The calibration verification Summary Form VII is used to report the results of the Performance Evaluation Mixtures (PEM), instrument blanks, and Individual Standard Mixtures A and B analyzed at the beginning and end of a twelve hour sequence. The laboratory must submit this form for each twelve hour sequence analyzed.
- G.2. Complete the header information on each Form VII required according to the instructions in part A.
- G.3. Enter the initial calibration date(s) analyzed. Give inclusive dates if initial calibration is performed over more than one date.
- G.4. On Form VII PEST-1, enter the EPA Sample No., Lab Sample ID, Date Analyzed, and Time Analyzed for the instrument blank that preceded the twelve hour sequence (PIBLK). For the PEM that initiated or terminated the twelve hour sequence (PEM), enter the EPA Sample No., Lab Sample ID, Date Analyzed, and Time Analyzed.
- G.5. In the table, report the retention time for each analyte in the PEM as well as the retention time windows. For each analyte in the PEM, enter the amount of the analyte calculated to be in the PEM, in nanograms to three decimal places, under "CALC AMOUNT". Enter the nominal amount of each analyte in the PEM under "NOM AMOUNT". Calculate the relative percent difference between the calculated amount and nominal amount for each analyte according to Exhibit D. Report the values under "RPD". Calculate the percent breakdown for endrin and 4,4'-DDT, and the combined percent breakdown in the PEM according to Exhibit D. Enter the values for the breakdown of endrin and 4,4'-DDT in their respective fields immediately under the table.
- G.6. Form VII PEST-2 is used to report the results of the analyses of the instrument blank and the midpoint concentrations of Individual Standard Mixtures A and B that, along with the PEM, bracket each 12-hour period of sample analyses. One copy of Form VII PEST-2 must be completed each time the Individual Standard Mixtures are analyzed, for each GC column used. The form is completed in a fashion similar to Form VII, entering the EPA Sample No., Lab Sample ID, Date Analyzed, and Time Analyzed for the instrument blank immediately preceding the Individual Standard Mixtures A and B, and for the standards themselves. The upper table on the form contains the retention time and amount data for Individual Standard Mixture A compounds. The lower table contains the data for Mixture

B. enter the data in these tables in a fashion similar to that for the PEM. Complete copies of Form VII PEST-1 and PEST-2 for each standard reported on Form VIII PEST.

H. Pesticide Analytical Sequence (Form VIII Pest)

- H.1. This form is used to report the analytical sequence for pesticide analysis. At least one Form VIII PEST is required for each GC column used for pesticide/Aroclor analyses.
- H.2. The laboratory shall complete all the header information as in Part A. Enter dates of analyses for the initial calibration, GC column, ID, and Instrument ID, as on Forms IV, VI, and VII.
- H.3. At the top of the table, report the mean retention time for tetrachloro-m-xylene and decachlorobiphenyl calculated from the initial calibration sequence under "TCX" and "DCB", respectively. For every analysis associated with a particular analytical sequence starting with the initial calibration, enter the EPA Sample Number, Lab Sample ID, Date Analyzed, and Time Analyzed. Each sample analyzed as part of the sequence must be reported on Form VIII PEST even if it is not associated with the SDG. The laboratory may use the EPA Sample No. of "ZZZZZ" to distinguish all samples that are not part of the SDG being reported. Report the retention time of the surrogates for each analysis under "TCX RT" and "DCB RT". All sample analyses must be bracketed by acceptable analyses of instrument blanks, a PEM, and Individual Standard Mixtures A and B. Given the fact that the initial calibration may remain valid for some time (see Exhibit D), it is not necessary to report the data from 12-hour periods when no samples in an SDG were run. The laboratory must deliver the Form VIII for the initial calibration sequence, and Forms that include the PEMs and Individual Standard Mixtures that bracket any and all samples in the SDG. While the data for time periods between the initial calibration and samples in the SDG is not a routine deliverable, it must be made available on request during on-site evaluations, etc. Here again, non-EPA samples may be indicated with "ZZZZZ".
- H.4. Flag all those values which do not meet the contract requirements by entering an asterisk (*) in the last column, under the "*". If the retention time cannot be calculated due to interfering peaks, leave the RT column blank for that surrogate, enter an asterisk in the last column, and document the problem in the SDG Narrative.
- H.5. If more than a single copy of Form VIII PEST is required, enter the same header information on all subsequent pages for that GC Column and Instrument, and number each page as described in Part A.
- H.6. Form VIII PEST is required for each for each GC system and for each GC column used to analyze target pesticides/Aroclors.

I. Pesticide Cleanup Summary (Form IX PEST-1, PEST-2)

- I.1. This form summarizes the results of the checks performed for both cleanup procedures employed during the preparation of pesticide extracts for analysis. Form IX PEST-1 is used to report the results of the check of the Florisil cartridges used to process all sample extracts, and to associate the lot of cartridges with particular sample results. In this fashion, problems with a lot of cartridges may be tracked across many sample.
- I.2. Complete the header information on each Form IX required, according to the instructions in Part A.
- I.3. Enter the "Case No." and "SDG No." for the current data package, regardless of the original Case for which the cartridge check was performed. Enter the "Florisil Cartridge Lot Number". Enter under the "Date Analyzed" the date the Florisil cartridge check solution was analyzed.
- I.4. Enter "GC Column" and "ID" for the GC columns used to determine the recovery of the analytes in the Florisil cartridge check solution, under "GC Column (1)", and "GC Column (2)", etc., as discussed previously.
- I.5. In the upper table, enter the amount of spike added and spike recovered in nanograms for each analyte.
- I.6. Calculate to the nearest whole percent, and enter the percent recovery in the "% REC" field. Flag each spike recovery outside the QC limits with an asterisk (*). The asterisk must be placed in the last space in the "% REC" column, under the "#" symbol.
- I.7. In the lower table, enter the "EPA Sample No.", the "Lab Sample ID", and "Date Analyzed" for each sample and blank that was cleaned up using this lot of Florisil cartridges.
- I.8. Number the Form IX pages as described in Part A.
- I.9. Form IX PEST-2 summarizes the results of the calibration of the Gel Permeation Chromatography device (GPC) that must be used to process all soil sample extracts for pesticide/Aroclor analyses. Calibration of the GPC is required at least once every 7 days, and each time the GPC column is repacked.
- I.10. Complete all header information as in Part A. Enter an identifier for the GPC Column, and the date of calibration in the appropriate fields. Enter the two "GC Column" and "ID" fields, as discussed above.

- I.11. For each of the pesticide matrix spike compounds listed in the box in the upper portion of the form, enter the amount of the spike added to the GPC column in ng, and the amount recovered, also in ng. Calculate the percent recovery of each analyte, and enter these values on the form, to the nearest percent. Compare the recoveries to the QC limits shown on the form, and flag all those values outside the limits with an asterisk (*) in the column under the “#” symbol.
- I.12. For each sample in the data package that was subjected to GPC under this calibration, enter the EPA Sample No., Lab Sample ID, and the date of both analyses in the lower portion of the form.
- I.13. If more than one copy of Form IX PEST-2 is required, number all pages as described in Instruction A.
- J. Pesticide/Aroclor Identification (Form X PEST-1, PEST-2)
- J.1. This form summarizes the quantitations of all target pesticides/Aroclors detected in a given sample. It reports the retention times of the compound on both columns on which it was analyzed, as well as the retention time windows of the standard for that compound on both of these columns. In addition, it is used to report the concentration determined from each GC column, and the percent difference between the two quantitative results. Separate copies of Form X are used for single component analytes and multicomponent analytes.
- J.2. Copies of Form X are required for each sample, blank, matrix spike, and matrix spike duplicate in which target pesticides or Aroclors are detected. If none are detected in a given sample, no copy of Form X is required for that sample.
- J.3. Complete the header information as in Instruction A. Enter the GC Column, and ID for each of the two columns, one as GC Column (1), the other as (2), as described previously. Enter the Instrument ID associated with each GC column directly below.
- J.4. For each single component pesticide detected, enter the name of the compound under "ANALYTE" as it appears on Form I. Enter the retention times on each column of the compounds detected in the sample next to the appropriate column designation (1 or 2). Enter the retention time windows on each column from the initial calibration standard. These data must correspond with those on Form VI, and are entered in a similar manner. The lower value is entered under the "FROM" column, the upper value under the "TO" column.

- J.5. Enter the concentration calculated from each GC column under the column labeled "CONCENTRATION". The units are the same as those used on Form I, $\mu\text{g/L}$ for water sample, and $\mu\text{g/Kg}$ for soil samples. However, do not enter any units on Form X.
- J.6. Calculate the percent difference between the concentrations entered, and report it to a tenth of a percent under "%D".
- J.7. The lower of the two concentrations is reported on Form I for each pesticide compound. The lower concentration is used because, if present, co-eluting interferences are likely to increase the calculated concentration of any target compound. If the percent difference between the calculated concentrations is greater than 25.0 percent, flag the concentration on Form I, as described previously. This will alert the data user to the potential problems in quantitating this analyte.
- J.8. If more pesticide compounds are identified in an individual sample than can be reported on one copy of Form X, then complete as many additional copies of Form X as necessary, duplicating all header information, and numbering the pages as described in Instruction A.
- J.9. Multicomponent analytes detected in samples are reported on a separate version of Form X. Complete the header information and Instrument and GC Column fields as described above. For multicomponent analytes, it is necessary to report the retention time and concentration of each peak chosen for quantitation in the target analyte, in fashion similar to that for single component pesticides. The concentrations of all peaks quantitated (three are required, up to five may be used) are averaged to determine the mean concentration. Report the lower of the two mean concentrations on Form I. Flag this value as described previously, if the mean concentrations from the two GC columns differ by more than 25.0 percent.
- J.10. If more multicomponent compounds are identified in an individual sample than can be reported on one copy of Form X, then complete as many additional copies of Form X as necessary, duplicating all header information, and numbering the pages as described in Instruction A.

We are proposing the following deviations from OLM03.1 for the CLP analyses of PCBs in Soil /Water samples for the NIROP - Fridley, Minnesota Project

Since we will not be analyzing these samples for pesticides, we are proposing that the pesticide portion of the run sequence be eliminated and the following modifications be performed

Sequence and Calibration:

Initial Calibration

Aroclor 1221@ 200 ng/mL
Aroclor 1232@ 100 ng/mL
Aroclor 1242@ 100 ng/mL
Aroclor 1248@ 100 ng/mL
Aroclor 1254@ 100 ng/mL
Aroclor 1016/1260 LOW@ 100 ng/mL
Aroclor 1016/1260 MID@ 500 ng/mL
Aroclor 1016/1260 HIGH@ 1000 ng/mL

-
-
-
-

10 samples

Continuing Calibration

Aroclor 1016/1260@ 100 ng/mL

Standard and Surrogate Information:

Each of the 100 and 200 ng/mL PCB standards would contain the surrogates TCMX and DCB at 20 ng/mL. The Aroclor 1016/1260 MID level standard would contain the surrogates at 10 ng/mL and the Aroclor 1016/1260 HIGH level standard would contain the surrogates at 100 ng/mL

Quality Control:

All water samples and QC would be spiked with 1 mL of a 200 ng/mL TCMX/DCB surrogate solution (or equivalent solutions producing a 200 ng spike amount) and soil samples would be spiked with 2 mL of the surrogate solution.

Matrix Spike/Matrix Spike duplicate samples would be spiked with 1 mL of a 5 ug/mL Aroclor 1016/1260 spike solution instead of with the normal pesticide spiking solution.

Additionally, a laboratory spike control sample, containing Aroclor 1016/1260, will be processed with each batch.

Quantitation:

All sample quantitations will be based upon single point standards as specified in OLM03.1. Dilutions will be performed whenever the calculated concentration exceeds 10X the concentration of the low level PCB standard.

Data Package:

The following forms would not be included:

- 6D & 6E "PESTICIDE INITIAL CALIBRATION OF SINGLE COMPONENT ANALYTES
- 6G "PESTICIDE ANALYTE RESOLUTION SUMMARY"
- 6H "PERFORMANCE EVALUATION MIXTURE (PEM)"
- 7D & 7E "PESTICIDE CALIBRATION VERIFICATION SUMMARY"
- 9A & 9B "PESTICIDE FLORISIL CARTRIDGE CHECK AND PESTICIDE GPC CALIBRATION"
- 10A "PESTICIDE ID SUMMARY FOR SINGLE COMPONENT ANALYTES"

A new form would be included that documents the linearity of the surrogate compounds and Aroclor 1016/1260 mix at three concentration levels. This would be equivalent to a form 6.

A new multicomponent continuing calibration form would be generated. This would be equivalent to a form 7.

The above procedural changes will supersede the Laucks SOP LTL-8082 for the duration of the project.



Reviewed by Monica Carr, Laucks Organic Supervisor

4/9/97

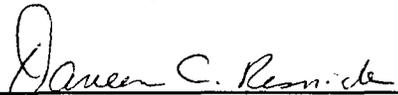
Date



Approved by Harry Romberg, Laucks QA Manager

4-9-97

Date



Approved by Daneen Resnick, Brown & Root

4/11/97

Date

Other Approval

Date

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-9128

Procedure for the Determination of the Oxidation-Reduction Potential in Water or

History:

Date

04/09/97

by: Bill Lundberg
Bill Lundberg

Date: 4/9/97

ed by: Harry Romberg
Harry Romberg, QA Officer

Date: 4-9-97

ed by: Karen J. Kotz
Karen Kotz, Laboratory Director

Date: 4/9/97

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1. Introduction and Scope

1.1 Method Description

- 1.1.1 This method covers the procedure for the electrometric measurement of oxidation-reduction potential (ORP) in water or soil.
- 1.1.2 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.2 Definition of Terms

- 1.2.1 Oxidation-Reduction potential is defined as the electromotive force between a noble metal electrode and a reference electrode when immersed in a solution.

2. Equipment List and Standards

2.1 Equipment

- 2.1.1 pH meter.
- 2.1.2 Reference electrode - a calomel, silver-silver chloride nonflowing junction type.
- 2.1.3 Oxidation-Reduction electrode - a silver electrode or equivalent noble metal electrode.

2.2 Reagents

- 2.2.1 Water: ASTM Type II
- 2.2.2 Aqua Regia- Mix 1 volume of reagent grade concentrated nitric acid with 3 volumes of reagent grade hydrochloric acid.
- 2.2.3 Nitric Acid, reagent grade (1 + 1) - Mix equal volumes of concentrated nitric acid and water.
- 2.2.4 Sulfuric Acid - reagent grade.
- 2.2.5 Calcium Chloride - prepare a 1:1 calcium chloride solution with deionized water.

2.3 Standards

- 2.3.1 Phthalate Reference Buffer Solution ($\text{pH}_s = 4.00$ at 25 degrees C) - Dissolve 10.12 grams of potassium hydrogen phthalate in water and dilute to 1 liter.
- 2.3.2 Phosphate Reference Buffer Solution ($\text{pH}_s = 6.86$ at 25 degrees C) - Dissolve 3.39 grams of potassium dihydrogen phosphate and 3.53 grams of anhydrous disodium hydrogen phosphate in water and dilute to 1 liter.
- 2.3.3 Redox Standard Solution; Ferrous-Ferric Reference Solution - Dissolve 39.21 grams of ferrous ammonium sulfate, 48.22 grams of ferric ammonium sulfate and 56.2 ml of sulfuric acid in water and dilute to 1 liter. The solution should be stored in a closed

glass or plastic container. The Ferrous-Ferric Reference Solution is fairly stable with a measurable oxidation - reduction potential.

- 2.3.4 Redox Reference Quinhydrone Solutions - Mix 1 liter of pH 4 buffer solution (see 2.3.1) with 10 grams of quinhydrone. Mix 1 liter of pH 7 buffer solution (see 2.3.2) with 10 grams quinhydrone. Be sure that excess quinhydrone is used in each solution so that solid crystals are always present. These reference solutions are only stable for about 8 hours so they must be prepared fresh for each day of analysis. The following table lists the nominal millivolt redox readings:

Nominal ORP of Reference Quinhydrone Solutions						
	ORP = v mV					
Buffer Solution- Nominal pH	4			7		
Temperature, °C	20	25	30	20	25	30
Reference Electrode						
Ag/Ag Chloride	268	263	258	92	86	79
Calomel	223	218	213	47	41	34
Hydrogen	470	462	454	295	285	275

3. Safety precautions and Waste Disposal

3.1 Safety Precautions

- 3.1.1 All standards, samples and sample solutions should be handled as if they are hazardous substances.
- 3.1.2 Refer to the instrument manufacturer's manual for routine instrument precautions.
- 3.1.3 Routine precautions include an awareness of the moving parts on the instrument you're using. These parts are often charged with power from an electrical component or with high pressure gas and have the potential to do harm if not used properly.
- 3.1.4 Caution must be taken when handling acids to prevent burns.

3.2 Waste Disposal

- 3.2.1 Waste segregation and disposal from the point of collection is further covered in the Laucks SOP on hazardous waste disposal.

4. Calibration and Quality Control

- 4.1.1 Before using electrode type meters allow them to warm up thoroughly. Bring them to electrical balance by carefully following the manufacturer's instructions. Set the scale or range to the millivolt level expected in the test solution.

4.1.2 Verify the sensitivity of the electrodes by noting the change in millivolt reading when the pH of the test solution is altered. The ORP will increase when the pH of the test solution decreases and the ORP will decrease if the test solution pH is increased. Place the sample in the beaker and agitate the sample. Insert the electrodes and note the ORP or millivolt reading. Add a small amount of a dilute NaOH solution and note the value of the ORP. If the ORP drops sharply when the caustic is added, the electrodes are sensitive and operating properly. If the ORP increases sharply when the caustic is added, the polarity is reversed and must be corrected in accordance with the manufacturer's instructions. If the ORP does not respond as above when the caustic is added, the electrodes should be cleaned and the procedure repeated.

4.1.3 Duplicate Readings

4.1.3.1 Perform a minimum of two successive readings on different sample portions per section 5.1.5 and report both results.

Operation procedures

5.1.1 After the assembly has been checked for sensitivity wash the electrodes with three changes of water or by means of a flowing stream from a wash bottle.

5.1.2 Preparation for water samples:

5.1.2.1 Place the sample in a clean beaker or sample cup and insert the electrodes. Immediately proceed to 5.1.4.

5.1.3 Preparation or soil samples:

5.1.3.1 Place approximately 5 grams of homogenized soil in a clean beaker or sample cup. Add 1:1 Calcium Chloride/deionized water solution to the soil in sufficient quantity to make a slurry.

5.1.3.2 Gently stir the slurry for approximately 2 minutes. Immediately proceed to 5.1.4.

5.1.4 Provide adequate agitation throughout the measurement period. Read the millivolt potential of the solution allowing sufficient time for the system to stabilize.

5.1.5 Measure successive portions of the sample (repeating the sample preparation steps outlined above) until readings on two successive portions differ by no more than 10 mV.

5.1.6 Calculations:

5.1.6.1 If the meter is calibrated in millivolts, read the oxidation-reduction potential directly from the meter scale. This ORP is related to the reference electrode used in the measurement.

- 5.1.6.2 Calculate the oxidation-reduction potential of the sample, in millivolts, referred to the hydrogen scale as follows:

$$E_h = E_{obs} + E_{ref}$$

where:

E_h = Oxidation-reduction potential referred to the hydrogen scale, mV,

E_{obs} = Observed oxidation-reduction potential of the silver reference electrode, mV,

E_{ref} = Oxidation-reduction potential of the reference electrode as related to the hydrogen electrode, mV.

6. Reports

6.1 Data Reporting

- 6.1.1 Report the ORP to the nearest 10 mV. Also report on the benchsheet the pH at the time of measurement.
- 6.1.2 All standard and reagent preparation must be documented in the Inorganics logbooks. All standards and reagents must be traceable to the original stock or neat material.
- 6.1.3 The analyst must record the following information on the analytical benchsheet: date, analyst initials, Laucks sample identification number, sample and quality control results.
- 6.1.4 Copies of the above documentation must be placed in each applicable workorder file for long term document storage.

7. References

- 7.1.1 Standard Practice for Oxidation-Reduction Potential of Water, ASTM D1498-76 (Reapproved 1981).
- 7.1.2 Phone conversation with Daneen Resnick (Brown & Root) from Rock Vitale, April 8, 1997 - modifications to the method to obtain soil ORP measurements.

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-9202

Title: **Total Suspended Solids (Non-Filterable Residue) Using EPA Method 160.2 /
Standard Methods 2540D and Total Volatile Suspended Solids Using Standard
Methods 2540 E.**

Revision history:

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0	7/11/94
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CONTROLLED

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Introduction and Scope

Method Description

Scope and Application

This method is applicable to drinking, surface, and saline waters, domestic and industrial. The practical range of the determination is 4 mg/l to 20,000 mg/l. The detection limit, for, is generally reported as 2 mg/l unless a sample volume greater than 100 mls is used.

A well-mixed sample is filtered through a standard glass fiber filter. The filter and residue are dried to constant weight at 103°C-105°C.

The filtrate from this method may be used for Total Dissolved Solids (Filterable residue).

If volatile suspended solids are to be determined, the filter and residue are then ignited at 550°C and the loss on ignition determined.

Interferences

Samples high in dissolved solids (filterable residue), such as saline waters, brines and wastes, may be subject to positive interferences due to soluble material which has not been completely washed from the filter. Care must be taken to ensure that an appropriate filtering apparatus has been selected and the filter adequately washed in order to minimize this possibility.

Samples which are very high in suspended material or which have certain particle sizes may plug the filter causing difficulty in filtering. It may be necessary to reduce sample size in order to reduce this tendency.

This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

Sample Collection, Sample Storage, Holding Times

No preservation of the sample is necessary. Refrigeration or icing to 4°C, to minimize biological decomposition of solids, is required. Analysis should begin as soon as possible and should in no case exceed 7 days from the date of collection. All exceptions, whether due to laboratory or client cause, must be recorded on a Holding Time Violation Report (HTVR).

Definition of Terms

1 This section defines terms and acronyms as they are used in this SOP. Other terms, such as MS/MSD or method blank, are not defined here since it is assumed that the user of this SOP already understands their more general meaning.

W - Deionized water - Lab reagent water. This water should be free of virtually all analytes.

MDL - Method detection limit - The lowest concentration a sample which will yield a positive result that is greater zero at a known level of confidence. MDLs are empirically determined by Laucks, although there is no known way to determine the MDL for the TSS or TVSS analyses.

MRM or LCS - Standard Reference Material or Laboratory Control Sample. This is a material of approximately the same matrix as the samples, containing a known and usually certified amount of target analyte and which is prepared and analyzed in the same manner as a typical sample. This sample is used to demonstrate that the analytical system is in control. It may be considered to be a blank spike for most inorganic analyses and is preferred over artificially spiking blank materials. This type of sample is rarely analyzed at Laucks for TSS and there is no known source of TVSS material.

Sequence - A set of samples analyzed in a chronologically continuous group.

Total Suspended Solids (TSS) (nonfilterable residue)- Those solids which are retained on a glass fiber filter of the appropriate retentive ability and dried to constant weight at 103-105C.

Total Volatile Suspended Solids (TVSS) - Suspended solids which are volatile (burn off) at a temperature of 550°C.

Equipment List

glass fiber filter discs, 4.7 cm without organic binder, Gelman A/E or equivalent. Laucks currently uses Pro Weigh 47 mm glass fiber filters from Environmental Express which are designed for TSS analysis. They are pre-washed and pre-weighed and require no additional preparation.

membrane filter funnel with the capability of adequately supporting 4.7 cm. filters

distillation flask

Drying oven. set at 103°C-105°C.

Muffle furnace set at 550°C ± 50°C

Desiccator charged with active silica gel desiccant

Analytical balance, capable of weighing to 0.1 mg.

3. Safety precautions and Waste Disposal

3.1 Safety Precautions

3.1.1 All standards, samples and sample solutions should be handled as if they are hazardous substances.

3.1.2 Refer to the instrument manufacturer's manual for routine instrument precautions.

3.1.3 Routine precautions include an awareness of the moving parts on the instrument you're using. These parts are often charged with power from an electrical component or with high pressure gas and have the potential to do harm if not used properly.

3.1.4 Electrical shock - All instruments present the possibility of electrical shock. The operator should take all precautions including ensuring that all instruments are operated with fully grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.

3.1.5 Routine precautions include an awareness of elevated temperatures of both the oven and any samples which have recently been removed from the drying oven or especially the muffle furnace. The temperatures involved in this analysis can cause severe burns if adequate care is not taken.

3.2 Waste Disposal

3.2.1 No waste should be generated from this procedure. Sample residues may be washed out and discarded down the sink.

Quality Control

Method Blanks

1. Criteria:

1.1 Method blanks are used to verify contamination free reagents and apparatus. They are prepared with every set of samples prepared at the same time or at least one blank every 20 samples which ever is more frequent. The method blank is prepared by pouring the same amount of deionized water through a filter as one would a typical sample (generally 100 mls.). Any TSS above the detection limit is reported. Method blank control limits are such that contamination would not exceed twice the detection limit. If 100 ml samples are used, Laucks generally considers the detection limit to be 2 mg/L with method blank control limits of 4 mg/L.

1.2 In making a determination of whether or not the analysis is in control, the analyst should usually be normalizing the blank to whatever volume was used for any sample. It is assumed that any blank is due to washings from the filter and apparatus and is actually independent of sample volume. In other words, the control limit for this analysis is actually 0.4 mg. If blank contamination exceeds that value, the TSS (or TVSS) of samples must be ten times that weight corrective action should be taken.

1.3 If TVSS is being determined, the filters are processed in the same manner only are also heated to 550°C. Otherwise, the detection limits, criteria, and corrective actions are the same as TSS.

2. Corrective action

2.1 Corrective action may necessitate re-preparation and re-analysis of the sample set. For example if TSS or TVSS were found in the blank but not in any of the associated samples, then the sample group may not require re-analysis. In addition, if sample levels exceed 10 times the blank, the level of contamination may be considered insignificant. In any case, if re-analysis is being undertaken, the analyst must first discuss the issue with the Quality Control Officer. In cases where blank contamination exceeds the control limit, a narrative comment must be made which documents the corrective actions taken.

3. SRM or LCS

3.1 Criteria

3.1.1 Analysis of a reference material is not normally required for TSS analysis and no known material is available for TVSS. An SRM/LCS analysis will generally be analyzed only if specifically required for a project. If not otherwise specified in that contract, it would typically

be analyzed at a frequency of once per 20 samples. Vendor specified control limits would be used for any such material.

4.2.2 Corrective Action

4.2.2.1 Re-analysis of all associated samples may be required if this sample exceeds it's limits. The QC Officer should be consulted for any other corrective actions and all instances of out-of-control events and any actions taken must be documented in the QC narrative of the report.

4.3 Sample Duplicate

4.3.1 Criteria

At least one duplicate sample per 10 samples is required. RPD values are calculated as follows:

$$RPD = \frac{|S1 - S2| * 100}{(S1 + S2)/2}$$

where

S1 = measured concentration in the initial analysis

S2 = measured concentration in the duplicate analysis

4.3.1.1 The RPD control limits are detailed in the Quality Control Database (QC_DB) and will change from time to time. For samples with values which are less than 5 times the detection limit, the control limit is equal to 5 times the detection limit. For values greater than 5 times the detection limit, the control limit is a calculated percent RPD.

4.3.2 Corrective action.

4.3.2.1 If a trend in out of control RPD values is observed, the methods used must be examined to determine the source of variance. Once this source is identified, the method must be changed so that samples can be analyzed with a predictable reproducibility. If integrity of reported sample values is in doubt, re-analysis of all associated samples may be called for. Corrective actions should be discussed with the Quality Control Officer.

5. Operation procedures

5.1 Sample Analysis

5.1.1 Analysis sequence

Method Blank

SRM or LCS (if required)

up to 20 samples plus duplicates

5.1.2 Analytical Operation

5.1.2.1 Preparation of glass fiber filter disc if Environmental Express Pro Weigh filters are being used: Remove the filter from its aluminum weighing dish and place the disc on the membrane filter apparatus with the wrinkled side up. While vacuum is applied, rinse the disc with a small amount of deionized water in order to seat the disk in the filter device.

5.1.2.2 Preparation of glass fiber filter disc if pre-washed and pre-weighed filters are NOT being used: Place the glass fiber filter on the membrane filter apparatus (if 4.7 mm filters are being used) or insert into bottom of a suitable Gooch crucible (if 2.4 cm filters are being used) with the wrinkled surface up. While vacuum is applied, wash the disc with three successive 20 ml volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Remove filter from membrane filter apparatus (if 4.7 mm filter) or both crucible and filter if Gooch crucible is used, and dry in an oven at 103°C-105°C for one hour or at 550°C ± 50°C if TVSS is to be determined. Remove to desiccator and store until needed. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg). Weigh immediately before use. After weighing, handle the filter or crucible/filter with forceps or tongs only. As in the procedure for the pre-weighed filters above, wet the filter slightly before use in order to properly seat it in the filtration apparatus.

5.1.2.3 Assemble the filtering apparatus and begin suction, taking care to have wet the filters as described in either procedure above. Shake the sample vigorously and rapidly transfer 100 ml to the funnel by means of a 100 ml graduated cylinder. If this volume takes longer than 5-10 minutes to pass through the filter, sample volume must be reduced such that the filtration time will not be exceeded. If that volume is less than or equal to 10 mls, it should be dispensed with a 10 ml Mohr (graduated glass) pipet which has a wide enough tip opening so as not to inhibit the passing of solid pieces of material.

5.1.2.4 Filter the sample through the glass fiber filter, rinse the graduate and filter with three successive 10 ml portions of deionized water, allowing the rinsate to pass completely through the filter between washings, and continue to apply vacuum for about 3 minutes after filtration is complete to remove as much water as possible.

5.1.2.5 If the sample contains large pieces of material which make it difficult or impossible to achieve a representative, homogeneous sample, it may be necessary to thoroughly mix the sample in a blender prior to filtration. If this is done, however, care should be taken to assure that air bubbles aren't entrained in the measured sample volume to the extent that it could affect the actual volume dispensed. In other words, let the bubbles and subsequent foaming subside before dispensing the sample.

5.1.2.6 Carefully remove the filter from the filtration device, taking care not to leave pieces of filter on the support apparatus, and place it in the aluminum weighing dish appropriate to that filter and sample.

5.1.2.7 Dry the filter for at least one hour at 103°C-105°C.

5.1.2.8 Remove the filter and aluminum dish from the oven and place in a desiccator to cool. The samples MUST be cooled prior to weighing or the apparent weight will be affected.

5.1.2.9 Repeat the cycle of drying, desiccating, cooling and weighing until the filter/dish attain a constant weight, changing by no more than 0.5 mg.

5.1.2.10 Record the final weight for calculation of TSS.

5.1.2.11 If TVSS is to be determined, repeat steps through using a muffle furnace pre-heated to 550°C ± 50°C. Record the final weight for calculation of TVSS.

5.2 Quantification

5.2.1 Residue concentrations are calculated using the following equations:

$$\text{TSS} = \frac{(W_f - \text{tare}) \times 1000}{V_i}$$

$$\text{TVSS} = \frac{W_f - W_a \times 1000}{V_i}$$

where:

V_i = volume of sample used in mls

W_f = weight of dried residue & filter

W_a = weight of ignited residue (after ignition @ 550°C) & filter in mg

tare = tare weight (weight in mg of filter before filtration of sample)

5.2.2 TSS and TVSS are generally reported on a mg/L as received basis.

6. Reports

6.1 Data Packet Organization

6.1.1 The data package for this analysis consists of the data sheet and a quality control database (QC_DB) report form.

6.2 Quality Control Reports

6.2.1 All results for quality control tests are entered into the lab data base using the QC_DB program. Printouts of all data entered need not be included in the package. However, all must be referenced on the report form. This includes the blank and duplicate results and any other QC which might have been analyzed by special request (such as an SRM/LCS).

6.3 Sample Result Reports

6.3.1 Data Qualifying Flags

6.3.1.1 Sample report results are qualified with data qualifying flags. These flags have the following definitions:

CODE	Definition
-------------	-------------------

U	: The analyte of interest was not detected, to the limit of detection indicated.
----------	--

Appendix I

QC Summary Table

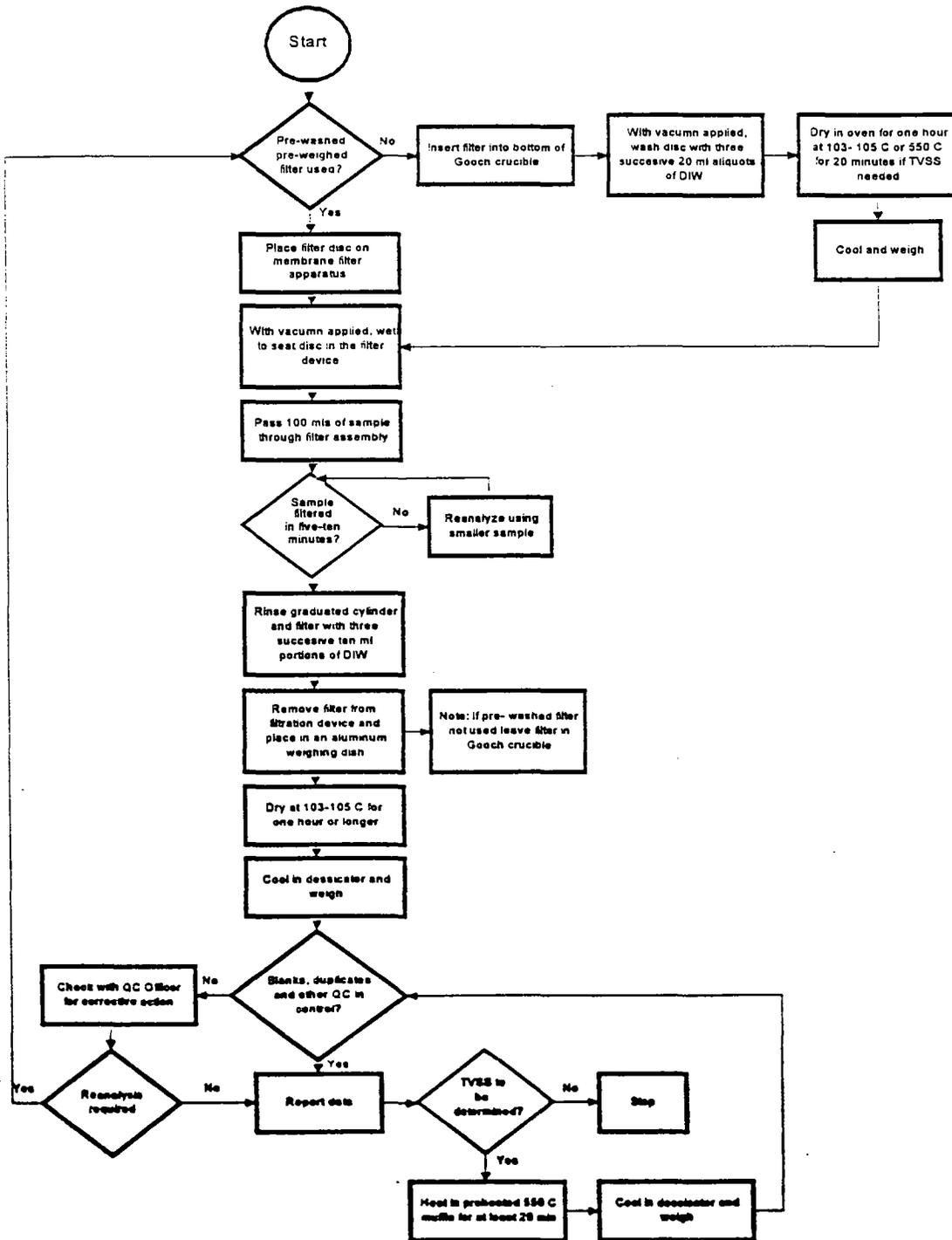
Laucks Testing Laboratories
Method EPA 160.2 / SM 2540D & E QC Requirements and Corrective
Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Method Blank	None	<4 mg/L or no more than twice the detection limit	5% frequency (1 per 20 samples)	Re-analyze all samples <10x the actual weight of the solids. Consult QC Officer for any other actions	QC_DB report form with appropriate commentary
Duplicate % Difference	None	See current control limits catalog or QC_DB database	10% frequency (1 per 10 samples)	Discuss with QC Officer. If impact appears serious, may need to re-analyze samples	QC_DB report form with appropriate commentary
Standard Reference Material (SRM) Recovery	None	Within vendor supplied limits or 90%-110% recovery	If required, at frequency specified, or 5% if not specified	Discuss with QC Officer. If impact appears serious, may need to re-analyze samples	QC_DB report form with appropriate commentary

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Appendix II

Flow Chart
 Total Suspended Solids (TSS) and Total Volatile Suspended
 Solids (TVSS)
 EPA 160.2 and/or SM 2540D&E



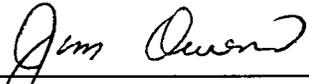
LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-9301

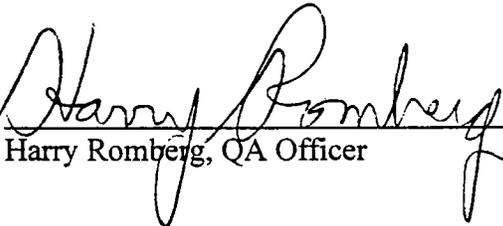
Title: **Spot Test for the Presence of Sulfide in Soil.**

Revision history:

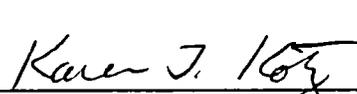
<u>Number</u>	<u>Date</u>
0	04/09/97

Written by: 
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Date: 4-9-97

Reviewed by: 
Harry Romberg, QA Officer

Date: 4-9-97

Approved by: 
Karen Kotz, Laboratory Director

Date: 4/9/97

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1. Introduction and Scope

1.1 Method Description

1.1.1 This method covers the procedure for the qualitative determination of sulfide in soil.

2. Equipment List and Standards

2.1 Equipment

2.1.1 Test tube, 10 to 20 ml.

2.1.2 150ml. to 250 ml. beaker

2.1.3 Filter paper, laboratory grade

2.1.4 Graduated cylinder, 5 or 25 ml.

2.1.5 Lead Acetate test paper - use commercially available lead acetate paper or prepare it in the following manner. Soak laboratory grade filter paper in saturated lead acetate solution until wetted. Remove from the solution and air dry.

2.2 Reagents

2.2.1 Hydrochloric acid - prepare a 20 - 30 % solution of hydrochloric acid in deionized water.

2.2.2 Saturated lead acetate solution - add approximately 20 grams of lead acetate to a beaker. Add 100 ml. of room temperature deionized water and stir.

3. Safety precautions

3.1 Safety Precautions

3.1.1 All standards, samples and sample solutions should be handled as if they are hazardous substances.

4. Quality Control

4.1 Laboratory Duplicate

4.1.1 At least one sample duplicate per 10 samples is required.

4.2 Corrective Action

4.2.1 The duplicate portion of the sample should reproduce the same qualitative results as the initial aliquot. If the duplicate results do not confirm the first analysis the sample should be mixed thoroughly and two new aliquots taken for confirmation

5. Operation procedures

- 5.1.1 Add approximately 1 - 2 grams of representative soil to a test tube or other appropriate container. If the soil is lumpy, gently break up the sample using a mortar and pestle, if necessary.
- 5.1.2 Moisten previously prepared or purchased lead acetate paper with a few drops of water.
- 5.1.3 Add approximately 5 mls. of the 20 - 30% Hydrochloric acid to the test tube and shake or mix for about ten seconds.
- 5.1.4 Immediately cover the test tube with the wetted lead acetate paper.
- 5.1.5 If sulfide is present the lead acetate paper will turn black within 3 to 5 minutes. The odor of Hydrogen sulfide may also be observed.

6. Data Reporting

- 6.1.1 All reagent preparation must be documented in the Inorganics logbooks. All reagents must be traceable to the original stock or neat material.
- 6.1.2 The analyst must record the following information on the analytical benchsheet: date, analyst initials, Laucks sample identification number, sample and quality control results.
- 6.1.3 Copies of the above documentation must be placed in each applicable workorder file for long term document storage.

7. References

- 7.1.1 Standard Methods for Chemical Analysis, Fifth edition, Volume One - The Elements, by Wilfred Scott, pp. 903 - 904.

ANALYTICAL METHOD AM18ANALYSIS OF C₁-C₄ HYDROCARBONS IN WATER1.0 Scope and Application

1.1 Method AM18 may be used to determine the concentration of dissolved gases in water samples. Specifically, Method AM18 may be used to determine the dissolved concentration of the following light hydrocarbon gases:

methane
ethane
ethylene
propane
propylene
i-butane
n-butane

1.2 This method is recommended for use by, or under the supervision of, analysts experienced in sample preparation, the operation of gas chromatographs and in the interpretation of chromatograms.

2.0 Summary of Method

2.1 Analysis of the C₁-C₄ hydrocarbons in a water sample is accomplished by transferring 30 ml of the sample plus 10cc of helium into a 50cc gas tight syringe. After equilibration, the headspace gases are analyzed with a gas chromatograph, using a backflush pre-column 10 port valve configuration and a flame ionization detector (FID). The sample (and standard calibration gas) is introduced into the columns by the mechanical injection of a sample loop. The data is transferred to a microcomputer where it is converted to digital format, stored, and processed using a chromatography data system (Chrom Perfect Direct, Justice Innovations).

3.0 Interferences

3.1 Ambient air is a potential source of "interference". Concentrations of methane in ambient air are typically 1.5 parts per million by volume (PPMV). Other light hydrocarbons may also be present at concentrations levels of concern. The analyst must take great care to ensure that air is flushed from the 50cc gas tight syringe before sample preparation and that no air has entered the syringe or needle prior to injection of the sample into the gas chromatograph.

3.2 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. An unrestricted flow of pure helium from a 10 psig source should be allowed to flow through the sample loop for 30 seconds prior to each analyses.

3.3 The analyst should demonstrate the absence of carryover contamination by analysis of the contents of the sample loop when purged with helium. This demonstration should be performed prior to the analysis of a sample set and when carryover contamination is suspected (after high samples). In the event that 'ghost peaks' (peaks similar to previous sample) appear when a pure helium sample is analyzed, measures should be taken to eliminate the carryover contamination.

3.4 Extra peaks in a chromatogram can be actual peaks from a previous run. Contamination from late eluting peaks can occur when the time between successive injections is too short.

3.5 The analyst should be certain that all peaks have eluted from the previous analysis prior to analyzing any sample or standard. If samples or standard chromatograms contain suspected 'extra peaks' the sample should again be analyzed after a clean baseline is established.

4.0 Apparatus and Materials

4.1 Sample vials: 40 ml VOA glass vials (QEC #2112-40ml or equivalent). Vials should be free of all hydrocarbons and compounds of interest prior to use.

4.2 Septa: Foil faced silicon (Integrated Liner Technologies, Inc.).

4.3 Syringe: Hamilton 50cc locking gas tight (#1050TLL or equivalent).

4.4 Gas Chromatograph: The chromatograph is equipped with the following: column oven, pre-column, analytical column, flame ionization detector, injection port, sample valve and sample loop. The column and detector for determination of C₁-C₆ hydrocarbons are a granular 3 ft. x 3/16 in. alumina analytical column and a flame ionization detector. The alumina column is protected against contamination by heavy organics by a 3 in. x 3/16 in. pre-column which is back-flushed after butanes have entered the analytical column. This arrangement allows rapid turn-around for consecutive analyses and a clean baseline for accurate, reproducible results. The flame ionization detector is of a special design which allows considerably more sensitivity than commercially available models.

4.5 Data Collection: The output of the chromatograph is directed to a microcomputer where the signal is converted to digital format, stored, and processed using a chromatography data system (Chrom Perfect Direct, Justice Innovations, Palo Alto, CA).

5.0 Sample Preparation and Analysis

5.1 Remove the sample (VOA) vials from the refrigerator. Let the samples reach ambient temperature over a period of 2 hours.

5.2 Using a clean 50ml gas tight, locking syringe withdraw 30ml of water from the bottom of the sample vial.

5.3 Withdraw 10cc of helium from a reservoir and lock the syringe.

5.4 Shake the syringe by hand (or use a wrist action shaker) for five minutes.

5.5 With the syringe in a vertical position, slowly inject the 10cc of headspace gas into the gas chromatograph sample loop through a septum fitting. The sample loop should be switched into the carrier gas flow stream (ten port valve activated) immediately after the sample loop has been filled with sample at atmospheric pressure. The flow through the sample loop is monitored by a flow meter connected to the sample loop vent port on the gas chromatograph.

6.0 Calibration and Results

6.1 The standard calibration gas should be introduced in the same manner as described in section 5.5 above. Measured peak areas are converted to concentrations in parts per million by volume using certified commercial gas standards traceable to NIST standards. (Matheson Gas Products Inc., or Scott Specialty Gases). Dilutes may be made to achieve multi point calibration curves.

6.2 At the beginning of a project or sample set, standards of appropriate calibration ranges will be run at least three times or until the results agree with a percent standard deviation no greater than 10%.

6.3 The instrument response (for any one subsequent standard in section 6.1 above) must not vary by more than 20%.

6.4 Concentration of analytes in the headspace gas in PPMV are converted to the original analyte concentration in the water (ng/l) using the following formula:

$$C_{NO} = \frac{(P) (V_G) (MW_X) \left(\frac{V_T}{V_G} - 1 + H_X\right)}{(R) (T) (H_X) (wt_w)} \times C_H \times 10^{12}$$

where:

- C_{NO} = original concentration of compound dissolved in water in nanogram per liter
- C_H = concentration of compound in headspace gas in parts per million by volume
- MW_X = molecular weight of compound
- H_X = distribution coefficient for compound X at room temperature
- T = Room temperature (295.5 deg. K)
- P = pressure = 1 atm
- R = the gas constant = 82.07 cc atm / mole °K
- V_G = volume of headspace gas
- V_T = volume of liquid plus volume of headspace gas
- wt_w = weight of the water

7.0 Quality Control

7.1 If the parameters set forth in section 6.3 are not met, the analytical program will be terminated until the cause is determined and a solution is effected.

7.2 The analyst should demonstrate the absence of ambient air and other contaminants in the sample preparation system by filling a sample syringe with helium and injecting 10cc of helium into the sample loop in the same manner as a sample. The results of this 'syringe blank' should demonstrate that C_1 - C_4 hydrocarbon concentrations are below the minimum detection levels.

7.3 Before and during sample analysis, instrument blanks (sample loop filled with flush helium) should be analyzed to assure the absence of interferences as described in section 3.0 above.

7.4 Standards analyzed during the course of analyzing samples may be averaged into the calibration table as well as being used for peak identification. All chromatograms should be examined by an experienced analyst.

7.5 Throughout analysis the gas samples are injected mechanically utilizing a sample loop to achieve a uniform sample size from a flow

directly from the sample preparation syringe. The uniform sample size assures consistent and accurate results.

7.6 The water sample is withdrawn from the 40ml VOA vial through the septum using a 5 inch large bore luer lock needle while replacing the water with pure helium. The 30ml of sample is withdrawn from the bottom of the 40ml vial and the remaining sample is discarded.

7.7 Calibration records are generated and stored. All such records will be maintained in the laboratory during the course of the project and there after as determined by the client.

8.0 Instrument Conditions

8.1 Gas Chromatograph:

Injection Temp. ambient
Flame Ionization Detector Temp. ambient
Oven Temp. 100 deg. C. isothermal
Initial F.I.D. Signal Range 10E9
Carrier Gas Regulator 24 psig.
Hydrogen Pressure 22 psig.
Flame Air Pressure 25 psig. (1.0 scfh)

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #LTL-1002

Title: Document Tracking and Control

Revision history:

Number	Date
1.0	05/15/95
2.0	12/27/95

Written by:

Harry Romberg
Harry Romberg, QC Officer

Date:

12-27-95

Approved by:

Karen J. Kotz
Karen Kotz, Laboratory Director

Date:

12/28/95

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SOP UPDATE FORM 13

1. Introduction and Scope

- 1.1. The purpose of this SOP is to describe the system under which Laucks creates and tracks controlled documents. This insures that the latest, approved version is in use and that prior versions are kept on file but are not available for unauthorized use. It forbids the use of unapproved or expired copies of methods or procedural documents. This includes but is not limited to procedural SOPs, QA documents, and analytical methods. Other documents may be included under this system at Laucks discretion.
- 1.2. Laucks recognizes two types of documents.
- SOPs are considered to be administrative (such as this document or others dealing with data review or sample entry) or they may be analytical procedures (methods).
 - Guidance and other miscellaneous documents may be generally broader in scope and utility than SOPs, examples being the laboratory QA Manual or Chemical Hygiene Plan.
- 1.3. The protocol for initiating new documents is outlined, as well as the process for their approval. The tracking process is also outlined as is distribution to appropriate individuals and replacement of outdated copies with updated versions.
- 1.4. This SOP does not attempt to describe the actual creation of documents except to require that certain elements be present in order that the document may be tracked and controlled. Other SOPs describe the structure or other elements required for a specific type of document.

2. Operation Procedures

2.1. Initiation and Updating of Documents

- 2.1.1. In order to track the status of documents, it is necessary to first be aware of what documents are in the process of being created, reviewed or revised. In order to do this, the Document Control Form is used (see Appendix A). Prior to beginning the creation or revision of any SOP or other controlled document, this form should be filled out. It will be kept on file in the QA Department so that it will be known which documents are in the process of being written or revised, and who is the primary responsible person for creating, reviewing or revising it.
- 2.1.2. The form must be filled out by either the individual responsible for the creation or revision, their Department Supervisor, or Division Manager. Creation or revision of documents

may also be assigned by the Laboratory Director, Technical Director, or QA Officer to specific individuals. The form, however, must be approved and kept on file by the QA Department.

- 2.1.3. Copies of this form will be given to the responsible individual and the appropriate Division Manager. Originals will be kept on file in the QA Department. This is in order to make sure the responsible parties are all informed of the initiation of the creation or revision process. This form must be filled out as soon as it is determined that the creation or revision of a document is necessary and a responsible party has been assigned. These forms will also be issued approximately annually in order to initiate the review process for existing SOPs.
- 2.1.4. It is recognized that some documents may have been written prior to completion of the Document Control Form or that it may be decided that some documents which are already in existence should be placed into the document control system. Unless these documents are ready for immediate approval, and acceptance by the Lab Director, QA Department and/or other responsible parties, in other words, not in a draft or review status, the document control form should be filled out.
5. Shortly after the Document Control Form is approved and distributed by the QA Department, an entry will be made in a database maintained by QA which tracks the status of that document. All documents which have been previously approved but are currently in the process of being revised will remain in force until revisions have been completed and approved.

2.2. Tracking and Control of Existing Documents

- 2.2.1. Most documents, particularly SOPs and administrative documents, will be assigned document numbers beginning with LTL. The scheme for numbering documents then proceeds as follows:

LTL-1000	QA / Administration
LTL-2000	Health and Safety
LTL-3000	Organic Extractions
LTL-4000	Sample Control,
-4100	Project Management
-4200	Document Management and Reporting
LTL-5000	Computer Systems (LIMS / MIS)
LTL-6000	Miscellaneous

LTL-7000	Metals Digestion
-7100	ICP Analyses
-7200	ICP/MS Analyses
-7300	Graphite Furnace Analyses
-7400	Flame Atomic Absorption Analyses
-7500	Cold Vapor Atomic Absorption Analyses
-7600	Gaseous Hydride Atomic Absorption Analyses
LTL-8000	Gas Chromatography, Volatiles
-8100	Gas Chromatography, Semivolatiles
-8200	GC / Mass Spectrometry
-8300	HPLC
-8400	Other Organic Analyses
LTL-9000	Conventional Chemistry- Titrimetric Analyses
-9100	Conventional Chemistry- Spectrophotometric / Instrumental Analyses
-9200	Conventional Chemistry- Gravimetric Analyses

- 2.2.2. Original documents will always be given a revision number of 0. Subsequent revisions, no matter how minor the revision, will be incremented by one.
- 2.2.3. In addition to the numbering and revision documentation, the document must also be given a title which will uniquely identify the document content. If the document is an analytical method, the method reference should be incorporated into the title. One example of this might be "Organochlorine Pesticides and PCBs by SW 846 Method 8080."
- 2.2.4. The database, as a minimum, will track the document number, revision number, title and SOP Manual distribution. In addition, other information may be tracked where appropriate and might include responsible individual, current status (first draft, first review, final revision, final review, complete, etc.), and any other details that may appear necessary in order to facilitate completion of the document.
- 2.2.5. SOPs, Methods, and many other documents should have header information which clearly indicates the document number, revision, date of revision, document replaced by revision and, usually, page number. The header may vary from but should contain all appropriate information similar to the following:

SOP No: LTL-xxxx
Revision: 1
Date: 12/27/95
Page: x of xx
Replaces: 0

- 2.2.6. Once a document has successfully undergone review and been signed-off by the author of the document and all of the other appropriate individuals (Laboratory Director, QC Officer, and, where appropriate, Technical Director, Division Managers, etc.), it is added to the SOP list. Only approved documents and their most currently approved revisions are noted on these lists. These lists are broken down by department and distributed to department supervisors with the distribution date indicated. New lists are distributed whenever a new document or revision is added.
- 2.2.7. A database is maintained by the QA department which tracks the revision history of all documents. This database includes both current documents and their predecessors. Outdated documents and prior revisions are kept on file, with the intent of incorporating them directly into the database, but are generally not made available to analysts.
8. Copies of the most current documents are kept on file in the QA Department and departmental specific documents are kept by the departmental supervisor in ring-binders which are available to all analysts and other appropriate staff. These departmental copies are stamped in red with a Controlled Document Stamp (See Appendix B). These copies, which are tracked by the QA department, will be replaced when a newer version has been completed and signed-off. The color of the Controlled Document Stamp will be black on subsequent secondary copies and will not be directly tracked by the QA department as these documents are considered uncontrolled.
- 2.2.9. It is the Departmental Supervisor's responsibility to ensure that their staff have copies of the most recent version of any document available to them. Keeping copies of outdated versions is inappropriate as they may be inadvertently used by uninformed individuals. When revised versions are issued, the old versions will be collected from the SOP books. In addition, the SOP book table of contents will be updated to reflect the revised SOP(s).
- 2.2.10. It is inappropriate for any individual to be working from an unapproved copy of a method or procedure.
- 2.2.11. It is inappropriate to make copies of the copies which are not stamped in red with the Controlled Document Stamp.

- 2.2.12. When documents are distributed to the departmental supervisor, a copy of the signature list(s) for the specific document(s) is also distributed. The signature lists are returned to the QA department when completed.
- 2.2.13. Departmental supervisors will insure that the most recent version of all appropriate documents are made available to all affected staff members. When this occurs, three things must happen.
- Newly distributed versions are placed in the SOP manuals.
 - The signature lists for the current document are signed and dated. In addition, as staff new to a particular task (SOP) are trained, the departmental supervisor will ensure that they have read and signed the signature list for that SOP.
 - The departmental supervisor is responsible for ensuring that all outdated versions of SOPs are discarded or destroyed.
- 2.2.14. Note that although any person capable of performing a documented task should be in possession of or have access to a current, officially assigned copy, the possession of a copy of any SOP or method does not imply that the individual in possession is qualified to perform the task detailed. They must still be properly trained in the techniques involved.
- 2.2.15. Note that versions of methods or SOPs which have been given to regulatory agencies or clients are uncontrolled in that they will not be updated except by specific arrangement.

2.3. Storage and Filing of Controlled Documents

- 2.3.1. Controlled documents will be kept by the QA Department. Master copies of the documents will be stored in a secure file and will generally not be used except to act as the reference copy and make intermediate "reproduction" copies.
- 2.3.2. Reproduction copies will be used to make subsequent copies for distribution to the laboratory and other authorities. These will be filed in QA but may not be stored in the same secure manner as the master copies.
- 2.3.3. Both master and reproduction copies will be filed in order of their SOP number as defined previously.
- 2.3.4. Electronic versions of all controlled documents are also kept on file by QA. These versions are stored in an area of the laboratory network which has limited access to designated individuals. These electronic copies will be given names as closely matched as

possible to their document or SOP number. Original documents and revisions will be given the extension .R0 or .R1, etc. to indicate their revision number. Should multiple files be necessary to create a given document, they will be incorporated into a subdirectory with similar naming conventions.

- 2.3.5. Copies of these electronic versions of SOPs will be distributed to individuals who have been assigned a revision. No other copies of these controlled documents should be kept by laboratory staff in order that unapproved copies of the document do not proliferate.
- 2.3.6. When a document has been revised and the outdated version has been removed from circulation, the master copy of the outdated version will be stamped with the "Replaced Version" stamp (Appendix C) to ensure that it is never inadvertently used as a current version. In addition, replaced versions will be filed in the "history" file which is separate from the current versions.

2.4. Review and Updating of Documents

- 2.4.1. In order to facilitate updates to documents without violating the practices outlined in the SOP, and in order to insure all approved updates have indeed been incorporated into the document, an "SOP Update" form (Appendix D) must be used. A copy of this form is located in Appendix D. This form may be filled out at any time by an analyst or supervisor. Before the change can be brought into practice, however, it must be approved by QA. QA may also choose to consult the area supervisor, Division Manager, or other senior staff before incorporating the procedure into the routine practice. A copy of this form will be kept with the laboratory controlled copy AND a copy must be filed with QA. When it is time to update the SOP, changes outlined on these forms will be incorporated into the revision.
- 2.4.2. SOPs should be reviewed approximately annually. Items addressed in the "SOP Update" forms will then be incorporated into the SOP itself. In addition, any other updates determined at the time of the review will be added. Each review will be documented on the Document Control Form (Appendix A).

SOP No: LTL-1002
Revision: 2
Date: 12/27/95
Page: 9 of 14
Replaces: 1.0

Appendix A

Document Control Form

SOP No: LTL-1002
Revision: 2
Date: 12/27/95
Page: 10 of 14
Replaces: 1.0

Laucks Testing Laboratories
DOCUMENT CONTROL FORM

- Generate new document
- Modify existing document
- Review existing document

Document No.: _____

Document Title: _____

Assigned to: _____ Date: _____

The aforementioned document has been reviewed and does not require modification at this time:

Reviewer: _____ Date: _____

Purpose for generation or modification of document and comments on review:

QA Approval: _____ Date: _____

Appendix B

Document Control Stamp

<p>Controlled Document</p> <p>Individuals must not perform work using this document unless they have signed the master and have been assigned a numbered copy. Unassigned copies will not be updated when changes occur.</p> <p>No. _____</p> <p>Assigned to: _____</p>
--

Appendix C

Replaced Version Stamp

**This document has
been replaced by:**

Revision: _____

on
Date: _____

SOP No: LTL-1002
Revision: 2
Date: 12/27/95
Page: 13 of 14
Replaces: 1.0

Appendix D

SOP Update Form

SOP No: LTL-1002
Revision: 2
Date: 12/27/95
Page: 14 of 14
Replaces: 1.0

Laucks Testing Laboratories
SOP UPDATE FORM

Document No.: _____

Document Title: _____

The following changes have been reviewed and determined to be necessary to the implementation of the above document.

Submitted by: _____ Date: _____

Approved by (QA): _____ Date: _____

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP # ~~LTL-COG~~ ^{DK-1226/95}
LTL-1003

Title: Chain-of-Custody and Documentation Procedures

Revision history:

<u>Number</u>	<u>Date</u>
1.0	02/13/95

Written by: Harry Romberg
Harry Romberg, Quality Control Officer

Date: 2-13-95

Reviewed by: Mike Nelson
Mike Nelson, Technical Director

Date: 2-13-95

Approved by: John Buerger
John Buerger, Laboratory Director

Date: 2/13/95

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LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP No. LTL-1003

Previous SOP No. LTL-COC

Title: Chain-of-Custody and Documentation Procedures

Rev: 1

Laucks is in the process of re-numbering our SOPs. As an interim measure, this page serves as the cover page for those SOPs whose header information has not been updated. This page details the title, the SOP number that it is being controlled under, and the previous SOP number. The previous SOP cover sheet has been manually corrected to reflect the change but each page header will reflect the old numbering system. As SOPs are revised, the full header and cover page will be updated.

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1. Introduction and Scope

1.1. Description

- 1.1.1. This SOP is intended to describe the chain-of-custody process at Laucks, for all samples from the point of receipt until the time of sample disposal. It does not address actual sample receipt, entry and log-in, nor does it address any aspect of samples analysis or reporting of results except as it pertains to maintaining the chain-of-custody. The chain-of-custody process is described only for samples requiring secure storage and strict chain-of-custody documentation.
- 1.1.2. The location of all samples requiring secure storage must be known at all times over the course of their possession by Laucks. Failure to maintain these conditions may result in invalidation of data on legal grounds, regardless of the technical level of data quality.
- 1.1.3. This process is restricted to use by, or under the supervision of analysts experienced in the process described. Each analyst or other individual requiring possession of the samples for any reason must understand the necessity of this documentation chain and be familiar with the process. Any person requiring access to the samples outside of the secure storage area must check them out using the described procedures.
- 1.1.4. Virtually all analytical staff and many others employed by Laucks are considered authorized personnel and may have access to one or more of the secure storage areas as needed for performance of their duties, at the discretion of the individual, and depending upon the nature of their duties. Removing of the samples or any aliquots thereof from the secure areas, however, requires completing the forms provided for this purpose. Individuals who are not Laucks employees will not have access to samples except under the direct observation and accompaniment of staff members.

1.2. Definition of Terms

1.2.1. Custody - A sample is considered under custody if:

- It is in the possession of an authorized person
- It is in view after being in the possession of an authorized individual
- It was in the possession of an authorized individual who then locked it up
- It is in a designated secure area which is accessible only to authorized personnel.

1.2.2. Chain of Custody - The process by which custody of a sample is maintained and documented throughout the period that the sample is in the possession of the laboratory. Any

changes in the possession (custody) of the sample must be documented in order that the chain-of-custody can be properly maintained.

2. Equipment List

- 2.1. Secure Storage Custody Log(s), see Appendix A

3. Safety Precautions

- 3.1. Safety Precautions

- 3.1.1. No safety precautions are necessary for adherence to the items addressed by this SOP. However, in handling actual samples while operating under this document, all standards, samples and sample solutions should be handled as if they are hazardous substances.

4. Operation procedures

1. Identification of Samples Requiring Strict Chain-Of-Custody
 - 4.1.1. Almost all samples entering the laboratory come with chain-of-custody logs, either generated by the client or by Laucks. Often these chains-of-custody are intended only for clear identification of testing parameters, rather than actual custody maintenance. These custody logs, however, will always be signed, timed and dated by the person checking the samples in and entering them into the laboratory database.
 - 4.1.2. Actual internal chain-of-custody procedures will be followed for all project and other work which require such procedures. These are usually identified as CLP work or work which require similar deliverables. These samples will usually, although not always, arrive with custody seals on the coolers and sometimes even the sample containers themselves. All work under the HAZWRAP, NEESA, or Army Corps of Engineers require these procedures, regardless of the type of deliverables requirements, as does any work involving pending legal action. If it is uncertain whether or not strict chain-of-custody should be maintained, these procedures should be followed.

4.2. Initiating Internal Chain-Of-Custody

4.2.1. Internal chain-of custody procedures begin when the samples are logged into the laboratory database. When the samples are logged into the system, they are stored in the sample entry area, in the main laboratory, in one of 3 locations:

- The main walk-in cooler is for organic extractables which have not yet been transferred to the extractions laboratory and for inorganics which require refrigeration.
- The small refrigerator just outside of the walk-in is for volatiles sample storage.
- The locked "cage" in the log-in area is for samples not requiring refrigeration.

4.2.2. Additionally, samples requiring secure storage which are located in the walk-in will be on designated shelves. Those awaiting transferal to the organics extractions laboratory will be on their own designated shelf.

4.2.3. For samples being logged into both the non-volatiles areas and volatiles refrigerator, a carbon copy of the Secure Storage Custody Log will be created for that refrigerator and the volatiles samples will subsequently be logged in and out using that form.

4.2.4. Samples requiring secure storage are logged into any of these areas by the sample receiving representative using a Secure Storage Custody Log (Appendix A). Samples not requiring secure storage need not have this form completed. A custody log will be completed for each **workorder** for which samples require chain-of-custody procedures.

4.3. Maintaining Internal Chain-Of-Custody

4.3.1. When samples are logged out of storage areas, they will be signed out in the appropriate spaces by the person removing them.

- If they are being removed for analysis, the "**Action**" column should state the analyses being performed. When they are returned, the logsheet must also indicate such.
- If they are being removed for transferal to another location (extractions or one of the volatiles storage locations), the "**Action**" column should state where they are being transferred. Additionally, the "**Sample Numbers**" column should indicate which samples are being transferred (i.e. 1-10 volatiles, or 3-5 extractables).
- When samples are removed for final disposal, if all samples are being removed, the logsheet is signed and dated at the bottom of the page. If only certain samples are being disposed or to be even more clear, the "**Action**" column should indicate "disposed" and the "**Sample Numbers**" column should indicate which samples are being disposed.

4.3.2. When samples are signed into another storage location, this is done using an identical Secure Storage Custody Log. Samples which are subsequently removed from these areas for analysis or disposal should be signed out using the same procedures as above.

4.3.3. Any analyst removing samples from any secure storage area for the purpose of preparation or analysis or transferral to another department **must** sign the samples out using the Secure Storage Custody Log and must sign the samples back in when they are returned, or must sign them into another secure storage area. Samples must be in the possession of the analyst who signed them out at all times during this period and must not be left unattended. If samples are analyzed and then immediately disposed, as may be the case for some volatiles analyses, the "Action" column on the custody log should indicate "analysis and disposal."

4.4. Sample Disposal and Closing of the Internal Chain-Of-Custody

4.4.1. When samples have been signed out for final disposal the chain-of-custody process is considered to be complete. At least quarterly, the Secure Storage Custody Logs are collected by the Quality Control Department and collated into binders in order that the chain-of-custody can be tracked for all samples requiring this process, should such tracking be required at a later date.

SOP No: LTL-COC
Revision: 1.0
Date: 02/13/95
Page: 8 of 9
Replaces: none

Appendix A

Secure Storage Custody Log

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-1004

Title: **Documentation of Analyst Competence and Training**

Revision history:

<u>Number</u>	<u>Date</u>
1.0	01/31/95
2.0	12/27/95
3	6/23/96

Revised by: Harry Romberg
Harry Romberg, Quality Assurance Officer

Date: 6-23-96

Approved by: Karen J. Kotz
Karen Kotz, Laboratory Director

Date: 6/23/96

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1. Introduction and Scope

1.1 Description

- 1.1.1 This SOP describes the way in which analyst competence is initially documented and by which the analyst is considered capable to perform independent analysis. Two practices are in place at the time of this writing. One practice is designed primarily for analysts who have been employed doing an analysis for a significant period of time at Laucks and have demonstrated competence through the successful analysis of many samples, including one or more of the following: performance evaluation (PE) samples, reference materials, laboratory control samples, surrogates, etc. The other practice is primarily for analysts who have been performing a specific analysis for less time than is considered extended proof of competence. This practice involves the analysis of multiple aliquots of a PE sample and subsequent evaluation of the results.

1.2 Scope

- 1.2.1 *This SOP contains discussion of initial demonstration of competence through PE analysis and, for some analyses, P&A criteria. It also defines ongoing performance demonstration through the use of PE samples.*
- 1.2.2 *Specific elements of training in safety, QA, and in each department are maintained in separate files. However, quizzes and sign-off sheets from this training are included in the respective analyst's file as demonstration that such training occurred. Specifics of these types of training are not within the scope of this SOP.*

2. Definitions

- *PE - Performance Evaluation*
- *P&A - Precision and Accuracy*
- *Trainer - An individual who has documentation demonstrating experience recognition or successful completion of competency and has been performing the task/method for a minimum of 3 months experience for login, sample preparation, and reporting and a minimum of 6 months for analytical instrumentation operation and analysis reporting.*

3. Responsibilities

3.1 Analyst

- 3.1.1 *It is the responsibility of the analyst to complete all of the items of their required training in an appropriate timeframe as required by their manager, safety and QA.*
- 3.1.2 *The analyst must complete all demonstration of competency items outlined in this SOP in a manner consistent with the analytical SOP.*
- 3.1.3 *The analyst must analyze a PE study initially and on an ongoing basis (at least annually) for each method for which they are considered qualified.*
- 3.1.4 *For many analyses, the analyst must perform an initial Precision and Accuracy study as required.*

3.2 Supervisor

- 3.2.1 *It is the supervisor's responsibility to ensure that their analysts are all initially qualified to perform an analysis including ensuring that they have analyzed all required PE samples and performed all required P&A studies for the methods for which they will be doing analyses.*
- 3.2.2 *It is the supervisors responsibility to ensure that all analysts have participated in applicable QA and safety training.*
- 3.2.3 *It is the supervisor's s responsibility to ensure that on a continuing basis, at least annually, that analysts who are to be considered capable of performing an analysis, have performed within limits on at least one PE study for analyses for which such are available.*
- 3.2.4 *It is the supervisor's responsibility to ensure that other training has occurred, whether that means peer training, reading, quizzes, completed checklists, etc.*
- 3.2.5 *It is the supervisor's responsibility to develop and maintain current departmental training materials, such as checklists, quizzes, etc.*
- 3.2.6 *It is the supervisor's responsibility to ensure that the analyst's training file has been updated with the most current PE or P&A data as well as any quizzes or checklists that are considered part of their departmental training.*
- 3.2.7 *It is the supervisors responsibility to designate a qualified individual(s) to train personnel for their new task/assignment.*

3.3 QA

- 3.3.1 QA maintains training files (except for Extractions where the supervisor maintains the files due to the location of the extractions facility).
- 3.3.2 QA periodically audits training files to ensure appropriate training is being maintained.
- 3.3.3 QA reviews PE and P&A studies to ensure criteria have been met.
- 3.3.4 QA works with managers to assist in developing training materials.
- 3.3.5 QA provides training to staff in QA issues and ensures that documentation of this training is in the staff training file.

3.4 Trainer

- 3.4.1 Completes applicable staff training documents during the training process.
- 3.4.2 Reviews documentation with the individual and the supervisor to ensure timely and accurate review of progress and documentation.

Operation procedures

4.1 Recognition of Experience and Training

- 4.1.1 Many analysts have been performing their assigned duties for an extended period of time and have successfully analyzed many samples, reference materials, PE samples, matrix, blank, and surrogate spikes and have not only demonstrated their capabilities to achieve results which meet criteria but have demonstrated a thorough knowledge of all aspects of the chemistry involved, instrument performance and maintenance, the necessary data reduction requirements, quality control criteria, and documentation.
- 4.1.2 These analysts, at the discretion of the appropriate Division Manger, may be certified to independently perform their analytical duties. This is achieved using the Recognition of Experience and Training Form, an example of which is in Appendix A. This form contains space to note the analysis type (Cyanide, for example) and the methods by which they are considered competent (335.3 and 9012 perhaps, but not CLP). The dates from which they have been doing these analyses must also be noted on the form. The Division Manager then signs the form in order to certify that the analyst is considered adequately trained in the particular method or aspect of the job. The form must include the criteria used to designate someone as competent and attached to the form must be the applicable documentation to confirm the criteria has been met.

- 4.1.3 *Certification of competency must include the successful analysis of a performance evaluation (PE) sample where such are available or can be made in the laboratory by a supervisor. This sample will be blind to the analyst, must be analyzed independently by them and must be analyzed in accordance with the appropriate SOP. Greater specifics on these types of samples are given in the Laucks SOP entitled "Blind Spike Program" but will often be from a WP or WS study or from another commercial source. Analysts who have been performing analyses for any length of time at Laucks have almost certainly analyzed numerous PE samples which can be used for initial and ongoing demonstration of competency.*
- 4.1.3.1 *Adequate performance on a PE sample will be considered to be within the supplied statistical limits for that sample if from a commercial source or from method defined limits for an LCS or blank spike if from internally prepared material.*
- 4.1.4 *Precision and Accuracy (P&A) criteria using quadruplicate analysis are also a part of most organic SW846 and some other methods. Successful analysis of such samples will be considered to be within the reference method-specified criteria. Since Laucks own precision and accuracy limits must be within the method-specified criteria, the analyst should also be able to meet Laucks criteria as well as those of the reference method. However, as long as method criteria are met, the analyst may be approved for independent work as long as they are able to obtain satisfactory performance from the ongoing analytical QC for that analysis.*
- 4.1.5 It is acceptable to certify such capabilities on multiple forms and to certify for multiple analysis types and/or methods on one form. At the time of this writing, there may be no known materials which can be submitted as unknowns for some analyses. In this event, at the discretion of the Division Manager and Quality Assurance Officer, this form may also be used to qualify analysts. From the date of the first version of this SOP, however, this should not be done where materials are readily available and reasonably handled.
- 4.1.6 When this process is completed, the original of this form and a copy of all applicable documentation will be inserted into the analyst's training file which is maintained in the QA area for the 940 building and the Extractions Supervisor Office for the 921 building.

4.2 Demonstration of Capability to Perform Analysis

- 4.2.1 For analysts who are relatively new to their assigned tasks, *a greater degree of capability demonstration must be undertaken through the satisfactory completion of any internal departmental training documentation. This training will include specific training and documentation developed by that department and department manager and may include required reading, quizzes, and performance criteria at the discretion of the department manager and QA. Example checklists are provided as Appendix C.*

- 4.2.2 *In general, if an analyst has not passed the criteria detailed in 4.1, then he/she must proceed through the following:*
- 4.2.2.1 *A trainer is designated for the task/test*
 - 4.2.2.2 *One-on-one training occurs for the timeframe designated by the supervisor and applicable checklists.*
 - 4.2.2.3 *Training may also include required reading of SOPs and the QA Plan, quizzes, and subset task demonstrations.*
 - 4.2.2.4 *Progress is monitored and documented on applicable forms.*
 - 4.2.2.5 *Supervised training continues until the analyst is deemed ready for capability demonstration.*
 - 4.2.2.6 *Demonstration of analytical competency completion, however, will be the same. Performance Evaluation and/or P&A elements as described previously in 4.1.3 and 4.1.4.*
- 4.2.3 *Where P&A demonstration is not required and defined by the method, Laucks may choose to apply additional internal P&A criteria similar to a typical P&A study. The samples may be submitted by the QC Officer, the Division Manager, or an individual designated by one of the above. Four or more aliquots of a material will be submitted to the analyst as unknowns. The analyst must demonstrate the capability to achieve results within the recovery range specified by the manufacturer, if they are independent materials, or within laboratory recovery criteria if they are prepared in-house. In addition, the % RSD of the results must be within Laucks established RPD limits (or default RPDs if none exist for a specific target analyte).*
- 4.2.4 *It is recognized that some independent materials may not recover within manufacturers criteria, at least for a subset of the target analyte list, regardless of the experience and competence of the analyst, due to degradation of the material, arbitrary setting of the limits, determination of the "true" values by methods other than those used for the analysis, or other factors. In that case, the % RSD may be the major factor in evaluation and other considerations or action may be taken at the discretion of the QC Officer and/or Division Manager, such as how Laucks more experienced analysts have historically performed for a particular material.*
- 4.2.5 *Failure to meet criteria means that the analyst must continue to work under the close supervision of a trained analyst.*

- 4.2.6 Likewise, meeting these criteria may be determined to be only one step in the overall training process. Whereas this is demonstration that the analyst is capable of obtaining reliable results, the Division Manager or other supervisory personnel may determine that a more complete knowledge of the analytical process is in order, such as instrument maintenance capabilities, method troubleshooting, data reduction, proven performance on actual sample analysis, etc.
- 4.2.7 When such materials are analyzed, a Demonstration of Capability to Perform Analysis form is completed (see Appendix B). This form is designed for single analyte methods. For multi-analyte materials, a page may be attached which depicts all of the analyst's results and the control criteria. However, this is the final signature form and must accompany any summary pages or written evaluation which may be considered pertinent. Also attached should be copies of the supporting data or a data summary page which references the workorder under which the data may be found.
- 4.2.8 The date of analysis, the results, the recoveries, and the % RSD are recorded on the form (or the attached summary). If all analytes met or did not meet criteria, the appropriate box is checked. If not all criteria are met but the analyst was considered to have performed adequately, a narrative explanation *must* accompany the evaluation, either on the back of the form or as a separate, attached report.
- 4.2.9 Additionally, if the analyst, through the analysis of these samples is considered fully qualified to perform the analysis, the appropriate box is checked and the form signed by the Division Manager. If the Division Manager considers that the analyst is now capable of analysis but still requires additional experience and training before they are fully capable of independent analysis, a date is set to review performance. The additional experience or training required and the next performance review date are recorded on the form (with the appropriate box checked) and initialed.
- 4.2.10 If further training is still required, copies of these forms will be retained by QA in a file to be reviewed regularly to insure that this final analyst review occurs in a timely fashion. A copy of the form indicating interim status will also be retained in the staff member's training file.
- 4.2.11 When this process is completed, the original of this form will be inserted into the analyst's training files.

4.3 *Ongoing Demonstration of Performance*

- 4.3.1 *At least annually, after initial qualification, analyst proficiency must be demonstrated. Each staff member that performs a method must demonstrate their continued proficiency through analysis of single blind proficiency samples (another PE). WP, WS or*

commercial PE samples may be used to satisfy this requirement just as they were used for initial qualification.

- 4.3.2 *As with initial qualification, continuing performance must be documented in the analyst's training file. Ongoing competency can be documented using the Recognition of Experience and Training Form.*

5. References

Navv Installation Restoration Laboratory Quality Assurance Guide, Naval Facilities Engineering Service Center, February 1996

Laucks SOP

LTL-1011 Procedures for the Determination and Reporting of Detection Limits, Reporting Limits, Precision and Accuracy Studies, and Control Limits

Appendix A

Recognition of Experience and Training Form

Recognition of Experience & Training Form

Laucks Testing Laboratories

It is hereby recognized that _____
Employee Name

has demonstrated competence in the methodologies listed below. Through the successful analysis of numerous samples, including performance evaluation samples, matrix spikes, laboratory control samples, etc. and in the associated reduction of data as required by these methods, we certify this staff member as being capable of independent performance of the listed analyses.

Analysis Type	Method Numbers	Has Been Performing Analyses by These Methods Since	Has Demonstrated Competency by meeting the following criteria, with the hard copy of applicable information relating to this competency attached to this form

Division Manager

Date

SOP No: LTL-1004
Revision: 3
Date: 6/23/96
Page: 12 of 22
Replaces: 2

Appendix B

Demonstration of Capability to Perform Analysis Form

Appendix C

Example Training Checklists

Pesticide/Herbicide GC Semivolatile Analyst Training Verification Checklist

Analyst Name:	Date:	Trainer:	Supervisor:	Analyst:
Documentation				
able to use Standards Log				
able to use Instrument Run Logs				
able to use Instrument Maintenance Logs				
Methods				
able to read and understands SOPs for all applicable methods				
<i>list Method(s):</i>				
able to read and understands EPA Methods (SW846, CLP, 500 & 600 series)				
<i>list Method(s):</i>				
able to read and understands appropriate sections of GC Training Manual				
Instrument Operation/Maintenance				
knows location and use of Instrument Manuals				
knows basic GC theory				
able to use GC Control Pad to set temperature program				
able to use Autosampler Control Pad to set injection program				
able to change syringe, septa & injection port liner				
able to trim/change columns, install Y connector & perform leak check				
able to measure and set carrier and makeup gas flows				
able to bake column/injectors/detectors				
NON-ROUTINE: Able to change detectors				
NON-ROUTINE: Able to perform total system cleaning				
Analytical Performance				
able to prepare standards & pass standard QC acceptance criteria				
able to analyze breakdown check and apply QC acceptance criteria				
able to analyze and generate acceptable calibration curve				
able to analyze CCVs and apply QC acceptance criteria				
applies acceptance criteria for surrogates and spikes				
able to set up analytical runs (CLP & non-CLP) & acquire data				
able to get information on samples/analyses (test codes, MDLs, etc.)				
able to quantitate an analytical batch (standards, CCVs, QC & samples)				
knows how to confirm detection of analytes (peak ID, conf. col.)				
knows reanalysis and reextraction criteria				
able to perform sample dilutions (obtaining linear results)				
knows correct reporting limits for method(s)				
knows corrective action & documentation for out of control QC events				
able to produce a data package (In-house, CLP and SW-846)				
Validation (complete one or more of the following)				
has successfully analyzed four P&A samples				
has successfully analyzed two PE samples				
has successfully analyzed three each of two types of QC samples				

I certify that _____ has been an analyst in the GC semivolatile method and has demonstrated competency at the preceding tasks for the following methods (list below):

Our performance should be not satisfactory at the 3 month interval should be discussed with the analyst and further evaluation. Not satisfactory items should be re-evaluated at the end of the 6 month probationary period.

Laucks Testing Labs
GC Volatile Analyst Training Verification Checklist

Analyst Name:	Date:	Trainer:	Supervisor:	Analyst:
Documentation				
Able to use Standards Log				
Able to use Instrument Run Logs				
Able to use Instrument Maintenance Logs				
Methods				
Has read and understands SOPs for all applicable methods				
List Method(s):				
Has read and understands EPA Methods				
List Method(s):				
Has read and understands appropriate sections of GC Training Manual				
Instrument Operation/Maintenance				
Knows location and use of Instrument Manuals				
Knows basic GC theory				
Able to use GC Control Pad to set temperature program				
Able to use Autosampler Control Pad to set injection program				
Able to check system flows				
Able to trim/change columns & perform leak check				
Able to measure and set carrier and makeup gas flows				
Able to bake column/injectors/detectors				
NON-ROUTINE: Able to clean P&T and autosampler lines				
NON-ROUTINE: Able to change nickel tubing, resin and IPA				
Analytical Performance				
Able to prepare standards & pass standard QC acceptance criteria				
Able to analyze and generate acceptable calibration curve				
Able to analyze CCVs and apply QC acceptance criteria				
Applies acceptance criteria for surrogates and spikes				
Able to set up analytical runs & acquire data				
Able to get information on samples/analyses (test codes, MDLs, etc.)				
Able to quantitate an analytical batch (standards, CCVs, QC & samples)				
Knows how to confirm detection of analytes (peak ID, conf. col.)				
Knows reanalysis criteria				
Able to perform sample dilutions (obtaining linear results)				
Knows correct reporting limits for method(s)				
Knows corrective action & documentation for out of control QC events				
Able to produce a data package (In-house and SW-846)				
Method Validation (complete one or more of the following)				
Has successfully analyzed four P&A samples				
Has successfully analyzed two PE samples				
Has successfully analyzed three each of two types of QC samples				

I hereby certify that _____ has been an analyst in the GC volatile department and has demonstrated competency at the preceding tasks for the following methods (list below):

Items found to be not satisfactory at the 3 month interval should be discussed with the analyst and further training done. Not satisfactory items should be re-evaluated at the end of the 6 month probationary period.

Fuels GC Semivolatile Analyst Training Verification Checklist

Analyst Name:	Date:	Trainer:	Supervisor:	Analyst:
Documentation				
able to use Standards Log				
able to use Instrument Run Logs				
able to use Instrument Maintenance Logs				
Methods				
is read and understands SOPs for all applicable methods				
is read and understands EPA & State Methods				
is read and understands appropriate sections of GC Training Manual				
Instrument Operation/Maintenance				
knows location and use of Instrument Manuals				
knows basic GC theory				
able to use GC Control Pad to set temperature program				
able to use Autosampler Control Pad to set injection program				
able to change syringe, septa & injection port liner				
able to trim/change columns & perform leak check				
able to measure and set carrier and makeup gas flows				
able to bake column/injectors/detectors				
NON-ROUTINE: Able to change detectors				
NON-ROUTINE: Able to perform total system cleaning				
Analytical Performance				
able to prepare standards & pass standard QC acceptance criteria				
able to analyze RTM standard and set up elution range				
able to analyze and generate acceptable calibration curve				
able to analyze CCVs and apply QC acceptance criteria				
applies acceptance criteria for surrogates and spikes				
able to set up analytical runs & acquire data				
able to get information on samples/analyses (test codes, MDLs, etc.)				
able to quantitate an analytical batch (standards, CCVs, QC & samples)				
knows reanalysis and reextraction criteria				
able to perform sample dilutions (obtaining linear results)				
knows correct reporting limits for method(s)				
knows corrective action & documentation for out of control QC events				
able to produce a data package (In-house and SW-846)				
Method Validation (complete one or more of the following)				
is successfully analyzed four P&A samples				
is successfully analyzed two PE samples				
is successfully analyzed three each of two types of QC samples				

I hereby certify that _____ has been an analyst in the GC semivolatile training program and has demonstrated competency at the preceding tasks for the following methods (list below):

Any item to be not satisfactory at the 3 month interval should be discussed with the analyst and further action done. Not satisfactory items should be re-evaluated at the end of the 6 month probationary period.

Laucks Testing Labs
HPLC Semivolatle Analyst Training Verification Checklist

Analyst Name:	Date:	Trainer:	Supervisor:	Analyst:
Documentation				
Able to use Standards Log				
Able to use Instrument Run Logs				
Able to use Instrument Maintenance Logs				
Methods				
Has read and understands SOPs for all applicable methods				
List Method(s):				
Has read and understands EPA Methods (SW846)				
List Method(s):				
Has read and understands appropriate sections of HPLC Training Manual				
Instrument Operation/Maintenance				
Knows location and use of Instrument Manuals				
Knows basic HPLC theory				
Able to use solvent delivery system to set mobile phase program				
Able to use Autosampler Control Pad to set injection program				
Able to change filters and guard column				
Able to change columns & perform leak checks				
Able to measure and set mobile phase flows				
Able to prime pumps				
Able to prepare mobile phase (filter water, select correct solvent grade)				
Able to change Helium tank				
NON-ROUTINE: Able to change lamps				
NON-ROUTINE: Able to locate the high pressure build-up				
NON-ROUTINE: Able to change pump seal				
NON-ROUTINE: Able to clean flow cell				
Analytical Performance				
Able to prepare standards & pass standard QC acceptance criteria				
Able to analyze and generate acceptable calibration curve				
Able to analyze CCVs and apply QC acceptance criteria				
Applies acceptance criteria for surrogates and spikes				
Able to set up analytical runs & acquire data				
Able to get information on samples/analyses (test codes, MDLs, etc.)				
Able to quantitate an analytical batch (standards, CCVs, QC & samples)				
Knows how to confirm detection of analytes (peak ID, conf. col.)				
Knows reanalysis and reextraction criteria				
Able to perform sample dilutions (obtaining linear results)				
Knows correct reporting limits for method(s)				
Knows corrective action & documentation for out of control QC events				
Able to produce a data package (In-house and SW-846)				
Method Validation (complete one or more of the following)				
Has successfully analyzed four P&A samples				
Has successfully analyzed two PE samples				
Has successfully analyzed three each of two types of QC samples				

I am certifying that _____ has been an analyst in the HPLC semivolatle
 instrument and has demonstrated competency at the preceding tasks for the following methods (list below):

_____ found to be not satisfactory at the 3 month interval should be discussed with the analyst and further
 actioning done. Not satisfactory items should be re-evaluated at the end of the 6 month probationary period.

Laucks Testing Labs

Semivolatile Analyst Training Verification Checklist

I certify that _____ has been an analyst in the semivolatile GC/MS
 and has demonstrated competency at the following tasks:

Task:	Date:	Supervisor:	Analyst:
able to Log-on to the RTE system			
able to create and edit BLISTS			
able to create spectra and quant reports			
able to prepare sample extracts for analysis (including dilutions)			
able to do basic mass-spec tuning			
able to perform daily maintenance tasks			
able to change a helium tank			
able to enter data into SAM special tests and QC reports			
able to get a basic directory listing of files on the RTE			
able to use QAREA			
able to check a CCV standard for compliance to the method			
able to check DFTPP for compliance to the method			
able to use basic RTE EDIT commands (create and edit files)			
able to use basic RPN commands (EC, DR, PF, PBM, etc.)			
able to generate simple TIC data			
able to check spectra vs. standard spectra			
able to understand acceptance criteria for surrogates, spikes, & ISs			
knows the basic differences between In-House, CLP, and SW-846			
able to generate basic CHRO forms packages			
knows where to get information on samples (test codes, etc.)			
able to calculate RFs and results from raw data			
knows the types of extraction procedures used for ABNs			
knows basic GC/MS theory			
has read and understands the SOPs for all applicable methods			
knows corrective action for out of control QC events			

Order:	TICs?	Package SDG.	TICs?

GC/MS Semivolatile Analyst Competency Criteria

Task:	Criteria:
Able to Log-on to the RTE system	Observation
Able to create and edit BLISTS	Successfully create 4 BLISTS
Able to create spectra and quant reports	Done for 4 jobs
Able to prepare sample extracts for analysis (including dilutions)	Done for 4 jobs
Able to do basic mass-spec tuning	Submit 4 tune checks / observation
Able to perform daily maintenance tasks	Observation
Able to change a helium tank	Observation
Able to enter data into SAM special tests and QC reports	Done for 4 jobs
Able to get a basic directory listing of files on the RTE	Observation
Able to use QAREA	Observation
Able to check a CCV standard for compliance to the method	Observation
Able to check DFTPP for compliance to the method	Submit 4 tune checks
Able to use basic RTE EDIT commands (create and edit files)	Observation
Able to use basic RPN commands (EC, DR, PF, PBM, etc.)	Pass RTE quiz at 85%
Able to generate simple TIC data	Done for 4 jobs
Able to check spectra vs. standard spectra	Done for 4 jobs
Applies acceptance criteria for surrogates, spikes, & ISs	Done for 4 jobs
Knows the basic differences between In-House, CLP, and SW-846	Observation
Able to generate basic CHRO forms packages	Complete 2 packages w/o supervision
Knows where to get information on samples (test codes, etc.)	Observation
Able to calculate RFs and results from raw data	Correctly complete 4 examples
Knows the types of extraction procedures used for ABNs	Observation
Knows basic GC/MS theory	Has read training manual
Has read and understands SOPs for all methods	Observation
Knows corrective action for out of control QC event	Observation / has read SOPs

GC/MS Training Program

Criteria for Demonstration of Analytical Competency

Analyst Name: _____

The analyst must meet at least one of the following criteria to demonstrate analytical competency.

1. Successfully analyze four (4) precision and accuracy samples, which have been prepared according to the SW-846 criteria for the method validation, or, if this is not available, according to in-house criteria. The results must be within limits specified by the SW-846 method or, if unavailable, by in-house protocol. (Attach data to this sheet).

Completed on : _____ Supervisor: _____

2. Successfully analyze two (2) rounds of performance evaluation samples. The results must be "acceptable" for 90% of the total compounds analyzed in multi-compound methods. If two rounds of samples are not available within six (6) months, one round of PE samples and the criteria from section 3 below will be acceptable. (Attach data to this sheet).

Completed on : _____ Supervisor: _____

3. Successfully analyze three (3) each of any two (2) of the following QC samples (total of 6 QC sample results). The results must be within the control limits for all compounds analyzed. (Attach data to this sheet).

MS/MSD _____
SRM _____
Blank Spike _____

Completed on : _____ Supervisor: _____

In addition to analytical competency, non-analytical competency must be demonstrated by the criteria found on the Semivolatile Analyst 3rd Month Training Verification Checklist.

REPORT MANAGEMENT

Employee Name:

Date of Hire:

ACTIVITY Reporting	Approx. Training Schedule	SOP Number (where applicable)	Trainer Initials/Date	Trainee Initials/Date
Transcribing data from sub-fabs				
Reporting— Extractions Metals Semi-volatiles Volatiles				
Log-in new project folders				
Log-out complete folders				
Update SAM-reports/benchsheets				
Cover letters				
Faxing				
Logging data in folders				
Filing benchsheets/WOC forms				
Filing complete folders				
Archiving complete folders				
Updating Paradox files				
Copying reports				
Paginating reports				

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-1005

Title: Analytical Balances

Revision history:

Number	Date
LTL-0005 R1	09/25/86
LTL-0005 R2	11/3/87
3	06/22/96

Revised by: Harry Romberg
Harry Romberg, QC Officer

Date: 6-22-96

Approved by: Karen J. Kotz
Karen Kotz, Laboratory Director

Date: 6/22/96

UNCONTROLLED

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1. Introduction and Scope

1.1 General

- 1.1.1 The most important piece of equipment in any analytical laboratory is the analytical balance. The degree of accuracy of the data is directly dependent on the accuracy of weight-prepared standards and samples. The balance should be one of the most cared for instruments in the lab. However this is not often the case.
- 1.1.2 The purpose of this SOP is to insure the proper use and calibration of all analytical balances in the laboratory. It involves the daily use of a standard weight check and a weekly calibration with a class "S". The results of these checks are logged in a balance logbook, thereby maintaining a record of the accuracy of that balance.
- 1.1.3 On an annual basis, analytical balances are cleaned and general maintenance performed by a qualified service technician. This process occurs automatically in conjunction with the service provider and Laucks purchasing and QA. It is the intent of this SOP to delineate internal calibration practices and not to provide additional specifics on externally provided service.

2. Equipment List

- Analytical Balance
- Manufacturer's Manual
- Balance Record Book
- Class "S" Weights

3. Safety Precautions and Waste Disposal

3.1 Safety

- 3.1.1 So as not to expose themselves or other analysts to potential harm and in order not to cross-contaminate samples, it is critical that the individual analyst clean the balance and the balance area after each and every use of the balance.
- 3.1.2 The analyst must not assume that the person using the balance before them cleaned up after themselves adequately and should check the area thoroughly before using the balance and clean up the area if necessary to maintain safety and reduce potential contamination.
- 3.1.3 Weighing chemicals and samples is potentially hazardous. The analyst should take every precaution to avoid contact of any of these things with the skin, eyes, or through

inhalation. In addition, the analyst should take precautions to see that nearby analysts or those using the balance afterwards are inadvertently exposed.

4. Operation Procedure

4.1 Balance Setup

- 4.1.1 Most of the balances used at Laucks are of the electronic variety, although there are some mechanical balances. Although electronic balances tend to be somewhat more rugged than the mechanical variety, they are still subject to many of the same conditions which make the operation of all balances a critical component of their continued functioning.
- 4.1.2 The analytical balance is a fragile and delicate instrument, the operation of which is subject to shock, temperature and humidity changes. Mishandling and other insults also account for great loss in precision and accuracy (P & A). The following precautions should be observed in order to maintain and prolong the life of the balance.
- 4.1.3 Analytical balances should be mounted on a heavy, shockproof table, preferably one with a sufficiently large work surface. Although shock is less of a concern with electronic balances, they should still be treated with care. For virtually all of the balances currently used by Laucks, except for some of the less sensitive variety which have no leveling bubble, the balance level should be checked frequently and adjusted as necessary.
- 4.1.4 Balances should be located away from lab traffic and doors or windows where they might be subjected to drafts, sharp temperature changes and physical shock.
- 4.1.5 For mechanical balances, when the balance is not in use, the beam should be raised from the knife edges and in the lock (rest) position.
- 4.1.6 For all balances, nothing should be stored on the pan when the balance is not in use.
- 4.1.7 All doors to the weighing compartment should be closed.
- 4.1.8 Special precautions should be taken to avoid spillage of corrosive chemicals on the pan or inside the balance case. The interior should be kept scrupulously clean.

4.2 Balance and Weight Calibration

- 4.2.1 There are three levels of calibration; daily, weekly, and annual.
 - 4.2.1.1 **Daily** - The daily calibration is done by the first user of the day. The user places a tare weight on the balance equivalent to a tare typically used on that balance, weighs the daily standard (a class "S" weight typical of the weight used on that balance) and

records the weight in the balance record book. If the weight is outside the limits set for the standard, it must be brought to the attention of the area supervisor and QA.

4.2.1.2 **Weekly** - The balance will be checked with a range of class S weights each week by the laboratory balance custodian. If a reading for a given weight exceeds the limits for that weight, the balance custodian will bring it to the attention of the area supervisor and QA.

4.2.1.3 **Annual** - Each balance will receive annual servicing and calibration by a qualified balance service representative.

4.2.2 The weights to be used for checking the balances are Class "S" weights or equivalent.

4.2.2.1 The Class "S" Weights - These are the primary standards for checking the accuracy of the balance. They must be handled with care as they are calibrated and damage to the weights may result in inaccurate balance calibration. These weights must only be touched with the forceps supplied with the weights or with the clean white gloves also kept with the weights. The class "S" weights are sent annually to a qualified weight re-certification service, currently Denver Instruments, although another qualified service is allowable. During this time the calibrations will be suspended or other Class "S" weights used (if available) until the calibrated weights return.

4.3 Responsibilities

The user is to ensure the following tasks are accomplished during the time he or she uses the balance:

- The balance is clean before use
- The balance is level before use
- The balance has been returned to the proper position (for mechanical balances)
- In addition, all balances should be reset to zero when not in use.
- Prior to use, the user should insure that the daily calibration check has been done. If not, he or she must complete the task
- **After use, the user will insure the balance is clean and returned to the proper storage position.**
- The user will report any malfunction or failure of the daily check to the area supervisor.
- The user will mark and not use any balance which has failed calibration.

4.3.1 The balance custodian is the person assigned to perform the weekly calibration checks. The custodian's duties include:

- Performing the weekly calibration check
- Marking any balance which has failed the weekly check
- Informing the area supervisor of any balance which has failed the weekly calibration check.

4.3.2 The area supervisor will ensure that the following tasks are accomplished:

- Weekly and daily calibration checks are being performed. It is particularly important to ensure that if the individual assigned to perform the weekly checks (the balance custodian) is absent, that someone is trained and assigned to this duty.
- That any maintenance is performed for balances which do not meet specifications. This may include contact others, such as QA, to actually correct the problem.
- That any malfunctioning balance or balance which has failed calibration not be used until it is functioning properly.

4.4 Daily Calibration Check

4.4.1 The first user to use the balance each day is to perform the daily calibration check.

4.4.2 The user will insure he or she is familiar with the operation of the balance according to the manufacturer's manual.

4.4.3 The user checks the zero on the balance. If it is off the user will adjust it according to the manufacturer's manual.

4.4.4 The user will place a tare weight on the balance which is typical of weights used on that balance (such as an empty beaker or an empty VOA vial). The weight of the tare should be recorded, strictly for the record, and the balance zeroed on that weight, if it is a balance capable of zeroing on the tare (all electronic balances are so equipped). The weight of the tare is not a controlled value but is only used to indicate the level of the tare used.

4.4.5 A standard weight of a size commonly used on that balance must then be added and the weight relative to the tare recorded under the appropriate day of the week in the calibration logbook. He or she will also initial the entry (See Appendix I). The standard weight will be a class "S" weight or equivalent.

4.4.6 The daily weight, after taring, must not vary from its nominal value by more than the following amounts:

<u>Balance capable of weighing to:</u>	<u>must not vary by more than:</u>
0.1 gram	±0.2 gram
0.01 gram	±0.02 gram
0.001 gram	±0.002 gram
0.0001 gram	±0.0005 gram

- 4.4.6.1 **Example 1:** 1 gram samples are typically weighed into flasks with tare weights of 100 grams on a balance weighing to 0.0001 g. In order to perform the daily calibration check, a flask of about 100 grams is placed on the balance and the weight recorded. The balance is tared (set to zero) based on this weight. A 1.0000 gm. Class "S" weight is then placed on the balance with the flask and the weight recorded. This second weight must read within the limits of 0.9995 gm to 1.0005 gm.
- 4.4.6.2 **Example 2:** 30 gram samples are typically weighed into beakers with tare weights of 80 grams on a balance capable of weighing to 0.01 grams. In order to perform the daily calibration check, a beaker weighing about 80 grams is placed on the balance and the weight recorded. The balance is tared (set to zero) based on this weight. A 30.0000 gm. Class "S" weight is then placed on the balance with the flask and the weight recorded. This second weight must read within the limits of 29.98 gm to 30.02 gm.
- 4.4.7 If the user cannot obtain a weight within the control limits established for the standard weight, he or she will bring it to the attention of the area supervisor and QA. Nothing requiring accurate weight should be weighed on a balance that does not meet calibration specifications. Any balance exceeding criteria must be clearly marked until it can be brought into control.
- 4.4.8 An example logbook page is presented in Appendix I
- 4.5 **Weekly Calibration Check**
- 4.5.1 The balance custodian is the person responsible to perform the weekly calibration check and to report problems to the area supervisor or QA. The custodian may be a different person in each area and it is the responsibility of the area supervisor to ensure that a capable balance custodian has been assigned to each area for which they re responsible. It is the responsibility of the custodian to insure that the weekly check is done even if they are not present, such as for vacation, etc.
- 4.5.2 On the first day of the week, the balance custodian will perform a calibration check on each balance in the lab to which they are assigned. The results of these checks will be recorded in each balance calibration logbook. This check will be performed using the laboratory Class "S" weights.

recorded in each balance calibration logbook. This check will be performed using the laboratory Class "S" weights.

- 4.5.3 The balance custodian will locate the Class "S" weights and insure they are clean. They will be returned to their proper location upon completion of the calibration checks.
- 4.5.4 The balance custodian will insure the balance is clean.
- 4.5.5 The balance custodian checks the zero on the balance. If it is off he or she will adjust it according to the manufacturer's manual.
- 4.5.6 At a **minimum**, the balance custodian will weigh 3 weights over the range for which the balance is used. Additional weights should be used if the range used is large in order to span the range typically used for that balance. If a specific weight (i.e. 100 mg or 30 grams) is the most often used on that balance, that weight should be included in the range of calibration. The results will be recorded to the left of the entries for the daily calibration check on separate lines. The custodian will also sign and **date** the entry. The date must include the month, day and year (See Appendix I).
- 4.5.7 Criteria for the weights on the weekly calibration check are as follows:

↓Balance capable of weighing: ↓	True value of weight			
	<0.1000 - 1.0000	1.0000-9.99	10. - 50.	>50.
0.1 gram	inappropriate	±0.1	±0.2	±0.2
0.01 gram	±0.02	±0.02	±0.02	±0.02
0.001 gram	±0.002	±0.002	±0.002	±0.005
0.0001 gram	±0.0005	±0.0005	±0.0020	±0.0050

- 4.5.8 If the balance custodian cannot obtain a reading within the control limits established for the standard weights, he or she will bring it to the attention of the area supervisor and QA.
- 4.5.9 An example logbook page is presented in Appendix I
- 4.6 Annual Calibration Check
 - 4.6.1 The laboratory employs a reputable outside firm to perform annual maintenance and calibration of all of the analytical balances. The current firm is North West Instrument Services but any reputable vendor may be used if first approved by QA.

5. References

APPENDIX I

Sample Page from a Balance Logbook

Week of:

June 16 - June 22, 1996
Harry Rosenberg

6/17/96

Class Weight
S Reading

1.00 1.00
10.00 10.00
50.00 50.00
150.00 150.00

Mon.

Tue.

Wed.

Thur.

Fri.

June = 130

128.6

132.6

146.7

135

2pm = 2.00

2pm = 2.00

2pm = 1.99

2pm = 2.00

2pm = 2.00

June 23 - June 29, 1996

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP No. LTL-1006

Previous SOP No. LTL-0053

Title: Refrigerator, Freezer, and Oven Thermometer Calibration and Maintenance

Rev: 1

Laucks is in the process of re-numbering our SOPs. As an interim measure, this page serves as the cover page for those SOPs whose header information has not been updated. This page details the title, the SOP number that it is being controlled under, and the previous SOP number. The previous SOP cover sheet has been manually corrected to reflect the change but each page header will reflect the old numbering system. As SOPs are revised, the full header and cover page will be updated.

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #: LTL-0053-~~12/24/95~~
1006

Title: Refrigerator, Freezer, and Oven Thermometer
Calibration and Maintenance

Submitted by: Vicki Talksabout Date: 10/13/93
Vicki Talksabout

Approved by: Harry Romberg Date: 10/13/93
Harry Romberg, QCO

Approved by: Mike Nelson Date: 9/24/93
Mike Nelson, Chief Chemist

Approved by: John M. Buerger Date: 10/11/93
John Buerger, Lab Director

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1. INTRODUCTION - This SOP provides a description of initial calibration of thermometers used for refrigerators, freezers, and ovens and the system used to record the calibrations and locations of the thermometers.

2. SAFETY - During the calibration and data recording the analyst will be exposed to minimal safety hazards: boiling water, hot ovens, and mercury filled thermometers. It is incumbent on the analyst to exercise due care and caution while executing this SOP. The company will provide any protective equipment or clothing needed to assure employee safety.

3. MATERIALS AND SUPPLIES LIST

Ertco Standard Thermometer- Stored in QC Officer's desk
High temperature grease pen
Disposable gloves
500 ml Erlenmeyer flask
Glass rod
Crushed ice

4. IDENTIFICATION OF THERMOMETERS

4.1. Refrigerator and Freezer Thermometers.

4.1.1. Thermometers are purchased from Streck Laboratories, Incorporated. Thermometers are received with an individual serial number imprinted on the thermometer and a certificate stating that the thermometer was calibrated in accordance with standards traceable to the National Institute of Standards and Technology. The Streck thermometers are immersed in a glass vial of forty-nine percent ethylene glycol. The entire thermometer and vial assembly is further encased in a plastic sleeve to prevent breakage. Alternate thermometers may be purchased in the future if a thermometer superior to the Streck design should become available.

4.1.2. Certificates are logged in a binder labeled Certificates-Thermometers located in the QC department shelves.

4.2. Oven Thermometers.

4.2.1. Oven thermometers are purchased from commercially available sources such as VWR. At a minimum the thermometer should be a mercury filled thermometer and measure from zero degrees Celsius to 110 degrees Celsius. Most inorganic ovens require a thermometer capable of reading to at least 180 degrees Celsius.

4.2.2. Upon receipt, thermometers are marked with an ID number. Thermometers are marked using a special grease pen that will survive high temperatures. Currently, thermometers numbered one through five are used in inorganic ovens while six through eight are located in extractions.

4.2.3. If an oven thermometer is replaced, its successor will be the same number followed by a alpha sequence character. For example, the first replacement of thermometer 5 will receive the ID number of 5A.

5. CALIBRATION OF THERMOMETERS

5.1. Calibration of the standard thermometer.

5.1.1. The standard ERTCO thermometer is recalibrated yearly. The standard thermometer is currently recalibrated every September.

5.1.2. It is only necessary to perform the thermometer recalibration at one point. The ice point, 0 °Celsius, is considered a "fixed point" in liquid-in-glass thermometry and is therefore chosen as the recalibration point.

5.1.3. Before recalibration, the standard thermometer must remain at room temperature for seventy-two hours.

5.1.4. Preparation of the ice bath.

5.1.4.1. Materials needed will include: a 500 milliliter

Erlenmeyer flask, a glass rod, crushed ice sufficient to fill the Erlenmeyer flask, and a minimal amount of water.

5.1.4.2. Fill the flask with crushed ice and add minimal amount of water to create a slurry. Stir the ice water slurry with a glass rod and immerse the thermometer.

5.1.4.3. Put as much ice in the flask as possible.

5.1.4.4. Allow the bath to equilibrate for five minutes with occasional stirring.

5.1.4.5. When the temperature has remained stable for at least two minutes record the ice-point reading.

5.1.5. If the ice-point reading is found to be higher or lower than the previous calibration reading, all other readings will be higher or lower, respectively, by the same amount.

5.2. Calibration of refrigerator thermometers.

5.2.1. Streck (Temp-Chex) refrigerator thermometers are calibrated upon receipt and yearly thereafter. All currently used thermometers are recalibrated every July. When a thermometer has been recalibrated, a small color coded sticker is attached. The color code will correspond to a particular yearly calibration. For example, fall 1993 calibrations, correspond to a gold color sticker. Thus an analyst can easily know his/her thermometer is currently calibrated.

5.2.2. Thermometers are placed in the GC/MS locked volatiles refrigerator (R-04). This refrigerator was chosen due to the fact that it is not frequently opened.

5.2.3. At the same time the ERTCO standard thermometer is also placed in the volatiles refrigerator. The standard thermometer is placed in an Erlenmeyer flask of water.

5.2.4. The thermometers are allowed to equilibrate for forty-eight hours and the temperatures read and recorded. Read the temperature of the standard thermometer first, then the individual Streck thermometers.

5.2.5. The difference in the Streck thermometer reading from the standard thermometer reading and the actual Streck thermometer temperature reading is recorded to the nearest 0.1 °C into a logbook. Each thermometer has a page in the logbook identified by the thermometer's serial number. The logbook page lists the purchase date, the current location of the thermometer and the thermometers calibration history. This logbook was initiated in December 1992, so information prior to this date may not be contained in the logbook.

5.2.6. It is important to allow the thermometers to equilibrate for the full forty-eight hours if the thermometer has been stored at room temperature, or incorrect temperature deviation results may be obtained. If the thermometer has been in use at ordinary refrigerator temperatures, twenty-four hours is sufficient.

5.2.7. A minimum of one calibrated refrigerator thermometer shall be kept on hand as a spare.

5.3. Calibration of freezer thermometers.

5.3.1. Streck (Temp-Chex) freezer thermometers are calibrated upon receipt and yearly thereafter. All currently used thermometers are recalibrated every July. When a thermometer has been recalibrated, a small color coded sticker is attached. Thus an analyst can easily know his/her thermometer is currently calibrated.

5.3.2. Thermometers to be calibrated are placed in the GC/MS volatiles freezer (F-05). This freezer was chosen due to the fact that it is not frequently opened.

5.3.3. At the same time the ERTCO standard thermometer is also placed in the volatiles freezer. The thermometer being calibrated and the standard thermometer will need to be placed on the same freezer shelf.

5.3.4. The thermometers are allowed to equilibrate for forty-eight hours and the temperatures read to the nearest 1 °C and recorded. Read the temperature of the standard thermometer first, then the individual Streck thermometers. The standard thermometer should be measured first as the standard thermometer is not encased in liquid as the Streck thermometers are. This

will cause the standard thermometer's temperature to rapidly change when the freezer door is opened.

5.3.5. The difference in the Streck thermometer reading from the standard thermometer reading and the actual Streck thermometer temperature reading is recorded into the logbook page referenced by the serial number of the individual thermometer.

5.3.6. It is important to allow the thermometers to equilibrate for the full forty-eight hours if the thermometer has been stored at room temperature, or incorrect temperature deviation results may be obtained. If the thermometer has been in use at ordinary freezer temperatures, twenty-four hours is sufficient.

5.3.7. A minimum of one calibrated freezer thermometer shall be kept on hand as a spare.

5.4. Calibration of oven thermometers.

5.4.1. Oven thermometers are calibrated upon receipt and yearly thereafter. All currently used thermometers are recalibrated every August. When a thermometer has been recalibrated, a small color coded sticker is attached. Thus an analyst can easily know his/her thermometer is currently calibrated.

5.4.2. Thermometers to be calibrated are placed in a boiling water bath.

5.4.3. At the same time the ERTCO standard thermometer is also placed in the boiling water bath. The thermometers will read a temperature slightly above 100 degrees Celsius if the bulbs of the thermometers are resting directly on the bottom of the beaker while the hotplate is in a heating mode.

5.4.4. The thermometers are allowed to equilibrate for four-five minutes and the temperatures read to the nearest 1 °C and recorded in the thermometer logbook. The difference in the thermometer reading from the standard thermometer reading and the actual thermometer temperature reading is recorded into the logbook page referenced by the number of the individual thermometer.

6. RECORDING AND STORING OF DATA- Data for refrigerator/freezers and ovens is recorded into a logbook.

6.1. Refrigerator and freezer thermometer logbook.

6.1.1. Each thermometer has a page in the logbook identified by the thermometer's serial number. The logbook page lists the purchase date, the current location of the thermometer and the thermometers calibration history. This logbook was initiated in December 1992, so information prior to this date may not be contained in the logbook.

6.1.2. The thermometer calibration history includes the actual temperature recording of the thermometer being calibrated, the deviation in degrees from the standard thermometer reading, the date, and the initials of the person performing the calibration.

6.2. Oven Thermometer Logbook

6.2.1. Each oven thermometer has a page in the logbook identified by the thermometer's number. The logbook page lists the purchase date, a description of the type of the thermometer, the current location of the thermometer and the thermometers calibration history. This logbook was initiated in December 1992, so information prior to this date may not be contained in the logbook.

6.2.2. The thermometer calibration history includes the actual temperature recording of the thermometer being calibrated, the deviation in degrees from the standard thermometer reading, the date, and the initials of the person performing the calibration.

6.3. Standard Thermometer Logbook

6.3.1. The standard Ertco thermometer has a page in the logbook. The logbook page lists the purchase date, a description of the type of the thermometer, the current location of the thermometer and the thermometers

calibration history.

7. SPECIFICATION LIMITS AND CORRECTIVE ACTIONS

7.1. Specification Limits.

7.1.1. Princo Instruments Inc. specifies a +/- 1 ° Celsius specification limit on the Streck refrigerator thermometers. (Princo Instruments is the actual manufacturer of the thermometers.)

7.2. Corrective Actions.

7.2.1. If there is any visible break in the mercury, this must be corrected before calibration. Currently Clyde Ambacher in inorganics is handling repair of thermometers with mercury breaks.

7.2.2. Every three months a cold storage audit is performed. As part of this audit, all thermometers are checked for mercury breaks and other deterioration. If mercury breaks are discovered the thermometer is replaced with the calibrated spare and the faulty thermometer is repaired and recalibrated or replaced.

7.2.3. If a refrigerator or oven thermometer deviates from the standard thermometer by more than +/- 2 ° Celsius it should be repaired or replaced. If this is a new thermometer, the possibility of a mercury break should be doublechecked. If no mercury break or other easily discernible cause can be found, the thermometer should be returned to the manufacturer for replacement. If this is a used thermometer, undergoing yearly recalibration, the thermometer should be replaced.

7.2.4. If a freezer thermometer deviates from the standard thermometer by more than +/- 5 °Celsius it should be repaired or replaced. If this is a new thermometer, the possibility of a mercury break should be doublechecked. If no mercury break or other easily discernible cause can be found, the thermometer should be returned to the manufacturer for replacement. If this is a used thermometer, undergoing yearly recalibration, the thermometer should be replaced.

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7.2.5 If the standard thermometer ice point deviates from 0.0 ° Celsius all temperature readings taken with the standard thermometer will have to be adjusted accordingly.

8. REFERENCES

8.1

U.S. Department of Commerce
National Institute of Standards and
Technology
NIST Special Publication 819
August 1991
A Procedure for the Effective
Recalibration of Liquid-in-Glass
Thermometers

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Date: 09-07-93
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Appendix I- Sample Logbook Page

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP No. LTL-1007

Previous SOP No. LTL-0045

Title: Maintaining Instrument Records and Logbooks

Rev: 1

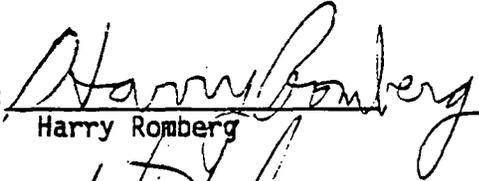
Laucks is in the process of re-numbering our SOPs. As an interim measure, this page serves as the cover page for those SOPs whose header information has not been updated. This page details the title, the SOP number that it is being controlled under, and the previous SOP number. The previous SOP cover sheet has been manually corrected to reflect the change but each page header will reflect the old numbering system. As SOPs are revised, the full header and cover page will be updated.

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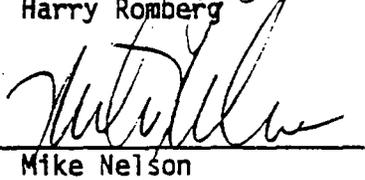
LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #: LTL-0045-⁰⁷⁶ ^{12/26/95}
1007

Title: Maintaining Instrument Records and Logbooks

Submitted by: 
Harry Romberg

Date: 9-9-91

Reviewed by: 
Mike Nelson

Date: 9/9/91

Approved by: 
Jim Owens

Date: 9/9/91

UNCONTROLLED

SOP No: LTL-0045
Revision: 1.0
Date: 9-5-91
Page: 2 of 14
Replaces: None

TO: Users of this SOP

After you have read this SOP you need to sign the operators statement which is attached to the master copy. See the QCO for access to this copy.

SOP No: LTL-0045
Revision: 1.0
Date: 9-5-91
Page: 3 of 14
Replaces: None

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SOP No: LTL-0045
Revision: 1.0
Date: 9-5-91
Page: 4 of 14
Replaces: None

SECTION I - Introduction and Scope

The maintenance of instrument logbooks is essential to monitoring instrument performance and throughput and in tracking analyses. It is also important to confirming instrument performance at the time of specific analyses and in monitoring ongoing or periodic performance degradation and the steps taken to correct or prevent such occurrences. Several systems are in place at Laucks, the differences being primarily dependent on the specific instrument and analysis types. This SOP will discuss what is expected in each.

NOTE: All errors in all logbooks must be altered by a single-line crossout which must also be initialed and dated. No erasures, overwriting, white-out or multiple-line crossouts (blacking out) are acceptable.

SECTION II - Equipment List

- 1) maintenance logbook
- 2) analytical run logbook (where appropriate)
- 3) pen (pencil is NOT allowed)

SECTION III - Safety precautions

No safety related precautions need be observed in the performance of this SOP. However, special precautions are needed for the instruments and related chemistries. These precautions should be outlined in the respective operational SOPs.

SECTION IV - Operation procedures

1.0 General

1.1 All errors in all logbooks must be altered by a single-line crossout which must also be initialed and dated. No erasures, overwriting, white-out or multiple-line crossouts (blacking out) are acceptable.

2.0 Maintenance Manuals

2.1 All instruments at Laucks from GC or GC/MS systems to ICPs, AAs, spectrophotometers, ion chromatographs, etc. have instrument maintenance manuals associated with the specific instrument.

2.2 Maintenance manuals are bound notebooks with the specific instrument and, if appropriate where multiple similar instruments are involved, instrument names or numbers printed on the outside cover. If there are multiple books for an instrument, which may be the case for instruments which have been in service for a long time, especially if they have required extensive, ongoing maintenance, the notebooks should be clearly numbered on the cover as #1, #2, etc.

2.2.1 As a general rule, loose leaf or 3-ring bound notebooks are not acceptable. The exception to this rule is for maintaining copies of professional service call paperwork or if specific forms have been created for monitoring maintenance activities. Such paperwork must be dated. Note of the service should still be made in the bound notebook associated with that instrument.

2.3 With a few basic rules, these maintenance manuals are free-form with no specific format but MUST include any and all maintenance associated with the particular instrument.

2.3.1 The maintenance manual must contain the DATE any service or maintenance was performed on the instrument and exactly WHAT that operation was. This includes everything from changing a part to cleaning an instrument orifice or changing a chromatographic column or instrument tubing. It should include everything from the simplest maintenance to the most complex, including any professional service calls.

2.3.1.1 Where maintenance is routine, some books use codes for the most common service operations. These codes must be clearly defined either on the front, inside cover of the maintenance manual or on the first page. If there are multiple books, these codes must be so defined in EACH book.

2.3.2 If the maintenance was performed because of a specific problem (not just routine, ongoing maintenance) the problem should be described in at least one entry in the maintenance book as well as the work performed at any one time, and the outcome of that maintenance, that is whether or not it was successful or what occurred when the work was performed.

2.3.3 In order to aid in monitoring instrument performance changes, service or equipment changes may also be noted in instrument run logs. However, this information is supplementary. ALL maintenance must be recorded in the maintenance manual.

2.3.4 Each entry should be INITIALED by the person making the entry.

3.0 Instrument Run-Logs

3.1 Instrument run-logs come in two essentially different forms, with variations depending upon the specific instrument. In any form, a copy of the daily run log must accompany the data from each laboratory workorder for any samples associated with that sequence.

3.1.1 GC, GC/MS, HPLC, and GPC run-logs are in bound, pre-printed, sequentially page-numbered books. They are identified by the specific instrument type and, if appropriate where multiple similar instruments are involved, instrument names or numbers printed on the outside cover. If there are multiple books for an instrument, which may be the case for instruments which have been in service for a long time, especially if they have required extensive, ongoing maintenance, the notebooks should be clearly numbered on the cover as #1, #2, etc.

3.1.1.1 They include places to record all relevant sample and data file IDs, performance criteria, sample type and size, additional comments pertinent to the specific analyses, and analyst initials. All appropriate information must be filled out and the page dated. Examples of these logbook forms are located in Appendices I (GC/MS), II (GC and HPLC), and III (GPC).

3.1.1.2 In addition to the appropriate header information for each analytical GC, GC/MS, HPLC or GPC run, all of the pertinent information should be filled out for each injection.

3.1.1.3 The samples, standards, calibration checks, reference materials, etc. should be listed IN ORDER.

3.1.1.4 Logbook information should be either completely filled out, or a logbook designed to incorporate all of the pertinent elements for that analysis so that all fields are filled in. Logbooks should contain all of the necessary information to track what analyses occurred, the processing order, and critical run parameters (such as what GC column was in use).

3.1.1.5 No empty space should be left between daily logbook entries. The end of the analytical sequence should be clearly marked, the most common acceptable method is to mark the space in the logbook after the last entry with a /E. If both of these criteria are met, it is not necessary to cross out unused space at the end of the analytical run. This space may be used for subsequent notes AS LONG AS the end of the sequence is clearly defined.

3.1.2 The other type of run-log typically in use is the individual, loose-leaf instrument run-log printout. Where the instruments themselves don't produce such printouts, handwritten run-logs are produced by the analyst. These are the log types typically in use in the Inorganics area of the laboratory.

3.1.2.1 A copy of the run-log is included with each data packet associated with that run.

3.1.2.2 As with the bound book format, the samples, standards, calibration checks, reference materials, etc. should be identified and listed IN ORDER.

3.1.2.3 Information critical to identifying the analytical run (date, analyst, analysis type) must be included in the header information. If multiple analytical runs were made in one day, they must be identified as run #1, run #2, etc. If the instrument is capable of time-stamping run data, this option should be utilized, although it need not be included in the run-log itself.

3.1.2.4 It is not a current labwide laboratory practice to maintain ongoing run-logs for inorganic instrumentation, although individual instrument analysts may choose to keep this information available either by archiving computerized information on diskette or by keeping hardcopy versions. As the daily run-logs are included with all data, it is not currently considered necessary. It is advisable, however, to maintain such records in a bound (3-ring binder is OK), organized format and not unbound, loose-leaf.

SOP No: LTL-0045
Revision: 1.0
Date: 9-5-91
Page: 8 of 14
Replaces: None

APPENDIX I
GC/MS Run Log

IS A

IS B

IS C

Run #	File Name	Sample #	Dilution		RT	Response	RT	Response	RT	Response
1	ALT7201									
2	H1109A	SSTD050	MS2-70-2	ORD 25						
3	MT7201									
4	H1109B	SSTD050	MS2-70-2	ORD 25						
5	MT7201									
6	H1109C	SSTD050	MS2-70-2	ORD 25	12.47	77061	16.28	181641	21.82	89817
7	H1109D	SSTD050	MS2-61-1	ORD DER 20	12.48	113027	16.29	270441	21.83	131253
8	H11090 HC-SFA	SBLK41	B020245441	16-2	12.49	71464	16.28	764818	21.83	79018
9	H11091	COMP1	9107B20-1		12.47	66036	16.28	148807	21.82	72983
10	H11092	COMP1MS	-1MS		12.48	66571	16.27	151500	21.81	75210
11	H11092 H11093	MSD	-1MSD		12.55	66354	16.36	160611	21.90	84808
12	H11094	COMP2	-2		12.47	62835	16.28	151014	21.82	73633
13	H11095	COMP3	-3		12.49	65236	16.30	153226	21.84	75655

6/9

11

8

LAUCKS TESTING LABORATORIES

Case #

ABN: 1

IS D

IS E

IS F

Run #	RT	Response	RT	Response	RT	Response	Data Reduction	Comments, Changes	Anal
1								100 - 33.5 - 33.2 - 1.47	BP
2								DETAP FAIL 441W	
3								100 - 33.3 - 31.0 - 1.29	
4								DETAP FAIL 441 ↓	
5								100 - 34.1 - 31.8 - 1.04	
6	26.45	134240	34.86	68027	—	—	HUEORD	OK.	
7	26.45	226661	34.87	107386	—	—	IFLORID6	*NOTE USES IS 640964	
8	26.45	124451	34.87	69954	—	—	ORDHUE 1 IFLORID6		
9	26.47	123829	34.87	81690	—	—		Needs 1:20 for TNT	
10	26.47	121864	34.87	72707	—	—			
11	26.55	146291	34.95	96307	—	—			
12	26.49	134842	34.86	96254	—	—		Needs 1:20 for TNT	
13	26.49	137342	34.83	90919	—	—	↓	Need > 1:20 for TNT	✓

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APPENDIX II
GC/HPLC Run Log

GC INSTRUMENT LOGSHEET

Case/lab number _____
 OPERATOR DSS DATE 8-9-91 CHROMATOGRAPHY REFERENCE PAGE _____
 COLUMN USED _____ OVEN TEMP _____ deg C ISOTHERMAL
 PACKED COLUMN FLOW RATE _____ ml/min FSCC LINEAR VELOCITY _____ cm/sec at _____ DEG
 CALIBRATION STD REFERENCE SE0809

reference peak

Seq #	Bot #	Run number	SAMPLE IDENTIFICATION	Dil	Ext val	K.T.	Resp.	Comments
1	2	*RAW03	HEXANE					
2	4	RE1302	PX2-48-3					
3	6	RE1303	PX2-48-2					
4	8	RE1304	PX2-48-1					
5	10	RE1305	EX4-37-2/570					
6	12	RE1306	BO807 GHRWMA					
7	14	RE1307	BO807 GHRWMA					
8	16	RE1308	#1 WELL GSP					
9	18	RE1309	#1 WELL MS					
10	20	RE1310	#1 WELL MD					
11	22	RE1311	PX2-48-1					
12	24	RE1312	ARCO 10000					
13	26	RE1313	ARCO 10000 MS					
14	28	RE1314	ARCO 10000 MD					
15	30	RE1315	PX2-48-1					
16	32	/E						
17	34							
18	36							
19	38							
20	40							
21	42							
22	44							
23	46							
24	48							
25	50							
26	52							
27	54							
28	56							
29	58							
30	60							

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Replaces: None

APPENDIX III

GPC Run Log

~~Reserved~~

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-1008

Title: QC Corrective Action

Revision history:

<u>Number</u>	<u>Date</u>
5	6/22/96
4	3/3/96
3 (LTL-0008)	6/29/89
2 (LTL-0008)	5/19/87
1 (LTL-0008)	12/12/86

Written by: Harry Romberg
Harry Romberg, Quality Assurance Officer

Date: 6-25-96

Approved by: Karen J Kotz
Karen Kotz, Laboratory Director

Date: 6/25/96

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1. Introduction and Scope

1.1 Purpose

1.1.1 The purpose of this SOP is to establish a system to identify, document and resolve out-of-control events.

1.2 Scope

1.2.1 An out-of-control event may be recognized by any member of Laucks. When they occur, the analyst, supervisor and Quality Assurance work jointly to solve and correct the problem. Out-of-control events are documented using an Out-of-Control-Event form or a Corrective Action form, or in a few selected instances, on a logsheet with space specifically for such actions. Corrective action resulting from an audit is also dealt with using its own Audit Response form but this action is elucidated in an SOP specific to that process.

2. Definition of Terms

2.1 This section defines terms and acronyms as they are used in this SOP.

2.1.1 **Corrective Action:** Action taken by an individual(s) to correct a problem as evidenced by either the failure of QC criteria or a more general problem which could affect performance of an analysis, the quality of service or other activity undertaken by the laboratory.

2.1.2 **Out-of-control event:** Any occurrence or condition failing to meet Laucks QC criteria or has the potential to impact data quality.

2.1.3 **QA/QC:** Quality Assurance/Quality Control

2.1.4 **Reagent blank:** a measured volume of reagents used in a method.

2.1.5 **Method blank:** a reagent blank that undergoes a preparation (digestion, extraction, distillation, etc.) step prior to analysis.

2.1.6 **RPD:** Relative Percent Difference

2.1.7 **LCS:** Laboratory Control Sample

3. OUT-OF-CONTROL EVENT PROCEDURE

3.1 Identifying an Out-Of-Control Event

3.1.1 The following is a list of examples of out-of-control events. This is not a complete list of all possible out-of-control events and many of those listed may be different for different methods. Specific criteria are given in analytical SOPs or in other QA documents. If there is doubt about whether a situation is out-of-control and must be responded to, consult with Quality Assurance.

3.1.1.1 GC/MS instrument tune criteria failing to meet criteria

3.1.1.2 Initial calibration linearity, depending upon the method used for calibration, correlation coefficient <0.995 (<0.990 for some fuels analyses) or percent RSD failing to meet method specifications.

3.1.1.3 Daily and continuing calibration verification or calibration blanks outside acceptable ranges as defined in their respective SOPs.

3.1.1.4 **NOTE:** If any of the above instances (3.1.1.1-3.1.1.3) occurs, analysis is stopped. No sample analysis can occur until the event is back in control. A corrective action form does not need to be filled out for these instances if identified at the analyst level and corrected before any data are affected.

3.1.1.5 Matrix spike, surrogate spike or blank spike recoveries outside acceptable ranges.

3.1.1.6 Unacceptable RPD value for MS/MSD or duplicate samples.

3.1.1.7 Unacceptable values for LCS's and QC samples.

3.1.1.8 A reagent blank containing a target analyte greater than the method reporting limit.

3.1.1.9 A method blank containing interference or a target analyte at a concentration greater than or equal to the method **reporting** limit.

3.1.1.10 **Note:** Samples which contain target analyte levels which are greater than 20 times the blank or which contain none of the offending analyte may be considered acceptable.

- 3.1.1.11 A sample received, prepared or analyzed past holding time.
- 3.1.1.12 A sample depleted before all required analyses are completed.
- 3.1.1.13 An extract blown down to dryness, spilled or otherwise compromised.
- 3.1.1.14 Contaminated reagents and glassware.
- 3.1.1.15 Equipment malfunction or instrument failure, such as cold storage unit temperature outside acceptable ranges and the loss of data acquisition.
- 3.1.1.16 Record keeping omissions, errors, and deviations from the record keeping standard operating procedures are also out-of-control situations

3.2 Responding to an Out-Of-Control Event

3.2.1 When an out-of-control event is recognized, each individual involved with the analysis in question has an interactive role and responsibility, these are as follows:

3.2.2 Analyst:

- 3.2.2.1 Must be able to recognize QC failure and immediately take the proper action or, if unsure of the appropriate response, notify the supervisor and work with the supervisor and Quality Assurance to solve the problem; also maintains QC charts.
- 3.2.2.2 The analyst is also responsible for performing the following steps to correct the problem:
- 3.2.2.3 Examine all calculations for correctness
- 3.2.2.4 Examine bench sheets for correctness
- 3.2.2.5 Check instrumentation and operating conditions to preclude the possibility of malfunctions or operator error
- 3.2.2.6 Verify integrity of spiking solution, laboratory control sample, or calibration standard
- 3.2.2.7 Re-analyze the sample

3.2.2.8 Take other actions as noted in the specific analytical SOP.

3.2.2.9 If these steps do not yield acceptable results, consult the supervisor.

3.2.3 Supervisor:

3.2.3.1 Must review all analytical and QC data for reasonableness, accuracy and clerical errors; also responsible for QC charts. Some of the above duties may be assigned to others, with supervisory oversight, if those others have been trained to observe the conditions which would initiate further investigation.

3.2.3.2 In an out-of-control event, the supervisor works with the analyst and Quality Assurance to solve the problem and prevents the reporting of suspect data by stopping work on the analysis in question and insuring that all results that are suspect are repeated, if possible, after the source of the error is determined and remedied.

3.2.3.3 If corrective actions do not yield results which meet specifications, it may be determined that sufficient action has been taken. The supervisor and QA will approve of such decisions and if it is determined that the data quality could be impacted, the supervisor will ensure that appropriate comments are reported with the data to the client.

3.2.4 Quality Assurance:

3.2.4.1 The Quality Assurance Officer or designee will work with supervisory personnel and/or analysts to solve out-of-control situations which are not routinely corrected at the bench.

3.2.4.2 In the event that an out-of-control situation occurs that is unnoticed at the bench or supervisory level, such as performance failure on a blind QC sample, Quality Assurance will notify the supervisor, help identify and solve the problem where applicable, insure the work is stopped on the analysis and no suspect data is reported.

3.2.4.3 Finally the Quality Assurance Officer or designee must review and approve all corrective action reports which cannot be resolved. If corrective actions do not yield results which meet specifications, it may be determined that sufficient action has been taken. The supervisor and QA will approve of such decisions.

3.2.4.4 If it is determined that the data quality could be impacted, the supervisor will ensure that appropriate comments are reported with the data to the client and QA will review said comments.

3.2.5 Project Manager:

3.2.5.1 The Project Manager is responsible for notifying the client of out-of-control events, such as missed holding times, raised reporting limits, matrix interferences, etc. which cannot be resolved without potential impact on either the data quality, the agreed upon or routinely reported results, or the timely and expected delivery date. It is not necessary to contact the client for events which are correctable and do not impact the final data quality, holding times or turn-around unless specifically requested by the client.

3.3 Corrective Actions

3.3.1 Appropriate corrective action depends on the type of analysis, the extent of the discrepancy, and whether the event is determinant or not. The corrective action to be taken for analytical QC failures is usually described in the specific analytical method but may also be determined by either the supervisor, Quality Assurance Officer, or by both in conference, if necessary.

3.3.1.1 Some items may not necessitate direct intervention of QA where standard practices are in place for some events, where the SOP or project or program QAP itself dictates the corrective action and where the action taken is the most conservative response practical. These types of events may be considered to have automatic QA approval and may not even require the completion of any related out-of-control event forms.

3.3.2 A corrective action can be as extensive as replacing a complete lot of contaminated extraction solvent, re-extracting and re-analyzing a complete batch of samples, due to reagent blank contamination; or as simple as recalculating a series of results because a wrong dilution factor was applied. Again, the appropriate corrective action must be determined on a case by case basis.

3.3.3 Data cannot be released until the system is in control or the QC failure can be attributed to a cause other than method performance. In the event the out-of-control event is due to matrix problems in the sample, and the system remained out of control, the data is flagged and supporting documentation is released to the client.

3.3.4 Corrective actions are considered adequate when the problem has been resolved and data can be reported or other actions taken from an in-control condition. Alternatively, it may be determined that the action taken was, as a minimum, all that was required by the method or that no further action was reasonable or possible that would improve the data. In these cases, the final decision must be approved by the supervisor and QA.

3.4 Documenting an Out-Of-Control Event

3.4.1 This is accomplished by completing one of the following

- A Corrective Action (CA) Form (See Appendix 1)
- A QC_DB Report Form (for Inorganics analytical QC only, see Appendix 2)
- An Out-Of-Control Event (OOCE) Form (lab use only, see Appendix 3)
- A Sample Receipt Form (for sample receipt events, see Appendix 4)
- An Audit Finding Report Form (QA use only, not shown here, see audit SOP)
- or logged onto a form which itself includes corrective actions (example, Cold Storage Logsheet, see Appendix 5).

3.4.2 CA forms are general and are for documenting corrective action taken to correct problems not associated with a particular analytical event.

3.4.3 Out-Of-Control Event (OOCE) Forms are filled out by **technical** laboratory staff only and are designed for documenting analytical QC failures and associated corrective actions. Where other forms, such as the Inorganics QC_DB Report Form, are used to document that the QC parameters were checked, any failures of QC and the decision to perform corrective action or continue data processing must be documented on the OOCE form. The checklist may then be attached to the OOCE form for final data submission.

Note: It is not necessary for analytical staff to document actions which were taken prior to processing samples or which do not affect reported data.

3.4.4 Audit Finding Reports are responded to by the assigned individual and signed off by QA or a designated individual (see the audit SOP).

3.4.5 All OOCE and Corrective Action Forms shall be filled in completely by the person observing the event. Actions taken may be filled in by either the initiating person or the person actually performing the corrective action. The descriptions of the event and any corrective actions taken should be detailed and specific. The OOCE form provides check boxes for most analytical events.

Note: Holding time violations due to laboratory error are annotated on the OOCE form. Holding time violations occurring due to receipt of samples beyond the criteria are documented on the sample receipt form only.

- 3.4.6 If the corrective action taken and annotated on the OOCE Form resolves the problem and allows data to be reported which is in control, the action is complete and only needs to be signed by the individual taking action and the individual initiating the action.
- 3.4.7 If the corrective action taken and annotated on the OOCE Form does not resolve the event and it is determined that no further action can or will be taken, the form must be signed by the analyst, supervisor, and QA.
- 3.4.8 Originals of all OOCE forms must be turned into QA. Copies must be included in each SDG or workorder in validatable packages and in the first workorder in the "samples affected" column for non-validatable data packages.
- 3.4.9 Any corrective actions taken which could either impact data directly, help to explain analytical decisions that were made in order to resolve analytical discrepancies, or which would help in the interpretation of the final data package must also be narrated in the final report. OOCE forms must be turned in with the data and the supervisor creating the narrative comment for that area will comment on any decisions resulting from failed QC which could impact data validity or interpretation.

Appendix I

Corrective Action Form

Laucks Testing Laboratories
Corrective Action Report

1) Problem Description:

Response tasked to: _____ on _____

By: _____ Response Requested By _____

2) Cause:

3) Action Taken:

Completed by _____ on _____

- Corrective actions will be reviewed 30 days after completion to verify problem has been corrected.
- No further action necessary

Reviewed by: _____ on _____

-
- 1) Person initiating corrective action fill out Part 1 and may fill out Part 2 if they are aware of the cause
 - 2) Original goes to person tasked with a response; one copy goes to QA Officer and another kept by person initiating corrective action
 - 3) Person tasked completes response in Part 2 (if not previously completed) and Part 3, signs response, and returns original to person initiating action
 - 4) Person initiating action determines if action corrects the problem and signs "Reviewed by." If action was insufficient, return to the person charged with responding without signing.
 - 5) Completed original goes to QA Officer

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Appendix 2

QC_DB Report Form

Laucks Testing Laboratories

QC_DB Report Form

Analyst _____

Checker _____

Test Code _____

QC Exceeds Control Limit
√ if yes

Corrective
Action Approved By _____

PBlk B _____ 96 _____

MS/MSD K _____ 96 _____

SRM R _____ 96 _____

Blk Spk S _____ 96 _____

MS/Dup M _____ 96 _____

Duplicate D _____ 96 _____

This report validates the following work orders

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Appendix 3

Out-Of-Control Event Form

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Appendix 4 .

Sample Receipt Form

Laucks Testing Laboratories, Inc.
SAMPLE RECEIPT LOG (1) CLP

P:\PM\Holly\docs\fax\ncmemo.doc 12/22/94

Initial once samples are checked in _____

DATE RECEIVED: _____
 TIME RECEIVED: _____
 CLIENT NAME: _____
 SDG # _____
 COC # _____

SAMPLE LOG-IN DATE: _____
 WORKORDER #: _____
 CLIENT PROJECT: _____
 AIRBILL ATTACHED?: (#) _____
 RECEIVED BY: _____

Non-Conformance: (Check applicable item(s)) _____ Client IDs affected: _____

- (1) Not enough sample sent for proper analysis. #s affected: _____
- (2) Sample Bottle received broken and/or cap not intact. _____
- (3) Custody seal: Absent _____ Present/Intact _____ Present/Broken _____
- (4) Any temperature out of compliance: _____
- (5) Sample received outside of holding time. _____
- (6) Sample not properly preserved. pH = ____ Wrong preservative used. _____
- (7) Illegible sample numbers or label missing from bottles. _____
- (8) Identification on bottle same as identification on paperwork: yes: ____ no: _____
- (9) Incomplete instructions received with sample(s). i.e.,
 no Request for Analysis. no Chain-of-Custody. _____
- (10) Samples received in improper container. _____
- (11) Samples held in field before receipt by Lab. Days (specify) _____
- (12) Air Bubble(s) in ____ of ____ samples for volatiles analysis. _____
- (13) Other _____

CORRECTIVE ACTION: (Check applicable item(s))

Correction action taken by:

- | | <u>Initials</u> | <u>Date</u> |
|--|-----------------|-------------|
| <input type="checkbox"/> (1) Client informed verbally (Client Services). | _____ | _____ |
| <input type="checkbox"/> (2) Client informed by memo/letter/fax (Client Services). | _____ | _____ |
| <input type="checkbox"/> (3) Sample processed "as received" (Sample Entry). | _____ | _____ |
| <input type="checkbox"/> (4) Re-sampling requested of client (Client Services). | _____ | _____ |
| <input type="checkbox"/> (5) Samples placed "on hold" until further notice (Sample Entry/Client Services). | _____ | _____ |
| <input type="checkbox"/> (6) NOTE IN NARRATIVE. See temperature/pH login sheet. (Sample Entry). | _____ | _____ |
| <input type="checkbox"/> (7) Other (Specify) _____ | _____ | _____ |

* When complete (within 24 hours of nonconformance) forward to QA. Original to be forwarded to initiator to be included in transmittal file.

Comments: _____

Appendix 5

Example Logsheet (Cold Storage)

Laucks Testing Laboratories, Inc.

Cold Storage ID #:

Location:

Year: **1996**

Correction Factor (add this number when recording the thermometer reading): _____ °C

Day	Month:				Month:				Month:			
	Time	Temp.	Initials	Actions	Time	Temp.	Initials	Actions	Time	Temp.	Initials	Actions
1												
2												
3												
4												
5												
6												
7												
8												
9												
10												
11												
12												
13												
14												
15												
16												
17												
18												
19												
20												
21												
22												
23												
24												
25												
26												
27												
28												
29												
30												
31												

Record Time and Temperature in the proper blocks and initial the entry each day of normal laboratory operation.

If refrigerator temperatures exceed 4°C±2°C or if freezer temperatures are warmer than -10°C, corrective action must be taken.

- Corrective action includes
- 1) Adjust the temperature of the thermostat
 - 2) Defrost the refrigerator or freezer
 - 3) Contact the appropriate laboratory maintenance personnel, the departmental supervisor, and/or the QA Officer
 - 4) One of the above may decide that professional maintenance is necessary or even that the cold storage unit must be disposed of.

Any and all actions **MUST** be recorded on this log sheet. If there is insufficient room, mark on the back of the page with the date the action occurred.

Samples **MUST NOT** be stored in units which are not maintaining the proper temperature.

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-1009

Title: **Blind Spike Program**

Revision history:

<u>Number</u>	<u>Date</u>
LTL-0048 Rev1.1	05/18/92
2	06/21/96

Written by: Harry Romberg
Harry Romberg, QA Officer

Date: 6-21-96

Approved by: Karen J Kotz
Karen Kotz, Laboratory Director

Date: 6/21/96

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1. Introduction and Scope

1.1 Description

- 1.1.1 This SOP provides a description of how blind spikes are generated, what types of analyses are monitored, how results are evaluated and how Laucks handles out of specification events.
- 1.1.2 Materials may be from a multitude of sources. The analyst will most often be aware that the sample is a blind spike but in no case should the analyst know the "true" value of the submitted sample. On occasion, at the discretion of QA, a double blind sample may be submitted (one which the analyst does not know is an evaluation sample).
- 1.1.3 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.2 Definition of Terms

- 1.2.1 **Blind Spike** - A proficiency sample which may or may not be known as such by the analyst but which contains a target analyte with a value which is not known.
- 1.2.2 **Double-Blind Spike** - A proficiency sample which is submitted to the analyst in such a way that it is thought to be a routine sample and which contains an unknown amount of target analyte.

2. Equipment List and Standards

2.1 Equipment

- 2.1.1 Pipets, flasks, containers etc. necessary to prepare spikes for submission.

2.2 Reagents

- 2.2.1 Deionized water, methylene chloride and other solvents or preservatives that may be required to prepare spikes. Some samples may be prepared by outside sources and only need to be submitted to the analyst.

3. Safety precautions and Waste Disposal

3.1 Safety Precautions

3.1.1 All standards, samples and sample solutions should be handled as if they are hazardous substances. During the preparation of blind spikes, the analyst will be exposed to a variety of reagent chemicals and solvents. In addition, preservatives contained in both reference materials and in sample bottles may pose health hazards. The health effects of these various chemicals may be ascertained by reading the appropriate material safety data sheets (MSDS). It is incumbent on the analyst to exercise due care and caution while executing this SOP. The company will provide any protective equipment or clothing needed to assure employee safety.

3.1.2 Many solvents also pose a fire hazard and should be treated with proper precaution.

3.2 Waste Disposal

3.2.1 Waste solvents are disposed in the appropriate waste solvent container.

3.2.2 No more blind spike material is used than is necessary for submittal of the sample so that it will not present a disposal hazard.

3.2.3 Waste segregation and disposal from the point of collection is further covered in the Laucks SOP on hazardous waster disposal.

4. Materials

4.1 Sources

4.1.1 Materials may be WS, WP or other materials from an external performance evaluation. Although these are not generated directly by the laboratory, they are blind samples in that the expected values and in many cases the constituents themselves are not known to the analyst beforehand.

4.1.2 Standard materials may be purchased from a vendor, such as Environmental Resource Associates (ERA), Analytical Products Group (APG), SPEX, Restek, Supelco or any other reputable vendor.

4.1.3 Materials may be purchased either as Performance Evaluation samples (values unknown to the laboratory), reference materials (values known to the laboratory), or as standard materials (values known to the laboratory). They may also be made up by supervisory or QA staff from materials of known content. In any instance, the value of the components

will be unknown to the analyst performing the analysis until completion of the evaluation.

4.2 Storage

4.2.1 Materials are stored as recommended by the manufacturer, most often at a temperature of $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$. Metals will generally be stored in dilute nitric acid and need not be refrigerated.

5. Operation procedures

5.1 Requirements and Scheduling

5.1.1 These requirements may be program and/or method-specific. Laucks specific training requirements and documentation are discussed in other SOPs and in the QA Plan. This SOP is intended primarily to document the practices and evaluation of results and not to dictate the specific analyst requirements.

5.1.2 Initially (as part of being considered able to independently perform an analysis), an analyst may be required to analyze a single blind Performance Evaluation (PE) sample. The analyst must process the samples independently, without direction or assistance in order to be considered proficient.

5.1.3 On an ongoing basis, at least annually, an analyst may also be required to demonstrate continuing performance by analyzing a single blind PE sample.

5.1.4 PE results may also be used as a supplement to a method verification process in order to verify the laboratory's ability to perform a method.

5.1.5 These PE samples may be from a performance evaluation study, such as an EPA Water Pollution (WP) or Water Supply (WS) study, an independent vendor PE, such as Environmental Resource Associates (ERA) or Analytical Products Group (APG), or it may be prepared by an area supervisor from a known material. Blind PE samples will almost always be prepared as aqueous solutions except in limited circumstances, such as fuel hydrocarbons, where soil samples are periodically analyzed. ERA, APG or other sources of materials will be used where components are not present in WP, WS or other "official" PE samples. Acceptable results from programmatic samples, such as those for HAZWRAP, Army Corps of Engineers, or NFESC may be used to qualify analysts or to otherwise demonstrate performance, even though in some instances an actual value may not be provided by the agency.

- 5.1.6 WP and WS program samples are analyzed semiannually (WP in approximately June and November, WS in approximately April and September). Supplementary PE samples for analytes not present in these samples (such as fuels or GC/MS semivolatiles) are generally obtained from APG, ERA or a similar vendor and are generally analyzed along with remedial samples (if any) resulting from WP failures (results being obtained approximately 3 months after submittal of the WPs). Other external PE samples from programs such as NFESC, HAZWRAP, or the Army Corps of Engineers may be analyzed at the discretion of those programs but be used for evaluation. The precise schedule for submittal of all but programmatic samples is at the discretion of QA in order to meet laboratory needs to qualify analysts or methods or to meet other requirements.
- 5.1.7 One set of PE samples may be used to qualify several analytical staff. For instance, one person may extract a sample and be so qualified. Several analysts may process the extract independently and also be qualified. If multiple analysts do process the extract, however, there must be no collaboration between analysts until the results have been received by QA.
- 5.1.8 In any instance, the values of the components must not be divulged to the analyst(s) prior to analysis. Furthermore, if a PE sample contains one or more components from a multi-component analysis (such as a semivolatiles or pesticide mixture), the analytes themselves must not be divulged.
- 5.1.9 Blind spikes should be analyzed in at least duplicate so that reproducibility can be determined as well as recovery. All results should be reported for each determination where the analysis was otherwise in control. Evaluation of replicates is a laboratory option and is rarely required of any external performance evaluation program.
- 5.1.10 Blind spikes are typically determined for the following analyses (in water excepts as noted):
- ICP metals
 - ICP/MS metals
 - Graphite furnace metals (Pb, As, Se, Tl)
 - Mercury
 - GC Volatiles
 - Gas/BTEX water & soil
 - Diesel water & soil
 - Petroleum Hydrocarbons (418.1) water & soil
 - Pesticides
 - GC/MS Volatiles
 - GC/MS Semivolatiles

- PNAs
- Explosives
- Cyanide
- Total Organic Halogens
- Total Organic Carbon
- Phenolics
- Ion Chromatography (F, Cl, NO₃, SO₄)
- NO₃/NO₂ Automated Cd reduction
- others at the discretion of QA

5.1.11 Where other method references are very similar to those above, the same PE analysis may be considered adequate documentation for both methods. Other blind PE studies may be conducted at the discretion of QA.

5.1.12 Samples will be given a laboratory ID number and test code when they are submitted to the laboratory and should be tracked in the same manner as a routine sample. Results will be compared against vendor-supplied, method-specific, or laboratory-derived limits as noted in the Evaluation and Reporting section.

6. Evaluation and Reporting

6.1 Data Package Organization

6.1.1 Paperwork must be completed as it would for routine samples, documenting preparation, calibration, and analysis and quality control. In addition, a summary page must be completed with the results of the sample and any replicate analysis. The summary page must contain the following elements:

- Analyst
- Date of analysis
- Preparation Technician (where appropriate)
- Date Prepared
- Analysis (Method*)
- Preparation (Method*)
- Components obtained from the analysis
- Results obtained from the analysis
- Replicates (where applicable) and associated RPDs

* At the discretion of QA, analysis and preparation methods may be considered sufficiently similar to qualify for more than one reference technique.

6.2 Evaluation

- 6.2.1 The data will be evaluated by QA with possible assistance from other supervisory staff. Data must meet the limits supplied by the vendor, if purchased or supplied as part of a PE program. If limits are not given by the vendor, method specific limits may be adopted or the laboratory may choose to accept recoveries based on internal QC limits.
- 6.2.1.1 All relevant components must be identified by the analyst, although in a few limited cases, similar components react in much the same fashion (i.e. similar retention times or patterns). In these instances, at the discretion of QA, the analyst may be allowed to re-evaluate the analysis.
- 6.2.1.2 If the analysis is a multi-component mixture, the results may be considered acceptable if 90% of the target analytes are quantified correctly.
- 6.2.1.3 Replicates will most often be evaluated where recovery exceptions occur or where it is determined by QA or the area supervisor that this reproducibility is a critical part of the analyst's evaluation. They will also be evaluated if it is so specified in the reference method. In these instances, the acceptability criteria are generally either the laboratory-derived RPD(s) or the reference method-specified criteria.
- 6.2.1.4 At the discretion of QA, the data may also be evaluated for completeness and documentation.

6.3 Remedial Actions

- 6.3.1 If the limits for the analyzed material have been exceeded, that performance criterion will be considered to have not been met. In such case, the data will first be re-evaluated by the analyst. If sufficient extract/digestate remains, this may include re-analysis.
- 6.3.2 If, after re-evaluation, the performance criterion still has not been met, the results from the entire analysis will be evaluated and if sufficient criteria have not been met, the analyst may be required to analyze another blind PE sample.
- 6.3.2.1 In some cases, the quality of the vendor-supplied material may be in question. In this instance or in the case where no more of a specific material is available in a timely fashion, a second source of performance evaluation material may be used.
- 6.3.3 Continued failure may result in either or both examining the analysis/preparation method for discrepancies or it may require re-training of the analyst if it is determined that the method and instrumentation is functioning properly. In either case, action must be

initiated immediately to insure that accurate results are being produced for actual laboratory samples.

- 6.3.4 In the extreme case, it may be determined after consultation with supervisory staff and laboratory management (including QA), that no analyses can be performed using that method or that analyst until there is demonstration of adequate performance.

7. Record Keeping

7.1 Analyst and Method

- 7.1.1 Records for all evaluations will be maintained by QA. Analyst evaluation will be maintained in the analyst's training file. Method evaluations will be kept separately but may mirror the analyst's evaluation.

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

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Title: Procedures for the Determination and Reporting of Detection Limits, Reporting Limits, Precision and Accuracy Studies, and Control Limits

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1. Introduction and Scope

1.1 Overview

- 1.1.1 This SOP describes the determination of Instrument Detection Limits (IDLs), Method Detection Limits (MDLs), Precision and Accuracy Studies, the setting of Reporting Limits and the determination and use of control limits. All are defined in the definitions section of this SOP.
- 1.1.2 In general, detection limits are the minimum amount of a target analyte that can be measured and determined to be greater than zero with a known degree of confidence. For purposes of this SOP, the known degree of confidence for MDLs will be defined as the 99% level. IDLs are based strictly on instrument response and MDLs on a sample processed through the entire preparation process. This SOP is based on information provided in 40 CFR Part 136, Appendix B, Definition and Procedure for the Determination of the Method Detection Limit, Revision 1.1.1 and in other sources such as the EPA Contract Laboratory Program (CLP) Inorganics Statement of Work (SOW).
- 1.1.3 Criteria for Precision and Accuracy (P&A) Studies are generally defined in the specific method, particularly those in SW 846. Where criteria are not so defined, Laucks has chosen to either use the criteria from similar methods or to set in-house criteria based on the judgment of senior management and QA. Where two methods are the same in technical detail and one does not provide P&A criteria, performance under the guidance of the method with specifications may be used to satisfy the performance criteria of both.
- 1.1.4 Control limits are determined initially for an analysis, generally using limits supplied in the method or defined by the program (such as CLP). After sufficient points have been accumulated the laboratory performs a statistical analysis of the data and computes the control limits which are based on 3x the standard deviation of recoveries (for accuracy limits) or relative percent differences (for precision limits). In some instances, warning limits may also be established using 2x the appropriate standard deviation.
- 1.1.5 This SOP is designed for applicability to a wide variety of sample types ranging from reagent water to solids containing the analyte. The MDL may vary as a function of sample type. Laucks rarely determines MDLs on any matrix other than soil or water. Other MDLs may be estimated based on these studies.
- 1.1.6 This SOP requires that a specific, detailed analytical method exist. When determining MDLs and P&As following this SOP, it is imperative that all sample processing steps included in the analytical method be included.

- 1.1.7 Where a specific method has requirements exceeding the requirements of this SOP, that method will take precedence. Where a reference method has stated detection limits, these are generally taken to be MDLs. This SOP is to be followed to validate a new method or to validate a change in a current method.
- 1.1.8 MDLs should be determined approximately annually for common procedures and as needed for procedures which may be performed on an infrequent basis. MDLs are determined on each instrument used for organic analysis.
- 1.1.9 PCB MDLs are to be performed for each PCB to be analyzed. At least one PCB MDL must be determined annually and all PCB MDL determinations must be performed within 3 years.
- 1.1.10 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis except in the case of P&A studies which are used to demonstrate the competency of the analyst.

1.2 Method Description

1.2.1 Detection Limits

- 1.2.1.1 For any metals method, the Instrument Detection Limit (IDL) must first be determined. The IDL may also be determined strictly for informational purposes for other methods but is not required. The IDL allows the analyst to assess the precision of the measurement system and to estimate the target concentration for the MDL study. IDLs are generally determined by analyzing 7 low-level standard replicates on 3 non-consecutive days and averaging the sample standard deviations from each of the three days.
- 1.2.1.2 In order to determine MDLs, a minimum of seven replicate measurements are made of a prepared sample matrix which contains approximately 1 to 5 times the estimated detection limit. A Student's t determination is made for the number of data points available, usually 7 (6 degrees of freedom), and the resulting standard deviation multiplied by that value to determine the MDL. All MDL data are entered into the laboratory MDL database.

Note: The CFR states that the recommended concentration levels used to determine the MDL be one to five times the MDL. It later implies that a level of up to 10 times the MDL is acceptable. Laucks considers up to 10 times the MDL to be an appropriate concentration although limited exceptions to this rule may be granted as long as the deviations are not great and they are approved by QA.

- 1.2.1.3 Reporting Limits (RLs) are set by the laboratory as limits that can be reliably reported on a consistent basis with a reasonable degree of confidence that the reported level is accurate. These limits may be set at the Practical Quantitation Limit (PQL) initially by using a multiplier times the MDL. The multiplier is often but not always defined in the method. After initial setting of the RL, it is rarely changed unless significant changes in the MDL occur which make it necessary to raise or lower the RL.
- 1.2.2 Precision and Accuracy (P&A) Studies are studies performed in order to demonstrate the laboratory's ability to perform a method and are also used to demonstrate analyst competency to perform the method. They generally involve the analysis of 4 replicates spiked at concentrations defined in the method. Adequate performance is most often defined in the reference method, although if the method performance has been demonstrated, analyst competency may be demonstrated in comparison to laboratory limits.
- 1.2.3 Control limits may be specified in a reference method or may be statistically determined by the laboratory from existing data. In general, laboratory determined limits for control samples must not exceed method specified limits. If laboratory determined limits do exceed method-specified limits, the entire system must be evaluated to improve method performance. In most instances, it is unacceptable for routine performance to exceed method-specified performance even if the laboratory is using method-specified control limits. This is because the laboratory cannot demonstrate adequate performance for all samples on a routine basis.

1.3 Definition of Terms

- 1.3.1 **Accuracy** - The degree of agreement of a measurement (of an average of measurements of the same thing), X, with an accepted reference or "true" value, T, usually expressed as the difference between the two values, X-T, or the difference as a percentage of the reference or true value, $100*(X-T)/T$, and sometimes expressed as a ratio, X/T. Accuracy is a measure of the bias in the system. Accuracy shall be calculated as follows:

$$\%R = \frac{C_s - C_u}{S} * 100$$

Where:

- Cs = Concentration of spiked sample
Cu = Concentration of unspiked sample
S = Expected concentration of spike in sample
%R = Percent recovery

1.3.2 **Control Limits** - Control limits may be specified in a reference Method (either as mandatory or guidance limits), or may be developed by the laboratory using internal performance data. Control limits represent acceptance criteria for determining whether an analytical system is in control (functioning within acceptable guidelines).

1.3.3 **Control Sample** - A QC sample introduced into the analytical process to allow evaluation of the measurement system. In general, it is best to use samples of a matrix similar to the samples being analyzed, where such are available. The control sample, however, will generally be free from interferences other than those inherent to the matrix itself.

1.3.4 **Degrees of Freedom** - The number of independent estimates that could be obtained from a specific set of data. In general, for a simple set of n independent values,

$$df = n-1$$

1.3.5 **IDL** - Instrument detection limit - The lowest concentration of a target analyte that can be measured and known to be greater than the instrumental background with a known degree of confidence. It may be used as a starting point for selecting MDL study spiking levels.

1.3.6 **MDL** - Method detection limit - The minimum concentration of a substance that can be measured and reported with a known degree of confidence (99% for our purposes) that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

1.3.7 **Mean** - The arithmetic sum of a set of observations divided by the number of observations.

$$\frac{\sum X_i}{n}$$

Where:

X_i = sample value for replicate i

n is the number of replicates

1.3.8 **P & A** - Precision and Accuracy - This often refers to a study conducted to validate a method or an analyst conducting a particular method.

1.3.9 **PQL** - Practical Quantitation Limit - The limit at which it is determined that the constituent can not only be detected but be accurately quantified. This limit is usually 2 to 10 times the MDL but may be even larger depending upon the constituent and the matrix. Factors are often taken from the published method but may be set by the

laboratory if published factors do not exist. These limits may also be used as the routine reporting limit (RL), unless otherwise contractually defined.

- 1.3.10 **Precision** - A measure of mutual agreement between individual measurements of the same property, usually under prescribed similar conditions. Precision is best expressed in terms of the standard deviation. Various measures of precision exist depending upon the "prescribed similar conditions".
- 1.3.11 **Reporting Limit (RL)** - A value greater than or equal to the MDL or the IDL which may be based on QA decision, the published method specifications, or project-specific requirements.
- 1.3.12 **Standard deviation** - A statistical measure of the variability of a set of sample observations. For the purposes of this SOP, the sample standard deviation is used. This is calculated using the formula:

$$s = \sqrt{\frac{\sum (X_i - \bar{X})^2}{n - 1}}$$

Where:

- s = the standard deviation estimated with $n-1$ degrees of freedom.
 X_i = sample value for replicate i
 \bar{X} = mean of all of the replicates
 n = the number of replicates

2. Equipment List and Standards

2.1 Equipment, Reagents and Standards

- 2.1.1 As appropriate for the given analysis.
- 2.1.2 Personal Computer with access to a spreadsheet program such as *Microsoft Excel* and the laboratory MDL database.

3. Safety precautions and Waste Disposal

3.1 Safety Precautions

- 3.1.1 Refer to the specific analytical SOP for appropriate safety precautions.

3.1.2 Waste Disposal

Refer to the specific analytical SOP for appropriate waste disposal practices. Waste segregation and disposal from the point of collection is further covered in the Laucks SOP on Waste Segregation and Disposal.

4. Calibration and Quality Control

4.1.1 Calibration is as appropriate to the specific method. No matrix spiking or other routine QA is required.

5. Responsibilities

5.1 Analyst

5.1.1 Each analyst is responsible for verifying a valid MDL study was performed and is available for each method they perform. In addition, each organic instrument analyst is responsible for verifying a valid annual MDL was performed on each instrument for each method they perform.

5.1.2 Each analyst is responsible for producing a one-time initial demonstration of precision and accuracy.

5.1.3 A metals analyst is responsible for assuring that a quarterly IDL study is produced on each instrument.

5.1.4 Each analyst is responsible for labeling MDL and P&A studies appropriately.

5.1.5 Each analyst is responsible for turning in a legible MDL, IDL, and P&A study to their supervisor for review and approval prior to final submittal to QA.

5.1.6 All of the analyst activities should be coordinated through the area supervisor.

5.2 Supervisor or Senior Analyst

5.2.1 Each area supervisor or senior analyst is responsible for coordinating the effective completion of the required studies. This may include but not necessarily be limited to helping determine appropriate concentration levels, coordinating the completion of the study within the timeline required by the method and/or the QA department, and scheduling the study around the analytical workload.

5.2.2 It is the responsibility of the area supervisor or senior analyst to insure that the analyst is performing the study within the guidelines of the method and to perform a review of the

final data prior to submission to QA. This review should include determination that appropriate spiking levels were used, that the data was properly computed and transcribed, and that any problems or concerns encountered during the study are documented.

5.2.3 It is the responsibility of the area supervisor to obtain the necessary information to update the control limits at a minimum of annually.

5.3 QA Department

5.3.1 It is the responsibility of the QA department to issue a Corrective Action notice to any department who fails to turn in acceptable MDL, IDL, or P&A studies.

5.3.2 It is the responsibility of the QA department to work with supervisors to schedule studies and to maintain files of all current and historical studies.

5.3.3 QA will review and provide the final sign-off that the study meets requirements.

5.3.4 QA will review and provide the final sign-off of reporting limits.

5.3.5 QA will bear the responsibility to maintain the statistically determined control limits and to ensure that they are within those specified in the reference method.

6. Operation procedures

6.1 General

6.1.1 All studies must be given laboratory LIMS ID numbers. Although they may be initially stored in QA, they will eventually be moved into the laboratory filing system and must have identification numbers in order to be able to retrieve the raw data. Identification numbers will be assigned by QA.

6.2 Instrumental Detection Limits (IDLs)

6.2.1 It is not necessary to perform actual IDL studies except for metals analyses. For metals analyses, they are performed quarterly on each instrument. Studies may be useful, however, to demonstrate instrument capabilities and as a tool for estimating the MDL.

6.2.2 As with all studies, a laboratory ID number should be assigned by QA for tracking purposes. In the case of metals IDLs, the same ID number may be assigned to all of the quarterly IDLs, rather than just one per instrument.

6.2.3 Actual IDLs studies are performed according to the CLP SOW by analyzing 7 replicates of low-level standards made up in the same matrix as all standards and not including any processing steps that would not ordinarily be performed on standards. The levels of those standards should be estimated from manufacturers detection limit specifications.

6.2.4 IDLs should be performed under the same instrumental conditions as will be used to perform actual analyses.

6.2.5 IDL studies must contain the following information (not necessarily in this order) for submittal to QA.

- Laboratory ID number
- Analyst who performed the IDL study
- Instrument name and ID which will distinctly identify that instrument
- Spike level
- Measured concentration of the 7 replicates (per day)
- Standard Deviation
- Mean
- Determined IDL
- Concentration Units
- Date(s) the study was analyzed
- Analysis (i.e. ICP, GFAA, etc.)
- Analysts signature & date signed
- Supervisor or senior analyst review signature & date signed

6.2.6 Spectrophotometry

6.2.6.1 The EPA/CLP SOW for metals requires that the IDL study be run on 3 non-consecutive days at least 7 times each day. It is prepared from an acidified aqueous standard solution made up at 3 to 5 times the manufacturers suggested IDL. The sample standard deviation (n-1) for each individual set of determinations is calculated and the final IDL is calculated as 3 times the average of the standard deviations for the three days. This may be performed using any commercial spreadsheet but care must be taken to insure that it is done using the sample standard deviation (n-1) calculation. For *Microsoft Excel*, this is the =STDEV() calculation. Ten percent of the calculations must be manually verified in order to demonstrate that the spreadsheet calculations are accurate.

6.2.6.2 If other spectrophotometric method IDLs are established by analyzing standards 7 times on 3 non-consecutive days, the calculation of the IDL is performed as described above. In addition, the EPA/CLP method does not prescribe the determination of MDLs. It is standard laboratory procedure to perform an MDL study (see section 6.3) approximately

annually for almost all routine methods of analysis, regardless of IDL frequency or other determinations.

6.2.7 Chromatography

6.2.7.1 The analyst should use the signal:noise method for determining concentrations to use for an IDL study. A preliminary estimate of 5x signal:noise is to be used; if necessary this will be adjusted and the study repeated.

6.2.8 Gas Chromatography/Mass Spectrophotometry

6.2.8.1 Mass spectral identification criteria are key in selecting target concentrations for the IDL study. The mass spectroscopist's experience in determining the minimum identifiable concentration must weigh heavily in selecting concentrations. All compounds must meet the spectral matching characteristics as called out in the analytical method for the IDL study to be valid.

6.2.9 It is strictly prohibited to compute MDLs based on IDL determinations.

6.3 Method Detection Limits (MDLs)

6.3.1 MDL studies must be performed annually for each method for inorganic analysis and for each method/instrument combination that will be used for organic methods.

6.3.2 MDL studies must also be performed when any major changes have been made in an instrument, such as a detector change.

6.3.3 Prior to beginning an MDL study, a laboratory workorder ID must be obtained from QA. The data generated from the study is then referenced to that workorder in the same manner as routine sample data.

6.3.4 MDL studies must contain the following information (not necessarily in this order).

- Laboratory ID number
- Analyst who performed the preparation
- Method number of the preparation (where applicable)
- Date(s) the study was prepared
- Analyst who performed the MDL study
- Method number of the analysis
- Date(s) the study was analyzed

- Instrument name and ID which will distinctly identify that instrument; this cannot be a data "channel" from the computer system but must distinctly and uniquely identify that instrument.
- Spike level
- Measured concentration of the 7 replicates
- Standard Deviation
- Mean
- Determined MDL
- Concentration Units
- Reporting Limits (RLs)
- Analysts signature & date signed
- Supervisor or senior analyst review signature & date signed

6.3.5 If it is determined from the study that the reporting limits must be changed (i.e. the MDL is near to or exceeds the RL), the QA Officer and the supervisor, possibly in concert with the Laboratory and/or Technical Director(s), must meet to determine the appropriate course of action. Reporting limits are intended to be at a level for which method precision and accuracy can be obtained. This generally cannot be done when the RL is close to the MDL

6.3.6 In order to determine the Method Detection Limit (MDL), it is first necessary to estimate what the MDL will be in order that the appropriate spiking levels may be used. How this estimate is made is immaterial to the actual MDL determination. Methods for making this determination may include any one or a combination of the following:

- estimating based on the instrument detection limit (IDL) as determined above or by any other means
- estimating based on the previous MDL
- estimating based on 3 times the instrument signal to noise ratio
- estimating based on analyst judgment

6.3.7 A solution is then prepared and spiked into a sample matrix, which is as free as possible of interference and target analytes, at a level that will result in a sample concentration equivalent to 1 to 5 times the estimated MDL.

Note: The CFR states that the recommended concentration levels used to determine the MDL be one to five times the MDL. It later implies that a level of up to 10 times the MDL is acceptable. Although the analyst should make his/her best effort to spike at a level from 1 to 5 times the MDL, Laucks considers up to 10 times the MDL to be a sufficient concentration. Limited exceptions to this rule may be granted as long as the deviations are not great and they are approved by QA.

6.3.7.1 Spiking levels which are determined to be less than 1x or greater than 10x the MDLs should in almost all circumstances be re-analyzed at a more appropriate spiking level.

6.3.7.2 Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interference concentrations are not detected at the estimated method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species. The interference concentration is presupposed to be normally distributed in representative samples of a given matrix.

6.3.8 Preparation of Spiked Samples

6.3.8.1 The MDL is almost always determined in reagent water or clean sand. Prepare a laboratory standard containing all analytes of interest at a concentration which is at least equal to or in the same concentration range as the estimated MDL. The analyte concentration should not exceed 5x the estimated MDL but allowances may be made up to 10x the determined MDL.

6.3.8.2 It is extremely rare that Laucks will perform studies for other than reagent water or soil. Soil matrix will almost always be represented by clean blank sand except for metals analyses where even clean sand contains levels of some metals which exceed the 10x acceptance criteria. For such analyses, reagent spikes are used containing only the digestion/preparation reagents. MDLs on other matrices will generally only be performed upon specific client request.

6.3.9 Calculation of recovery statistics

Note: All values are used without correcting for native concentration. As previously mentioned, if blank correction is a part of the method, the average blank value is used for correcting analyte concentration measurements. In almost all methods, however, blank correction is forbidden.

6.3.9.1 The sample standard deviation is calculated as follows:

$$s = \sqrt{\frac{\sum (X_i - \bar{X})^2}{n - 1}}$$

where:

s is the standard deviation estimated with n-1 degrees of freedom.

X_i = sample value for replicate i
 \bar{X} = mean of all of the replicates
 n is the number of replicates

6.3.9.2 The Student's t statistic is determined for $(n - 1)$ degrees of freedom at the 99% confidence interval (CI). A Student's t table for the 99% CI is provided in Appendix 1. For most data sets, using $n=7$ sample readings, the t value is 3.143.

Note: In some cases, it may be determined that it is useful to prepare an additional sample so that, in case of laboratory accident, at least 7 are available for statistical analysis. Whether or not this is done, all samples analyzed **must** be used in the statistical evaluation unless there is a strong reason to reject one or more of the data sets, such as obvious contamination, abnormally poor surrogate recovery, or spilled sample. It is inappropriate to reject data which do not have an overriding reason to do so. The reason for rejection must be clearly documented in the data file. If more than 7 points are used in the MDL determination, the current MDL database will not accommodate the calculation. In this case, the determinations will necessarily be done using a spreadsheet program.

6.3.9.3 The MDL determination then becomes:

$$MDL = t_{99\%CI} * s$$

where:

$t_{99\%CI}$ = the Student's t value at the 99% confidence interval
 s = the sample standard deviation as calculated above

6.3.9.4 The MDL, standard deviation and Student's t statistic for the appropriate number of replicates at the 99% CI are automatically calculated when using the Laucks MDL database.

6.3.10 Methodology Exceptions/Specifics

6.3.10.1 Wet Chemistry

6.3.10.2 The MDL for all titrimetric determinations is set as the value determined by 0.2 ml of titrant at the method specified titrant strength and sample aliquot size. This would include all tests such as versenate hardness, alkalinity, argentometric or mercurimetric chloride, titrimetric COD, etc. Karl-Fisher moistures would be an exception to this; the MDL is taken to the value determined by 0.05 ml of titrant, the method specified titrant strength, and sample size.

6.3.10.2.1 The MDL for all gravimetric residue determinations (total solids, total suspended solids, etc.) is set as the value determined by a weighing of 0.2 mg at the method specified sample size.

6.3.10.3 GC and Gas Chromatography/Mass Spectrophotometry

6.3.10.3.1 The prime consideration in GC/MS determinations is the ability to make compound confirmation based on spectral identification criteria. For SIM methods this does not apply.

6.3.10.3.2 Likewise, for PCB and other multi-peak GC analyses, pattern recognition may also dictate what can actually be determined. For either situation, analyst interpretation may be in order to confirm actual compound identification. Such interpretation must be noted in the data.

6.4 Reporting Limits

6.4.1 Reporting Limits are generally determined in one of four ways:

- Administrative decision
- Set equivalent to the Practical Quantitation Limit (PQL)
- Project Specific Requirements
- The low standard

6.4.2 The administrative decision method is generally based on what the laboratory considers to be a limit which can be obtained on a consistent and reliable basis. Values obtained from statistical determinations of MDLs, for instance, cannot always be confirmed by spectral identification, pattern matching, standard response, or analytical spike recovery. In this instance, the laboratory may choose an RL which is more readily identifiable as a level for which a compound can be so identified and reliably quantified. Administrative decision may also be considered to be a part of the PQL option.

6.4.3 The PQL option is set as a factor times the MDL. This factor may either be set forth in the published method or it may be set by the laboratory. In order to be able to provide consistent and routine reporting limits, the laboratory will generally not reset PQLs when MDLs are re-determined unless the MDL changes by a factor of more than twofold.

6.4.3.1 If it is determined from the study that the reporting limits must be changed (i.e. the MDL is near to or exceeds the RL), the QA Officer and the supervisor, possibly in concert with the Laboratory Director and/or Technical Director, must meet to determine the

appropriate course of action. Reporting limits are intended to be at a level for which reliable identification and reasonably accurate quantitation can be obtained. This generally cannot be done when the RL is close to the MDL.

- 6.4.4 Project Specific RLs are derived from project requirements and are contractually agreed upon between the laboratory and the client. In any event, the agreed upon limits **cannot** be less than the MDL or IDL.
- 6.4.5 On occasion, the low standard defines the RL. The decision to use this technique may be any combination of method specific requirements, laboratory decision, or project-specific requirements. In no case will the RL determined from the low standard be lower than the statistically determined MDL.
- 6.4.6 Reporting Limits are generally detailed in the Detection Limits Database and the LIMS system, unless set by project-specific agreement, in which case they are detailed in documents pertaining to that project and in the ProjQC database. The only persons given the capability to edit the approved limits are QA, LIMS system administrators, and the Technical or Laboratory Director. In most cases, only QA will actually perform any such editing. Note here that the EPA Contract Laboratory Program (CLP) requirements use specific contract required detection limits (CRDLs) or quantitation limits (CRQLs) and any project using the CLP methods will almost always also be reported using the CLP CRDLs or CRQLs. Any exception to the use of the CLP limits in these instances must also be noted in the ProjQC database and on any paperwork defining the details of the project.

6.5 Precision and Accuracy Studies

- 6.5.1 At a minimum, a one-time demonstration of precision and accuracy (P&A) must be performed for each method.
- 6.5.2 In some cases, it may also be required that an analyst will be required to perform a P&A study to be considered proficient and capable of independently performing a preparation or analysis.
- 6.5.3 P&A studies will be performed in accordance with the specific method. Where method-specific performance criteria are not specified, Laucks may choose to set criteria independently. Laucks' criteria, at a minimum, will meet those specified in a given method. Any determination to the contrary must be well documented and in direct consultation with QA and laboratory management.
- 6.5.4 All P&A studies must be turned in to QA after having undergone supervisory or senior analyst review.

6.5.5 All P&A studies must include the following information:

- Laboratory ID number
- Analyst who performed the preparation
- Method number of the preparation
- Date(s) the study was prepared
- Analyst who performed the analysis portion of the P&A study
- Method number of the analysis
- Date(s) the study was analyzed
- Instrument name and ID which will distinctly identify that instrument; this cannot be a data "channel" from the computer system but must distinctly and uniquely identify that instrument.
- Spike level
- Measured concentration of the 4 replicates
- Standard Deviation of the recovery tabulated against the published QA Acceptance Criteria Table, where available
- Average recovery tabulated against the published QA Acceptance Criteria Table
- Concentration Units
- Analysts signature & date signed
- Supervisor or senior analyst review signature & date signed
- Raw Data

6.5.6 The mean recovery and acceptance limits must meet the criteria given in the QC Acceptance Criteria Table at the end of each of the determinative methods, when available. Where criteria are not available Laucks may use internal acceptance criteria or defer to a similar technical method with P&A criteria and use this P&A criteria as guidance in establishing performance criteria.

6.5.7 Blank spike analyses are the commonly accepted P&A evaluation. In most methods where criteria are defined, 4 replicates must meet method-specified criteria for the **laboratory** to be considered capable of adequate performance.

6.5.8 The individual **analyst** must be able to analyze four replicates and meet laboratory blank spike control limits to be considered competent to perform the applicable analysis. For purposes of the P&A study, the analyst may be considered qualified if 90% of the analytes in a multi-analyte analysis meet laboratory criteria as long as all analytes meet the default method-specific criteria.

6.5.9 For the laboratory to be able to claim routine performance within specified limits, all analysts performing an analysis must be capable of that level of performance. All analysts must be routinely capable of performance within method-specified criteria and

will be evaluated against laboratory criteria, with further action and training in order if they are unable to routinely meet laboratory criteria.

6.6 Control Limits

- 6.6.1 Initially, when a new method is being implemented or there are insufficient data, the laboratory will use method-specified control limits for evaluation of data. If no such limits exist, the laboratory may elect to use specified limits from a similar method or may set default limits at the laboratory's discretion. These limits may be from the precision and accuracy study for that method. The determination for the suitability of setting any default limits not otherwise specified in a reference method is at the discretion of QA.
- 6.6.2 During the routine course of analysis, blank spike or laboratory control samples (LCS) and in many cases matrix spikes and matrix spike duplicates (or sample duplicates) will be analyzed. Spiking will occur at the levels specified in the respective methods, but will generally be somewhere in the middle of the calibration range.
- 6.6.3 When sufficient data have been gathered, generally at least 20 data points, the laboratory will undertake the determination of statistically-based control limits. These control limits are based on 3x the standard deviation of recoveries (for accuracy limits) or relative percent differences (for precision limits). In some instances, warning limits may also be established using 2x the appropriate standard deviation.
- 6.6.4 At a minimum, the control limits will be updated annually on a preparation/analysis/matrix specific basis. The number of data points and spiking levels used to obtain the new limits must be documented when forwarded to QA for approval.
- 6.6.5 If purchased from a commercial vendor, vendor-supplied control limits for a control sample will be considered adequate for default control limits if they are within the limits specified in the reference method. In addition, if the material is readily available and its composition does not change with every purchase, the laboratory will develop internal limits for that material. These limits may or may not be within the vendor-supplied limits but they **must** be within the method-specified limits.
- 6.6.6 In general, laboratory determined limits for **control samples** must not exceed method specified limits. If laboratory determined limits do exceed method-specified limits, the entire system must be evaluated to improve method performance. In most instances, it is unacceptable for routine performance to exceed method-specified performance even if the laboratory is using method-specified control limits. This is because even though the laboratory may be demonstrating adequate performance on the control material in any specific analytical run, it cannot demonstrate adequate performance for all samples in that run on a routine basis.

- 6.6.7 The laboratory may also calculate limits for matrix spike and matrix spike duplicate or replicate samples. However, these limits are primarily used to demonstrate method performance on a particular sample or sample-type relative to the routine laboratory sample and exceptions to these limits will generally be allowed as long as control sample limits are met.
- 6.6.8 The laboratory may be called upon to utilize control limits specified in a method or in a specific contract as designated in the LIMS ProjQC database or supplementary paperwork. The laboratory's overall performance will be considered adequate if internal control limits are within those specified in the reference method. Contractually defined limits will be used for the control samples analyzed under the contract and appropriate corrective actions taken but will not be used as a guide for routine laboratory performance.
- 6.6.9 For any particular project, if the laboratory exhibits exceptions to the method or contract-specified criteria, appropriate corrective action must be taken. Should routine laboratory control limits be within method or contract-specified criteria, and laboratory limits are exceeded but method or contract limits are met, the data may be reported but should be flagged. Where appropriate, corrective action may still be taken at the discretion of QA.

7. Reports

7.1 Data Package Organization

- 7.1.1 All work, with the exception of control limit computations, is performed under laboratory workorder ID numbers.
- 7.1.2 All data supporting the study are provided in a standard format specific to that method. In order to save paper, some items, such as the initial calibration, etc., may be referenced to other workorders. However, it must all be easily recoverable if full documentation is required, up until the standard laboratory data disposal date. Rationalizations for interpreting the results of any study and specific detail which might impact the study should be documented in the file as well.
- 7.1.2.1 Data files are prefaced with a copy of the summary report containing all of the elements previously noted in this SOP. Where laboratory database reports are available, a copy of the database report must also be kept on file by QA. All sign-offs will be handwritten.

8. References

40 CFR Part 136, Appendix B, *Definition and Procedure for the Determination of the Method Detection Limit. Revision 1.11*

EPA Contract Laboratory Program (CLP) Inorganics Statement of Work (SOW), ILM03.0.

EPA "600" Series Methods, section 8.1.1, 40 CFR, Part 136, App. A.

EPA SW846 "8000" Series Methods, section 8.6 and the specific methods

Navy Installation Restoration Laboratory Quality Assurance Guide, Naval Facilities Engineering Service Center, February 1996

Appendix I

Student's *t* Values

<u>n</u>	<u>degrees of freedom</u>	<u>t value at 99% CI</u>
2	1	31.821
3	2	6.965
4	3	4.541
5	4	3.747
6	5	3.365
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
12	11	2.718
13	12	2.681
14	13	2.650
15	14	2.624
16	15	2.602
17	16	2.583
18	17	2.567
19	18	2.552
20	19	2.539
21	20	2.528
22	21	2.518
23	22	2.508
24	23	2.500
25	24	2.492

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #: LTL-0033-~~12/24/95~~
1012

Title: Solvent QC Monitoring for Trace Residue Analysis

Submitted by: Harry Romberg
Harry Romberg

Date: 4-10-91

Reviewed by: Vicki Talksabout
Vicki Talksabout

Date: 4-11-91

Reviewed by: Mike Nelson
Mike Nelson

Date: 4/11/91

Approved by: Jim Owens
Jim Owens

Date: 4/15/91

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LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP No. LTL-1012

Previous SOP No. LTL-0033

Title: Solvent QC Monitoring for Trace Residue Analysis

Rev: 1

Laucks is in the process of re-numbering our SOPs. As an interim measure, this page serves as the cover page for those SOPs whose header information has not been updated. This page details the title, the SOP number that it is being controlled under, and the previous SOP number. The previous SOP cover sheet has been manually corrected to reflect the change but each page header will reflect the old numbering system. As SOPs are revised, the full header and cover page will be updated.

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Revision: 1.0
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TO: Users of this SOP

After you have read this SOP you need to sign the operators statement which is attached to the master copy. See the QCO for access to this copy.

SECTION IV - Operation procedures

Part 1. Initiation, Data Handling, and Record Maintenance

1.1 A new lot of any solvent must be sequestered by the supplier and the checking process initiated at least two weeks prior to using up the last of the previous lot of that solvent. A lot is defined as a batch of solvent with the same manufacturers lot number. This must be done in order to ensure that the lot has been released for analytical use BEFORE the remainder of an acceptable lot has been used up. If any solvent has failed, a second bottle may be tested for the failed parameter(s) in order to ensure the failure was not due to laboratory contamination. Failure of the second test is grounds to reject that lot for use in the laboratory.

1.2 When a lot has been formally designated as acceptable, enough should be ordered to last approximately 2 months in order to minimize the frequency of testing necessary. Any larger amount of hexane or acetone may be ordered, if desired and if the solvent locker will accommodate it. No more than 4 months supply of methylene chloride will ever be ordered, as typical methylene chloride recommended shelf-life is 6 months. For methylene chloride, multiples of a 27 case pallet will be most conveniently ordered and delivered in shrink wrap plastic. Thus, the palette may be easily set aside until testing has been completed. Methylene chloride should be kept cool and in an low light area to inhibit breakdown.

1.3 Alternatively, since it is unlikely that any lot will fail and to eliminate the time between acceptance and delivery, an appropriate supply (as defined above) may be ordered and sequestered at the laboratory for analysis. If said lot fails, however, the lot must be returned to the supplier and a new lot tested immediately. This lot **MUST** be kept separate from the current stock and very clearly marked so that it is not inadvertently used prior to acceptance. This distinction is the responsibility of the Extractions Supervisor. All solvent deliveries must be immediately reported to the Extractions Supervisor or designated alternate in order that this distinction be made.

1.4 The Extractions supervisor or designated representative initiates the checking process. When a bottle from a new, previously untested, lot of solvent is received, a Solvent Check Order form is filled out (Appendix I) designating the Manufacturer, lot number, solvent, tests to be performed and person initiating the testing. This form is given to the Sample Entry Clerk who creates a work order in SAM and gives it a work order number. One laboratory work order is established for EACH lot and type of solvent in order to very sharply distinguish between which are acceptable and which fail.

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SECTION I - Introduction and Scope

The purpose of this SOP is to define the method(s) used to check and document the purity of the major solvents used for trace residue analysis at Laucks. The solvents being tested are methylene chloride, acetone, and hexane. Specific techniques and equipment used for operations such as concentration and solvent exchange are not addressed in this document.

SECTION II - Equipment List

Glassware, reagents and equipment as delineated in the methods specific to the described task.

SECTION III - Safety Precautions

Typical precautions should be taken when handling any solvent. Some, such as methylene chloride are not flammable, but others, such as acetone and hexane are and should be treated with extreme caution. Long term health effects of solvent contact are generally unfavorable. Breathing of ANY solvent vapor should be minimized, as should any direct skin contact, by working in a well ventilated area (in or near a hood if necessary) and by using the provided gloves and, if necessary or desired, respirator masks.

Part 2. Solvent Analysis

2.1 Methylene Chloride Acidity

2.1.1 .01 N NaOH - To a 100 ml. volumetric flask, add 10 mls. of .1000 N sodium hydroxide from the buret of standardized NaOH in the Inorganics lab. Fill to the volumetric mark with deionized water, stopper, and mix very well. It takes several inversions of the flask to properly mix the solution (at least 10). This solution should be prepared immediately prior to analysis.

2.1.2 Neutral ethanol - Add 25 mls. of denatured ethanol to an Erlenmeyer flask. Add 2 or more drops of phenolphthalein indicator solution (1 gm. phenolphthalein/100 mls. ethanol). With a Pasteur pipet, add the .01 N NaOH solution dropwise until the ethanol turns slightly pink. Hold the flask against a white background to enhance the color. This solution should be prepared immediately prior to analysis.

2.1.3 Add 25 mls. of the methylene chloride to be checked to the flask containing the neutralized ethanol. Swirl. Do not shake too vigorously so that CO₂ from the air will not acidify the ethanol and cause a fading endpoint.

2.1.4 Add 900 uL of the .01 N NaOH. Swirl to mix well.

2.1.5 If the resulting color is pink, the methylene chloride passes (is not acidic). If it does not turn pink, it should be retested, preferably from a second bottle. If it fails a second time, it should be rejected or used only for cleaning. Failing solvent should NEVER be used for extraction purposes.

2.1.6 A "PASS" or "FAIL" is entered into the SAM report under the associated regular SAM test code, MECLAC. If the solvent fails, residue analysis SHOULD NOT be performed until a suitable acceptable lot is determined. The Extractions supervisor should see that any such failing lot has been terminated in SAM. Data and the report, however, should still be submitted to the QC Officer.

2.2 The residue checks are performed for EPA CLP Target Compound List (TCL) components for both pesticides/PCBs and semivolatiles (ABNs) as is appropriate for the solvent being checked.

2.3 In all cases, 500 mls. of the appropriate solvent is concentrated to 1 ml. in a Kuderna-Danish concentrator. No splitting of the concentrate occurs. Surrogates are not added.

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1.5 When testing has been completed, the lot will be officially designated as acceptable or failed by the QC Officer or Chief Chemist. This will be done by initialing the final report and contacting the Extractions supervisor. In fact, any lot will be considered acceptable which meets the criteria specified in Appendix II. As long as those criteria are met, the lot will be considered acceptable. The Extractions supervisor should be certain that a lot has been designated as acceptable prior to using it and should take whatever actions are necessary to ensure prompt analysis and acceptance before the last of the acceptable solvent has been used.

1.6 The data and report files will be maintained by the QC Officer in a designated location specific for this purpose.

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APPENDIX I

Solvent Check Order Form

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Replaces: none

2.4 Methylene Chloride - MeCl_2 is used for both ABN and pesticide/PCB analyses. A separate 500 ml. concentration is done for each analysis.

2.4.1 For the pesticide/PCB analysis, hexane is added and the solvent exchanged and concentrated down to 1.0 ml., which is submitted for analysis.

2.4.2 For ABN analysis nothing is added and the MeCl_2 concentrated directly down to 1 ml and submitted for analysis.

2.5 Acetone - Acetone is used for both ABN and pesticide/PCB analyses. A separate 500 ml. concentration is done for each analysis.

2.5.1 For the pesticide/PCB analysis, hexane is added and the solvent exchanged and concentrated down to 1.0 ml., which is submitted for analysis.

2.5.2 For the ABN analysis, the acetone is blown down to near dryness with nitrogen and brought up to 1 ml. with MeCl_2 and submitted for analysis.

2.6 Hexane - Hexane is used only in pesticide analysis. It will be concentrated 500 mls. to 1 ml. as stated and submitted for TCL pesticide analysis.

2.7 Acceptance criteria are compiled in Appendix III and are based on 500 mls of solvent concentrated to 1 ml. final volume. They are derived from EPA CLP criteria for acceptable blanks. The SAM report indicates the acceptance level, the level found and signifies whether the detected level (if any) passes (OK) or fails (FAIL).

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APPENDIX II

Solvent Acceptance Criteria

LAUCKS TESTING LABORATORIES

Solvent Check Order Form

Solvent: _____ Manufacturer: _____

Lot No: _____ Date: _____ Requested by: _____

SAM Number: _____

Tests to be performed:

Methylene Chloride: Acidity (MECLAC)
ABN QC (MSQCCK)
Pesticide/PCB QC (PXQCCK)

Acetone: ABN QC (MSQCCK)
Pesticide/PCB QC (PXQCCK)

Hexane: Pesticide/PCB QC (PXQCCK)

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Solvent Acceptance Criteria

<u>Semivolatile Compounds</u>	<u>Total ng in 1 ml.</u>
4-Nitrophenol	25000
Dibenzofuran	10000
2,4-Dinitrotoluene	10000
Diethylphthalate	50000
4-Chlorophenyl-phenyl ether	10000
Fluorene	10000
4-Nitroaniline	25000
4,6-Dinitro-2-methylphenol	25000
N-nitrosodiphenylamine	10000
4-Bromophenyl-phenylether	10000
Hexachlorobenzene	10000
Pentachlorophenol	25000
Phenanthrene	10000
Anthracene	10000
Carbazole	10000
Di-n-butylphthalate	50000
Fluoranthene	10000
Pyrene	10000
Butylbenzylphthalate	50000
3,3'-Dichlorobenzidine	10000
Benzo(a)anthracene	10000
Chrysene	10000
bis(2-Ethylhexyl)phthalate	50000
Di-n-Octylphthalate	50000
Benzo(b)fluoranthene	10000
Benzo(k)fluoranthene	10000
Benzo(a)pyrene	10000
Indendo(1,2,3-cd)pyrene	10000
Dibenz(a,h)anthracene	10000
Benzo(g,h,i)perylene	10000

Solvent Acceptance Criteria

<u>Semivolatile Compounds</u>	<u>Total ng in 1 ml.</u>
Phenol	10000
bis(2-Chloroethyl) ether	10000
2-Chlorophenol	10000
1,3-Dichlorobenzene	10000
1,4-Dichlorobenzene	10000
1,2-Dichlorobenzene	10000
2-Methylphenol	10000
2,2'oxybis(1-Chloropropane)	10000
4-Methylphenol	10000
N-Nitroso-di-n-propylamine	10000
Hexachloroethane	10000
Nitrobenzene	10000
Isophorone	10000
2-Nitrophenol	10000
2,4-Dimethylphenol	10000
bis(2-Chloroethoxy)methane	10000
2,4-Dichlorophenol	10000
1,2,4-Trichlorobenzene	10000
Naphthalene	10000
4-Chloroaniline	10000
Hexachlorobutadiene	10000
4-Chloro-3-methylphenol	10000
2-Methylnaphthalene	10000
Hexachlorocyclopentadiene	10000
2,4,6-Trichlorophenol	10000
2,4,5-Trichlorophenol	25000
2-Chloronaphthalene	10000
2-Nitroaniline	25000
Dimethylphthalate	50000
Acenaphthylene	10000
2,6-Dinitrotoluene	10000
3-Nitroaniline	25000
Acenaphthene	10000
2,4-Dinitrophenol	25000

Solvent Acceptance Criteria

<u>Pesticide/PCB Compounds</u>	<u>Total ng in 1 ml.</u>
alpha-BHC	5
beta-BHC	5
delta-BHC	5
gamma-BHC	5
Heptachlor	5
Aldrin	5
Heptachlor epoxide	5
Endosulfan I	5
Dieldrin	10
4,4'-DDE	10
Endrin	10
Endosulfan II	10
4,4'-DDD	10
Endosulfan sulfate	10
4,4'-DDT	10
Methoxychlor	50
Endrin ketone	10
Endrin aldehyde	10
alpha-Chlordane	5
gamma-Chlordane	5
Toxaphene	500
Aroclor-1016	100
Aroclor-1221	200
Aroclor-1232	100
Aroclor-1242	100
Aroclor-1248	100
Aroclor-1254	100
Aroclor-1260	100

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LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-1013

Title: Preparation, Storage, Shelf Life and Traceability Documentation of Standards and Reference Materials

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1	8/31/92
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Written by: Harry Romberg Date: 6-5-96
Harry Romberg, QA Officer

Reviewed by: Monica Carr Date: 6/6/96
Monica Carr, Organics Manager

Reviewed by: Bill Lundberg Date: 6/6/96
Bill Lundberg, Inorganics Manager

Approved by: Karen J. Kotz Date: 6/6/96
Karen Kotz, Laboratory Director

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3. Safety precautions and Waste Disposal

3.1 Safety Precautions

3.1.1 All standards and reference materials including neat or solutions should be handled as if they are hazardous substances.

3.2 Waste Disposal

3.2.1 Waste segregation and disposal from the point of collection is further covered in Laucks SOP on Hazardous Waste Disposal.

4. Operation Procedures

4.1 Preparation of Organics and Inorganics Materials

4.1.1 General consideration in standard preparations include:

- 4.1.1.1 Determine volumes and aliquots required using the concentration calculations in Appendix 1.
- 4.1.1.2 Choose volumes and aliquots which minimize the number of intermediate dilutions required to obtain final working concentration considering:
 - The inherent measurement error, i.e. no aliquots less than 20% of the volume of measurement device whenever possible.
 - The ratio of solvent:analyte
 - The amount of solution left over for disposal.
- 4.1.1.3 Be sure to use a solvent volume sufficient to dissolve all analytes.
- 4.1.1.4 The solvent used should be miscible with water when being used for sample spiking purposes. Most standards used in the extractions laboratory are prepared with methanol.

1. Introduction and Scope

1.1 Method Description

1.1.1 This SOP is intended to describe the way in which standards and reference materials are tracked, prepared, stored and maintained at Laucks, from the time of receipt of the neat or stock materials, solutions or their preparation to the point of use of the working standard. General descriptions of documentation of standard preparation may be present, it is not intended to define the actual method of preparation for each specific method. This is contained in the applicable analytical method SOP. The way in which these standards are tracked, however, is detailed along with the description of storage and shelf life guidance.

1.1.2 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described procedure of documentation.

1.2 Definition of Terms

1.2.1 Standard or Reference Material: these items are defined as any solution of an analyte at a known concentration prepared from purchased neat materials or stock solutions, or from intermediate solutions traceable to purchased materials. This includes calibration standards, independent laboratory control standards (LCS or SRM), spiking solutions, surrogate solutions, independent calibration verification standards.

2. Equipment Lists and Standards

2.1 Equipment

2.1.1 Equipment and reagents necessary for the preparation of any specific solution.

2.2 Standards

2.2.1 Standards as specified in each analytical SOP.

2.2.2 All standards must also be verified both qualitatively and quantitatively in order to satisfy EPA requirements for traceability. This may be accomplished by either (1) purchasing solutions which have been fully documented by a commercial vendor, or (2) following the recommended steps for traceability as outlined in the 3/90 CLP Organic statement of work.

2.3 Standards Logbooks

mark). Consult your supervisor if the compound is not in solution after sonication.

- The volumetric flask is diluted to the mark.
- If the analyte recrystallizes while stored in the refrigerator, the standard should be sonicated before use. Do not aliquot from a cloudy or opaque standard.
- In addition to the normal labeling of the standard, a separate label should be added indicating the need for sonication.

4.1.3.4 For volatiles, the flask is inverted and gently mixed three times after diluting to the mark.

4.2 Traceability Documentation for Organics and Inorganics Materials

4.2.1 All organic neat standard materials are logged into the NEATS database, as described in 4.2.5, when they arrive in the lab. No neat organic material should be used before it has been logged into the database. Inorganic stock materials are logged directly into the appropriate standards logbook. Examples of some NEATS database screens are provided in Appendix 3.

4.2.2 All standard, spike, or surrogate mixes which are diluted solutions, whether organic or inorganic in nature, are not logged into the database but are logged directly into the appropriate standards logbook.

4.2.3 The current controlled logbooks are identified in each area as follows:

- GC/MS Volatiles - MV# (used for standards made from neat materials, single analyte concentrates, or supplier provided standard mixes)
- GC/MS Semivolatiles - MS#
- Metals - ME#
- GC Pesticides - PX#
- GC Volatiles - VOA#
- GC & HPLC PNAs - BA#
- other GC & HPLC analyses - MA#
- Organic Extractions misc - EX#
- Technicon & Lachat Analyzers - TE#
- IR Oil and Grease - IN#

4.1.2 Proper Syringe/Pipette Technique

- 4.1.2.1 Choose an appropriate size syringe so that the measured volume is at least 2/3 of the total volume of the measurement device.
- 4.1.2.2 When selecting a pipette, choose volumetric pipettes only for the exact amount to be measured.
- 4.1.2.3 Always rinse a syringe (organics) at least ten times with the appropriate solvent in between measurements, and wipe the syringe with a Kim-wipe.
- 4.1.2.4 There should be no air bubbles. Either tap them away or discard the solution in the syringe/pipette and obtain another aliquot. Repeat this procedure as often as necessary to remove all bubbles. It may be helpful to use a GC septum with very small (<50 μ l) syringes.
- 4.1.2.5 For organics, when delivering the measured volume to the dilution vessel, fill the vessel 1/2 - 2/3 with the solvent to be used, add the measured aliquot directly into the solvent without touching the sides of the container, and fill to volume with solvent. A sub-surface injection is preferable whenever possible.

4.1.3 When preparing stock solutions from neats, the following steps should be taken.

NOTE: 99.9% of the time, stock standards will be prepared WEIGHT per Volume. DO NOT use Volume measurements for liquids unless EXPRESSLY TOLD to do so by your SUPERVISOR.

- 4.1.3.1 The dilution vessel (volumetric flask) and stopper should be triple solvent rinsed (last time with the solvent to be used for standard preparation) and allowed to dry completely.
- 4.1.3.2 The neat is weighed, to 4 significant figures, directly into the volumetric flask and the weight is recorded (to 3 decimal places for volatiles, one less than actually weighed in order to account for possible small losses due to volatilization). Stopper before weighing to avoid compound volatilization if dealing with solvents or volatile materials.
- 4.1.3.3 For components other than volatiles, the volumetric flask is filled about 3/4 full with dilution solvent and shaken until analyte is completely in solution.
 - If the analyte will not dissolve, the stoppered volumetric flask should be sonicated in the sonic bath until it does dissolve. (Because sonication heats the solution slightly, the solution should be allowed to cool before dilution to the

4.2.8 An example of the solution nomenclature used is a working ABN standard prepared on 11/13/91. The solution number assigned was MS 2-77-2. This label represents the following:

- MS - solution was made and used as a semivolatile mass spec standard
- 2- solution was logged into standard book #2
- 77- page number on which solution has been recorded
- 2- this denotes the second entry on page 77

4.2.9 All discrete measurements made during a standard preparation must be recorded in the log book, specifically, weights aliquots and final volumes.

Other pertinent data to be entered in the log book are as follows:

- Standard Name
- Parent material and concentration/purity
- Solvent/Diluent standard is prepared in
- Type of standard being prepared (i.e. inter-mediate, spike, working, calibration)
- Final concentration
- Date prepared/opened
- Expiration dates
- Analysts initials

4.2.10 The Laucks internal working material ID must be documented on the manual benchsheet, the analytical run-log or instrument printout to enable tracking back to the parent material. See Appendix 5 for examples of typical bench sheets with standards references.

4.3 Storage of Standards and Reference Materials

4.3.1 Always completely label solution with the following information:

- LAUCKS ID number
- Standard name
- Concentration
- Solvent/Diluent
- Technician's initials
- Date of preparation
- Expiration Date

- Ion Chromatography - IC#
- TOC/TOX - OC#

NOTE 1: # in the above table indicates a sequential number, beginning with 1, with each subsequent controlled book with that analysis code having the next higher integral value.

NOTE 2: This logbook number is for tracking standards only. The logbooks also will have a QA logbook number used for controlling logbooks which is independent of the standards tracking process.

4.2.4 All purchased stocks and subsequent standard preparations must be recorded in the appropriate database or log-book.

4.2.5 Upon receipt, each purchased neat material, stock, intermediate or working solution is entered into either the database (if an organic neat material) or a standards log-book and assigned a unique LAUCKS identification number. The information entered in the database or standards logbook must include:

- Analyte(s) name and vendor product ID (vendor ID must be given to unequivocally identify exactly what was used).
- supplier name
- supplier lot number
- concentration and/or purity
- expiration date (either vendor supplied, the analytical SOP or determined from the shelf life table in Appendix 2, in order of preference)

NOTE: In the case of the metals solutions which are supplied without an expiration date, the date opened and corresponding expiration date will be added when the standard is opened based on, in order of preference, the analytical SOP or Shelf Life table in Appendix 2.

4.2.6 After each material is logged it is labeled with the LAUCKS ID, date received, date opened (if the material is to be used from the same container more than once) and expiration date (if not already on the label). The accompanying vendor Certificates of Analysis, Purity or Authenticity are labeled with the Laucks ID and filed in a controlled laboratory notebook in the laboratory area. These certificates are then archived through QA when the notebook is full.

4.2.7 Every prepared stock, intermediate or working standard solution is entered into the standard log-book and assigned a unique LAUCKS ID number. The logbook entry must include the items detailed in section 4.2.9. Each material must be labeled with LAUCKS ID number, preparation date, expiration date and preparer's initials. Other items to be included on the label are listed in section 4.3.1. Examples of typical standards logbook entries are provided in Appendix 4.

4.3.2.5 Semivolatile Standards and Reference Materials

4.3.2.5.1 All standards solutions should be stored at a maximum temperature of 4 degrees C (± 2 degrees). Refer to the analytical SOPs for details as some analytes may drop out of solution if at cooler temperatures.

4.3.3 Inorganic Standards and Reference Materials

4.3.3.1 All metals standards are kept in a cabinet in the metals analysis lab. This is at room temperature. Expired standards that are kept for qualitative purposes are kept in the same room, in a different cabinet. These qualitative standards have a special label on the bottles denoting that they are not to be used for quantitative purposes. All other standards are kept at 4°C in a reach-in cooler in the inorganics lab. This cooler is dedicated to standards and SRMs only. No sample storage is allowed in this cooler.

4.4 Shelf Life

4.4.1 Expiration

- 4.4.1.1 If a parent material has an expiration date of month/year, then the material is considered usable through the end of that month. For example, 01/96, the material expires after 1/31/96. This guidance was obtained from various vendors.
- 4.4.1.2 All parent expiration dates MUST be entered into the standard log books and the expiration date for all resulting child materials must also be entered into the logbook and placed on the material label.
- 4.4.1.3 Note that no child solution may exceed the life of a parent solution or neat material. This stipulation may reduce the shelf life of a prepared solution from that listed in Appendix 2. For instance, if a stock solution is prepared from parent material that has an expiration date of 05/20/95 in 01/95, instead of having a six month shelf life (07/95) the solution will expire, 05/20/95, the same date as the parent.
- 4.4.1.4 See Appendix 2 for the Table of typical shelf life of standards and reference materials. This table is provided as guidance only. The vendor expiration date (if applicable) and the analytical SOP take precedence over any guidance set forth in the Table.
- 4.4.1.5 If a standard is past its expiration date it may be used for qualitative purposes only. The standards logbook must be edited to reflect this status and an additional label must be placed on the standard. This label must be bright in color and must clearly indicate that it is to be "Used for Qualitative Purposes Only".

4.3.2 Organic Standards and References Materials

4.3.2.1 Store in vial or bottle which minimizes head space.

4.3.2.2 Use amber or clear glass, screw tops with Teflon-liners when required, and store at, in order of preference, the temperature referenced in the analytical SOP or the temperature detailed below, in the assigned refrigerator.

4.3.2.3 Volatile Standards and Reference Materials

4.3.2.3.1 All standards solutions should be stored in the VOA freezer at -10°C to -20°C .

4.3.2.3.2 Most volatile standards are stored in the original ampules until used.

4.3.2.3.3 Standards are transferred to Mininert vials with Teflon lined septa for daily use and stored in the VOA freezer. When the standards are transferred, the information is recorded in the GC/MS Volatile Standards log book.

4.3.2.4 Other Volatile Standard Solutions

4.3.2.4.1 Some standards need to be prepared in the lab. Stock solutions are diluted using high purity MeOH.

4.3.2.4.2 To insure stability, standard solutions should be sealed in amber glass ampules

4.3.2.4.3 Rinse unsealed ampules with clean MeOH and place in oven to dry.

4.3.2.4.4 Cover ends of ampules with foil.

4.3.2.4.5 Dilute stock solution in high purity MeOH in a volumetric flask.

4.3.2.4.6 Mix gently.

4.3.2.4.7 Partially fill ampules with solution and recap with foil.

4.3.2.4.8 Use CO_2 to cool ampules until crystals form on sides.

4.3.2.4.9 Heat end of ampule with acetylene flame until glass begins to soften.

4.3.2.4.10 Gently pull end until seal is formed.

4.3.2.4.11 Label ampules and store in freezer.

4.3.2.4.12 Record the information in the Mass Spec VOA Standards Log Book (MV).

4.3.2.4.13 When standard solutions are used they should be transferred to Mininert cap vials with Teflon lined septa. The vials are stored in the VOA freezer until discarded.

Appendix 1

Example Calculations

1. Concentration Calculations from Neat Materials

HELPFUL hint: To keep yourself straight ALWAYS, ALWAYS include the units (mg, ml, etc.) in your calculations.

Example Calculations of Standard Concentrations:

Weight of Neat Material: 0.2500 gm
Volume of Solvent: 10 ml

To Calculate Concentration in mg/L (ppm):

1) Calculation in Steps.

$$A) \quad 0.2500gm * \frac{1000mg}{1.0g} = 250mg$$

A.1) Adjust the 250 mg for purity,

i.e. if purity = 90%, 250 mg x 0.9 = 225 mg

$$B \quad 10mls * \frac{1L}{1000mls} = 0.01L$$

$$C) \quad \frac{225mg}{0.01L} = 22500mg / L$$

2) Calculation as a Single Step.

$$\frac{0.2500gm}{10ml} * 0.90(purity) * \frac{1000mg}{1gm} * \frac{1000ml}{1L} = 22500mg / L$$

5. Standard Verification

5.1 Criteria

5.1.1 Standards are to have their concentrations verified before use whenever possible. The QC'ing of the standard is to be recorded in the applicable column in the standards logbook unless they are validated in the individual analytical run (such as confirmation by another standard from an independent source). Criteria for standards acceptability are in many cases defined in individual SOPs. In instances where they are not so defined, acceptability criteria are:

- 80% - 120% for organics
- 90% - 110% for inorganics

For Example: 100% = purity of 1.0
 86% = purity of 0.86

If the % purity is $\geq 97\%$, it is considered 100% pure for standards calculation.

3)

$$FC = \frac{W}{FV} * P * \text{Conversion Factors}$$

where;

W = Weight of neat material (g)

FV = Final Volume (ml)

P = Purity (%/100)

FC = Final Concentration (mg/L = ppm)

2. Intermediate and Working Standards (Standard Dilution)

$$(FC)(FV) X 1000 = (AV) (PC)$$

where;

FC: Final Concentration(s) in standard desired. Units= $\mu\text{g}/\text{mL}$.

FV: Final volume of the prepared standard. Units= mL .

1000: Conversion factor from mL to μL

PC: Parent Concentration (standard normally containing high concentrations and is diluted to desired final concentration). Units = $\mu\text{g}/\text{mL}$.

AV: Aliquot Volume of parent standard required to achieve final concentrations desired.

Units: μL (microliter).

a) Neats to Stocks

$$\frac{\text{Purity} * 1,000,000 * W}{FV} = FC$$

where;

1,000,000 = Conversion factor from gram to microgram

W Weight used in standard prep (g)

FV Final Volume (ml)

FC $\mu\text{g}/\text{ml} = \text{ppm} = \text{mg}/\text{L}$

Purity = % Purity/100

A. Volatiles:

Method	Expiration Date
SW 846 8240 B	Stock Standards: 6 months; gases weekly if unstable, or 6 months if prepared in nitrogen. Calibration standards prepared daily
CLP OLM01.9	Stock Standards: 6 months or sooner. Stock gas standards: 2 months or sooner Secondary dilution standards: 6 months or sooner (gases & reactive compounds: monthly or sooner) Calibration standards: weekly or sooner. IS, surrogate & matrix spike: fresh spiking solution weekly or sooner. Aqueous standards: 24 hours at 4°C or 1 hour at room temperature; 12 hours if stored on autosampler.
CLP OLM0 2.0-03.1	Stock Standards: 6 months or sooner. Gases & reactive compounds: 2 months Secondary standards: 1 month or sooner for gases & reactive compounds, e.g. styrene Other purgeables: 6 months or sooner IS, surrogate & matrix spike: fresh spiking solution weekly or sooner. Calibration standards: weekly or sooner. Standard solutions stored in ampulated glass vials for 2 years from preparation date or shorter if recommended by manufacturer. Once opened, expiration dates above apply. Aqueous standards: 24 hours at 4°C or 1 hour at room temperature; 12 hours if stored on autosampler.
10/92 Low Conc. CLP	Opened stock standards: weekly Aqueous standards: 24 hours. Stock Standards: 6 months or sooner Gases stock standards: 2 months or sooner Secondary dilution standards: 6 months or sooner (gases 1 month or sooner) Working calibration standards: weekly. IS: prepare fresh spiking solution every 3 months or sooner Surrogates: prepare fresh surrogate solution every 6 months or sooner
SW 846 8260A	Stock Standards: 6 months or sooner Gases: weekly if unstable or 6 months if prepared in nitrogen Working solutions: check frequently for degradation or evaporation Calibration standards are prepared daily

Appendix 2

Shelf Life Guidelines

NOTE: *IN NO CASE, will the Laucks' expirations date EXCEED the manufacturer's expiration date.

IN NO CASE, will a child solution have an expiration date that exceeds its parents.

TYPE OF STANDARD	INORGANICS	ORGANICS EXTRACTIONS	ORGANICS INSTRUMENTATION ^A
Purchased Neat	10 Years * ¹	5 Years * ¹	5 Years * ¹
Purchased Stock Solution	12 Months * ²	12 Months * ²	6 Months * ²
Prepared Stock Solution	12 Months	12 Months	6 Months
Intermediate Solution	3 Months	N/A	6 Months
Working Solution	2 weeks * ³	6 Months	3 Months
Purchased Working Solution		6 Months	3 Months

- * 1. Unless the manufacturers expiration date is less than the following, purchased neat standards shelf life will not exceed 10 years materials from the date of receipt for inorganics and 5 years from the date of receipt or 3 years from the date opened for organic materials, whichever is shorter.
- *2. Unless manufacturers expiration date is less than the following, purchased stock solutions or intermediates shelf life will not exceed 1 year from the date opened.
- * 3. Listed time is maximum. Specific shelf-life criteria are detailed in the individual SOPs.

NOTE: THIS IS A GENERAL PROTOCOL. WHERE POSSIBLE, VERIFY THE INTEGRITY OF THE WORKING STANDARD SOLUTION BY MEETING THE ACCEPTANCE CRITERIA SPECIFIED IN THE ANALYTICAL SOP FROM THE KNOWN TRUE VALUE WHEN ANALYZED AGAINST AN INDEPENDENT LABORATORY CONTROL STANDARD OR A CALIBRATION CURVE.

LAUCKS TESTING LABORATORIES

NEALS DATABASE PROGRAM

SEARCH BY ONE OF THE FOLLOWING PARAMETERS:

CAS Number	Bottle Number	
Chemical	Synonym #1	Synonym #2

Enter New Chemical

Open Report for Expiring Chemicals

SOP No: LTL-1013
Revision: 3
Date: 6/3/96
Page: 17 of 19
Replaces: 2

Appendix 3
Neats Database Screens

SOP No: LTL-1013
Revision: 3
Date: 6/3/96
Page: 18 of 19
Replaces: 2

Appendix 4
Logbook Examples

NEATS DATA ENTRY

Chemical: n-nitroso-diphenylamine CAS: 86-30-6

Synonym #1: Purity (%): 98.3

Synonym #2: Lot: 153-1508

Bottle #: NJG Source: ChemService

Old Bottle #: Catalog: O-374

Box: 2 Size (g): 2

Received: 4/3/96

Expires: 10/1/2000

Notes: For GC/MS SVOA MS/MSD

Previous Next

New

Exit

LAUCKS TESTING LABORATORIES, INC.
STANDARDS LOGBOOK

#	ANALYTE	ID or STOCK No.	STOCK CONC.	VOL/WT TAKEN	FINAL VOL.	CONC.	SOLVENT	PREP. DATE	INIT.	EXP. DATE	QCD (Initials)
4	2,4,6-TNT	M-8330-11	1000 PPM	10 uL	50 mL	200 PPB	DI H ₂ O	12/20/95	MLT	04/01/96	
L	HM X	M-8330-4	↓	↓	↓	↓	↓	↓	↓	↓	
01	1,3,5-TNB	M-8330-12	1000 PPM	10 uL	50 mL	200 PPB	Fluid Tcup #1	12/20/95	MLT	04/01/96	
	2,4-DNT	M-8330-2									
	RDX	M-8330-5									
	2,4,6-TNT	M-8330-11									
L	HM X	M-8330-4	↓	↓	↓	↓	↓	↓	↓	↓	
02	1,3,5-TNB	M-8330-12					Tcup #2 Fluid				
	2,4-DNT	M-8330-2									
	RDX	M-8330-5									
	2,4,6-TNT	M-8330-11									
L	HM X	M-8330-4	↓	↓	↓	↓	↓	↓	↓	↓	

fill 4-02-04
cont

LAUCKS TESTING LABORATORIES, INC.
STANDARDS LOGBOOK

#	ANALYTE	ID or STOCK No.	STOCK CONC.	VOL/WT TAKEN	FINAL VOL.	CONC.	SOLVENT	PREP. DATE	INIT.	EXP. DATE	QC'D (Initials)
1	SW 246 highstd	ME3-96-01 10/19/96	LTL-CAL-1	10 mls	100 mls		HCL 5% HNO ₃ 1% H ₂ O	5/23/96 4/23/96 4/2/96	KP	7/10/96	KP
		ME4-45-01 4/1/97	LTL-CAL-2	1 ml							
		ME4-32-02 3/14/97	LTL-CAL-3								
		ME3-66-05 7/10/96	1000 ppm Mo 7/10/96	↓							
		ME3-66-09 7/10/96	1000 ppm Pb 7/10/96	4 mls							
		ME3-97-08 11/17/96	1000 ppm Cu 11/17/96	↓							
		ME3-66-12	1000 ppm Zn	↓							
2	ABN SPE ICP/MS ICV3	ME4-30-01	ICP/MS KV1	500 ul	5 mL		10% HNO ₃ H ₂ O	4/3/96	ABN		
3	AS	ME3-81-9 2/2/96	1000 ppm	100 ul	5-11-96 10ml in 100ml	1 ppm	5% HNO ₃	4-3-96	HM	5-96	
4	ICP/MS STD1	ME4-30-01	ICP/MS	50 ul	5 mL		5% HCL H ₂ O	4/3/96 4 ABN	ABN		
5	STD2	↓	Stock Std	250 ↓	↓		↓	↓	↓		
6	STD3	↓		500 ↓	↓		↓	↓	↓		

ME4-48

SOP No: LTL-1013
Revision: 2
Date: 04/17/96
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Appendix 5
Bench Sheet Examples

LAUCKS TESTING LABORATORIES, INC.
STANDARDS LOGBOOK

#	ANALYTE	ID or STOCK No.	STOCK CONC.	VOL/WT TAKEN	FINAL VOL.	CONC.	SOLVENT	PREP. DATE	INIT.	EXP. DATE	QC'D (Initials)
1	IC ICWter ^{72 11/19/96} Cl	ERA 3412	—	—	260ml	129 mg/L	—	100g in 31/8/96	SK	Opened: 4/19/97 Exp: 4/19/97	
	F		—	—		6.47 mg/L	—				
	NO ₃		—	—		8.77 mg/L	—				
	SO ₄		—	—		110 mg/L	—				
2	Cal. Std. F	IC4-84-4	1000x	500 _{ul}	100ml	5x	H ₂ O	3/20/96	SK	4/3/96	
	Cl	.5	1000x	1000 _{ul}		10x					
	NO ₂	.7	100x	2000 _{ul}		2x					
	NO ₃	.3	1000x	500 _{ul}		5x 10x ^{72 4/21/96}					
	SO ₄	.6	1000x	2000 _{ul}		20x					
3	NO ₂ ICW	IC4-78-7	100x	1000 _{ul}	100ml	1x	H ₂ O	3/20/96	SK	3/27/96	
4	NO ₂ ICV	IC4-78-7	100x	1000 _{ul}	100ml	1x	H ₂ O	3/25/96	SK	4/1/96	

LAUCKS TESTING LABORATORIES
 ABN GC/M. OPERATIONS LOG

CASE # _____

PAGE 4883 -A

3/18/96

IS = MS334-1 DFTPP = MS334-4

IS A

IS B

IS C

RUN #	FILE NAME	CLIENT NAME	CLIENT SAMPLE#	LAB I.D. #	INJECTION INFO	RT	RESPONSE	RT	RESPONSE	RT	RESPONSE
1	MT7SD1										
2	HC18A	-	SSTD050	MS4-9-1	25. YARN	11.24	55075	14.99	159300	20.44	164485
3	HC18B	-	SSTD200	MS3-89-1	100.8 ^{way} / _{phenol}	11.22	59100	14.98	168403	20.42	100469
4	HC180	Kalama	B03139645VWLA	9603368-BLK	1000→1	11.23	58139	14.98	166207	20.43	99304
5	HC181	Kalama	S03139645VWLA	-SPK	1000→1	11.24	55723	14.99	155289	20.44	98643
6	HC182	Olympia	-	9603206-aDL	1:4 1000→1	11.24	52364	14.98	158592	20.44	107071
7	HC183	Kalama	-	9603368-01	1:2 100→1	11.24	56997	14.98	168568	20.46	103091
8	HC184	+	-	-DIDL	1:4 100→1	11.24	58386	14.15.00 ^{24.416}	173480	20.45	106213

~~3/19/96~~

File Name: SW846 Autosampler Type: TYPE TJA
Sample Positions: 257/300 QC Positions: 11/19 # Sets: 1
Use Station location is rack -1, pos. -1.

- Racks ---

Rack #	Type	Usage	#Pos Left	Analyses/Pos
1	Aux. (L) Rack	STD/QC/BLANK	11	10
2	Sample (13mm)	Samples	32	1
3	Sample (13mm)	Samples	75	1
4	Sample (13mm)	Samples	75	1
5	Sample (13mm)	Samples	75	1

- Sample Sets ---

Set #	Type	Prepare?	Description	Method	#Pos	Rack#	StartPos
1	,Y	No	UMC09,UMC11 RE-AS, TL	UMASOIL	43	2	1

- Preparation Info ---

Set #	Uptake	Uptake#2	Final	Dil.Factor
-------	--------	----------	-------	------------

Report As, TL

KP 4/10/96

Samples Prepared.

Rack #1

Row	Col	Sample Name	Set #	#Used	Type
1	1	ICV1 ME4-48-01	-NA-	1	QC Standard
2	1	STD4 ME4-48-01	-NA-	1	Standard
3	1	STD3 ME4-48-01 5ml/10mls	-NA-	1	Standard
4	1	STD2 ME4-48-01 1ml/10mls	-NA-	1	Standard
5	1	STD1 ME4-48-02	-NA-	1	Standard
6	1	STD0	-NA-	1	Standard
7	1	Blank	-NA-	7	Blank
8	1	CCV ME4-51-01	-NA-	6	QC Standard

...19 Not Used)

Rack #2

Row	Col	Sample Name	Set #	#Used	Type
1	1	CR111 ME4-45-02	1	-NA-	Sample
2	1	ICSAB11 ME4-52-05	1	-NA-	Sample
3	1	PBS1	1	-NA-	Sample
4	1	LCSS1	1	-NA-	Sample
5	1	03040-01	1	-NA-	Sample
6	1	03040-01D	1	-NA-	Sample
7	1	03040-01S	1	-NA-	Sample
8	1	03040-01L	1	-NA-	Sample
9	1	03040-02	1	-NA-	Sample
10	1	03040-03	1	-NA-	Sample
11	1	03040-01 5X	1	-NA-	Sample
12	1	03040-01D 5X	1	-NA-	Sample
13	1	03040-01S 5X	1	-NA-	Sample

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LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-1017

Title: Internal Audit Procedures

Revision history:

<u>Number</u>	<u>Date</u>
000	5/13/93
001	3/3/96

Written by: Harry Romberg
Harry Romberg

Date: 3/3/96

Approved by: Karen T. Kotz
Karen T. Kotz, Laboratory Director

Date: 3/3/96

UNCONTROLLED

1.4.4 SOP: Standard Operating Procedure

1.4.5 QA: Quality Assurance

1.4.6 QC: Quality Control

1.4.7 Audit: A planned and documented activity performed to determine by investigation, examination, or evaluation of objective evidence the adequacy of and compliance with established procedure, instruction, and other applicable documents and the effectiveness of implementation. An audit should not be confused with surveillance or inspection activities performed for the sole purpose of process control or product acceptance.

1.4.8 Auditor: Any individual who performs or assists in the performance of any part of an audit, including technical specialists.

1.4.9 Lead Auditor: An individual who is qualified to organize and direct an audit, report audit findings, and evaluate proposed corrective actions.

1.4.10 Finding: Departure from approved procedures, program requirements, or other applicable documents that have, or in the immediate future could reasonably be expected to have, an adverse effect on the adequacy or effective implementation of the Laucks QA program. This would be ranked as a **critical** discrepancy in the audit report.

1.4.11 Deficiency: Departure from approved procedures, program requirements, other applicable documents, or good management practices that, if not corrected in a timely manner, could reasonably be expected to have a future adverse effect on the adequacy or effective implementation of the Laucks QA program. This would be ranked as a **minor** discrepancy in the audit report.

1.4.12 Discrepancy: Departure from approved procedures, program requirement, or other applicable documents that have, or may have an adverse effect on the adequacy or effective implementation of the Laucks QA program. This includes findings and deficiencies found during the course of an audit.

1.4.13 Recommendation: An observation or advise given to enhance current practices by any individual or department of the Laucks QA program. This would be ranked as a **recommended** item in the audit report.

1. Introduction and Scope

1.1. Method Description

1.1.1. The purpose of this procedure is to provide instructions for planning, performing and reporting QA/QC audits within the laboratory.

1.1.2. This method is restricted to use by, or under the supervision of personnel experienced in the technique described.

1.2. Discussion

An Audit of the facility is performed for the following reasons:

1.2.1 To determine that contractual and regulatory obligations are fulfilled.

1.2.2 To determine that procedures and standards are being followed, and to insure good laboratory practice. These audits will include, but are not limited to the refrigeration unit temperatures, logbooks, balance calibrations, data, and standards traceability.

1.2.3 To establish that quality assurance objectives are met, including holding times, use of approved analytical methods, and stated objectives for precision and accuracy.

1.2.4 To serve as a management tool to evaluate appropriateness of quality assurance policies.

1.2.5 To identify potential or actual deficiencies for the purposes of evaluating compliance with requirements and providing the means for correction.

1.2.6 To determine that records are prepared and maintained as required.

1.3 Documentation and Frequency

Documentation required is specified in the text and the frequency shall be as required by the QA Manager, but at least one technical audit shall be performed annually for each department. This audit may take place in parts, with additional and more extensive audits being scheduled as deemed necessary.

1.4. Definition of Terms

1.4.3 This section defines terms and acronyms as they are used in this SOP.

2.3 Final review and sign-off of each Audit Finding Report may be performed by either the QA Manager, Lab Director or department supervisor or designee.

3. Safety precautions

3.1. Safety Precautions

3.1.1. Auditors must adhere to the general laboratory health and safety policies during the course of the audit.

3.1.2 Protective eyewear must be worn in all applicable locations at all times during the course of the audit.

4. Calibration and Quality Control

Not applicable.

5. Operation procedures

5.1 General

5.1.1 Audit personnel may be selected and assigned audit responsibilities commensurate with their training and expertise and the special nature of the activities to be audited.

5.1.2 Audit personnel are independent of any direct responsibility for performance of any activity which they will audit. Persons having direct responsibility for performance of the activities are not involved in the selection of an audit team.

5.1.3 Audit team members shall have received appropriate indoctrination and training for auditing.

5.2 Audit Planning

5.2.1 The QA Manager, or designee shall develop an audit plan which shall be the basis for the audit. The audit plan is documented on Audit Plan Form (Se Appendix I).

5.2.2 The QA Manager shall develop an audit checklist appropriate to the activity or area being audited. The checklist should contain auditable requirements extracted from the QA Manual.

2. Responsibilities

2.1 It is the responsibility of QA personnel, the auditor and audit leader to perform an audit according to this SOP and complete all documentation required for review.

2.1.1 QA Manager is responsible for the following:

- Approving each detailed audit plan
- Concurring with the adequacy of each audit report
- Issuing the audit report
- Tracking audit status through final closeout

2.1.2 If an audit team is used, the following responsibilities fall upon the Audit Team Leader. If an audit team is not used, the following responsibilities fall to the QA Manager:

- Developing the detailed audit plan
- Conducting pre-audit and post-audit conferences
- Supervising the conduct of the audit
- Preparing and signing the audit report

2.1.3 Management of audited departments is responsible for the following:

- Providing reasonable and timely access to personnel, facilities, and records, as required to support the audit process
- Providing timely and adequate response to audit reports, including determination and implementation of corrective actions, as required.
- Verifying initial implementation of corrective action for deficiencies in their areas, if applicable.

2.2 Audits and reports are to be performed by personnel in the laboratory who have demonstrated the ability to evaluate processes in the laboratory with emphasis on Quality Control and Quality Assurance.

5.4.1.2 Purpose and scope of the audit.

5.4.1.3 Audit team members (when applicable) and the people contacted during the audit.

5.4.1.4 Description of items, including the rank, type and detail of the audit finding requiring corrective action. The description of the items must be in sufficient detail to enable investigation, evaluation, and correction of the finding. (See Appendix II - Audit Finding Report Form) The report may also include the area affected (See Table in Appendix III) and Finding Type (See Table in Appendix IV)

5.4.1.5 Due date for completion of corrective action plans.

5.4.2 The QA Manager shall issue the audit report to the appropriate levels of Laucks management within four following the audit. This report shall include a copy of each finding, deficiency and/or recommendation.

5.5 Audit Closure and Follow-Up

5.5.1 The appropriate Laucks Management (departmental supervisors, laboratory director hall investigate the reported finding, deficiency or recommendation and do the following:

5.5.1.1 Determine the actions required to correct the discrepancy.

5.5.1.2 Evaluate each discrepancy to determine the root cause of the problem and any generic implications.

5.5.1.3 Determine the corrective action required to correct the discrepancy and to prevent recurrence.

5.5.1.4 Document corrective action and indicate corrective action commitment date.

5.5.1.5 Sign, date, and return the completed form to the QA Manager within the assigned time frame given in the audit report.

5.5.2 The QA Manager shall evaluate each discrepancy/recommendation response. Inadequate or indeterminate responses shall be returned for reexamination of the problem and revised corrective action.

5.5.3 The QA Manager shall verify the corrective action, as stated in the response, and make sure it has been implemented and accomplished as scheduled.

applicable SOP's or guidance documents, such as EPA SW846. Checklists are designed for each Department by the QA Manager and can be accessed by the QA Department.

- 5.2.3 The QA Manager shall ensure that the checklist provides an adequate means for indicating whether the question is satisfactorily answered.
- 5.2.4 Audits are scheduled in a manner to provide coverage and coordination with ongoing QA program activities.
- 5.2.5 Audits are scheduled at a frequency commensurate with the status and importance of the activity. Within the audit program, each department of the laboratory and each element of the Laucks-QA program is audited, at a minimum, at least once annually.
- 5.2.6 The QA Manager notifies the audited department, in writing, prior to the audit to provide the subject and scope of the audit, audit schedule, and audit team members, if applicable.

5.3 Audit Performance

- 5.3.1 The QA Manager and (when required) the appointed audit team members shall proceed through the audit checklist recording evidence of compliance, discrepancies, or recommendations.
- 5.3.2 During the audit, the QA Manager or appointed team member shall use their best judgment to determine if there is a need to audit at a greater depth than the checklist indicates. If this is the case, the checklist shall be modified accordingly.
- 5.3.4 Objective evidence is examined, and essential information is recorded, such as the identification of specific evidence examined, specific details of discrepancies or adverse conditions, and applicable references.
- 5.3.5 The QA Manager shall identify each finding, deficiency, or recommendation in a QA audit report. Findings, deficiencies and recommendations will be listed by department and sequentially numbered in the QA audit report.

5.4 Audit Report

- 5.4.1 The QA Manager or his designee shall prepare an audit report which should address the following:

- 5.4.1.1 Date and location (Laucks-department) of the audit.

- Training/Records
- Good Laboratory Practices
- Other

5.7.2 Explanations of Categories Listed Above

5.7.2.1 Logbook maintenance findings include but are not limited to the following: logbooks not being maintained in accordance with Laucks policy, improper entries into logbooks, improper error corrections, logbooks not being kept up to date.

5.7.2.2 Document Control Procedure findings include but are not limited to the following: documents being maintained in such a way that is non-complaint with Laucks document control procedures (this includes archives, SOPs, QAPs, Chemical Hygiene Plan, HTVRs, and forms), records being stored in work areas for longer than 6 months, improper handling of controlled procedures.

5.7.2.3 QC procedure finding include but are not limited to the following: temperatures of ovens and refrigeration units not being monitored in accordance with procedures, balances and pipettes not being verified as required.

5.7.2.4 Standard Operating Procedure and Quality Assurance procedure findings include any case where a procedure has not been followed in full and has not been documented on the applicable corrective action form.

5.7.2.5 Analytical methods findings involve cases where the approved and required analytical method has not been followed to the full extent and there is no documentation that communicates this.

5.7.2.6 Purchasing and procurement document control findings involve instances where the appropriate procedures have not been followed in full. This type of finding includes but is not limited to the following: un-approved use of standards or solvents, lack of certification documentation, etc.

5.7.2.7 Findings for standards preparation and standards documentation include but are not limited to the following circumstances: improperly prepared standards, improperly documented standard preparation, inadequate verification documentation, lack of documentation when procedures are not followed in full.

- 5.5.4 An interim status report of corrective action completion may be issued
- 5.5.5 After verification of corrective action, the QA Manager shall issue a report stating that all corrective action has been completed and the audit is closed.
- 5.5.6 If a stalemate is reached concerning either the validity or resolution of an audit finding, affected personnel escalate the concern to the appropriate level of management to effect a resolution.

5.6 Records

The QA Manager shall ensure that the following audit documentation is maintained on file:

- 5.6.1 Completed audit checklist.
- 5.6.2 Audit Report (includes findings, deficiencies and recommendations).
- 5.6.3 Corrective Action (response to discrepancies).
- 5.6.4 Records pertaining to the completion of corrective action.

5.7 Audit Discrepancy Tracking

- 5.7.1 Audit discrepancies will be categorized to facilitate tracking and trending of recurrent problems. The categories are as follows:
- Logbook Maintenance
 - Document Control Procedures
 - QC Procedures
 - Standard Operating/Quality Assurance Procedure
 - Analytical Method
 - Purchasing/Procurement Document Control
 - Standards Preparation/Documentation
 - Safety/Reagent Labeling or Storage

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Appendix I

Audit Plan Form

5.7.2.8 Safety and reagent/chemical labeling findings involve any deviation from approved safety and waste procedures and the chemical hygiene plan.

5.7.2.9 Training and training records findings involve lack of training records, and personnel performing analysis without appropriate qualification documentation.

5.7.2.10 Good Laboratory Practice findings involve significant figures, temperature monitoring, calibration techniques and other associated activities involved with safe and accurate laboratory practices.

6.1 References

Laucks Quality Assurance Plan

Applicable SOPs

Audit Database Tables

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Appendix II

Audit Finding Report Form

Audit Plan

Area to be Audited: _____

Lead Auditor: _____

Audit Team Members (if applicable): _____

Date of Audit: _____

Type of Audit: _____

Checklist(s) to be Used: _____

Individuals Contacted During the Audit: _____

Audit Debrief Date: _____

Report Issued Date: _____

Signature of Lead Auditor: _____

Signature(s) of Team Members: _____

Appendix III

Area Names

Audit Finding Report

Audit Number: Example	Finding Number: 1
Facility:	Audit Date:
Auditing Body:	Audit Type:
Lead Auditor:	Affected Area: GC-Semivolatiles
Related Findings:	
Finding Rank: Minor	Repeat Finding?: No
Finding:	
Corrective Action Response:	
Opened By:	Date Opened:
Response By:	Response Date:
Corrective Action By:	Scheduled Completion Date:
Verified By:	Date Verified:

Appendix IV

Finding Type

Depart	Department	DepartmentDescription	Sup ID #
ARCH	Archive	Archive of Documents in QA	0006
BP	Bottle Prep	Bottle Prep	0008
DM	Data Management	Data Management and Administrati	0008
EXT	Extractions	Extractions	0027
GCEF	GC-Extractable Fuels	Extractable Fuels by GC/FID	0038
GCS	GC-Semivolatiles	GC-Semivolatiles	0048
GCV	GC-Volatiles	GC-Volatiles	0038
MSS	GC/MS-Semivolatiles	GCMS-Semivoiatile	0048
MSB	GC/MS-Semivolatiles & Volatile	GC/MS-Semivolatiles and Volatiles	
MSV	GC/MS-Volatiles	GCMS-Volatile	0038
SAF	Health and Safety	Health and Safetv	0006
HPL	HPLC	HPLC	0038
IN	Inorganics	Metals and Wet Chemistry Office	0053
MIS	LIMS and MIS	LIMs and MIS	0070
MET	Metals	Metals and Metals Prep	0067
MTI	Metals Instrumentation	Metals Instrumentation	0067
MTP	Metals Preparation	Metals Preparation	0067
PM	Project Management	Project Management	0008
QA	Quality Assurance	Quality Assurance	0006
SM	Sales and Marketing	Sales Department	
SC	Sample Control	Sample Control	0008
SP	Soecial Chemistry	Special Chemistrv	0053
WC	Wet Chemistry	Wet Chemistrv	0053
YAK	Yakima Office	Yakima Office	0072

ID of Finding Type	Finding Type
BA1	Balance - Not Certified Annually
BA2	Balance - Not Checked Daily With Class S Weights or as used
BA3	Balance - Weights Not Certified Annually
BA4	Balances - Weights used for calibration do not correspond to weights used for analysis
CA1	Corrective Action - Procedures Not Developed
CA2	Corrective Action - NVC Not Being Tracked
DL1	Documentation/Logbooks - Error and Corrections not be documented correctly
DL2	Documentation/Logbooks - incomplete columns, not properly bound
DL3	Documentation/Logbooks - Not Maintained or used
DL4	Documentation/Logbooks - inadequate Review
DR1	Data Review - Not Being Performed
DR2	Data Review - Not Being Documented
DR3	Data Review - No SOP
DR4	Data Review - No QC Decision Matrix Available
EC1	Electronic Backup - Not Being Performed
EC2	Electronic Backup - Not Inventoried For Retrieval
GL1	Good lab practice - misc GLP items
MD1	Methods - No SOP/Cribsheet available at time of audit
MD2	Methods - SOP/Cribsheet in use not current controlled version
MD3	Method- controlled SOP/Cribsheet is not being followed or doesn't match current practice
MD4	Methods - The controlled SOP is Non-compliant with the referenced published method
MD5	Methods - SOP/Crib sheets in use & not controlled, meaning draft or handwritten SOPs in use
PE1	Performance Evaluation Samples - Results are outside warning limits, check for error
PE2	Performance Evaluation Samples - Results are outside control limits, not acceptable
PE3	Performance Evaluation Samples - Results included misidentified compounds, not acceptable
QA1	QA - QAP/SOP Document Control Not in Place or Used
QA2	QA - Precision and Accuracy Data Not Current
QA3	QA - MDL/IDL Not Current
QA4	QA - QC Limits Not Determined or Maintained
QA5	QA - Control Charts Not Developed or Maintained
QP1	QAPlan - No QAP Available
QP2	QAPlan - Outdated And Needs Revision
QP3	QAPlan - Has Major Discrepancies With SOPs or practices of the day
RC1	Records Control - Logbooks Not Controlled
RC2	Records Control - Filing not maintained per SOP
RC3	Records Control - No SOPs to describe System
RC4	Records Control - Not mentioned in QAP
RC5	Records Control - Archiving inadequate
SC1	Sample Control - Building not secured
SC2	Sample Control - COC not established or maintained per client requirements
SC3	Sample Control - Temp/pH not monitored for all regulatory samples
SF1	Safety - No SOP
SF2	Safety - Not Adhering to SOP or Chemical Hygiene Plan
SF3	Safety - Not Adhering to Good Lab Safety Practices
ST1	Stds/Reagents - No SOPs for preparation
ST2	Stds/Rgnts - Prep record inadeq./or not traceable
ST3	Stds/Reagents - Expiration Date Misused
ST4	Stds/Reagents - Not Labeled Properly in the laboratory
SW1	Software - Not Verified and Documented
TH1	Thermometer - NIST Not Available
TH2	Thermometer - NIST Not Evaluated Annually
TH3	Thermometers - Not Calibrated Annually
TH4	Thermometers - Correction Factor Not Applied or misapplied
TH5	Thermometers - Temp. Not Recorded Daily or As Used
TR1	Training - No Formal Program or Documentation
TR2	Training - Incomplete Forms (eg Proficiency, Hrs)
TR3	Training - Not Maintained Consistently

APPENDIX B

**LAUCKS TESTING LABORATORIES, INC., QUALITY ASSURANCE PLAN
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APPENDIX C

BROWN & ROOT ENVIRONMENTAL STANDARD OPERATING PROCEDURES

<u>SOP NUMBER</u>	<u>Title</u>
• CT-03	Data Validation
• CT-05	Database Records and Quality Assurance
• SF-1.6	Analysis For Volatile Compounds Using Purge-and-Trap Gas Chromatography (Field GC Analysis)



BROWN & ROOT ENVIRONMENTAL

STANDARD OPERATING PROCEDURES

Number CT-03	Page 1 of 101
Effective Date 03/01/96	Revision 3
Applicability B&R Environmental, NE	
Prepared Risk Assessment Department	
Approved <i>Ud.</i> D. Senovich	

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1.0 CLP ORGANICS FOR SOLID AND AQUEOUS MATRICES

1.1 CLP Organics by GC/MS

1.1.1 Volatiles (USEPA CLP Statement of Work (SOW) 3/90)

1.1.1.1 Applicability

CLP 3/90 volatile methodology is used to determine organic compounds in most matrices including groundwater, sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

The CLP 3/90 volatile Target Compound List (TCL) includes the following substances:

Acetone	Chloromethane	Methylene Chloride
Benzene	Dibromochloromethane	4-Methyl-2-Pentanone
Bromodichloromethane	1,1-Dichloroethane	Styrene
Bromoform	1,2-Dichloroethane	1,1,2,2-Tetrachloroethane
Bromomethane	1,1-Dichloroethene	Tetrachloroethene
2-Butanone	1,2-Dichloroethene (total)	Toluene
Carbon Disulfide	1,2-Dichloropropane	1,1,1-Trichloroethane
Carbon Tetrachloride	cis-1,3-Dichloropropene	1,1,2-Trichloroethane
Chlorobenzene	trans-1,3-Dichloropropene	Trichloroethene
Chloroethane	Ethyl Benzene	Vinyl Chloride
Chloroform	2-Hexanone	Xylenes (total)

This method is based upon a purge-and-trap, gas chromatographic/mass spectrometric (GC/MS) procedure. Prior to analysis, samples must be prepared according to the SOW.

1.1.1.2 Interferences

Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. Associated field quality control blanks are analyzed in order to monitor this.

Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe or purging device is rinsed with reagent water between samples. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination.

If sample or matrix interferences are encountered, a secondary or alternate analytical column may be used to resolve the compounds of interest.

1.1.1.3 General Laboratory Practices

A method blank consisting of organic free water spiked with surrogates and internal standards should be analyzed immediately following each daily calibration, and also after the analysis of every high concentration sample.

Matrix Spike/Matrix Spike Duplicate (MS/MSD) analyses should be conducted to determine the effects of sample matrix upon the compounds of interest.

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1.1.1.4 Sample Preparation

A purge- and -trap procedure is performed to prepare and extract volatile compounds from samples and to introduce those compounds into the GC/MS.

For highly volatile matrices, direct injection preceded by dilution should be used to prevent gross contamination of the instrumentation. For pastes, dilution of the sample until it becomes free-flowing is used to ensure adequate interfacial area. The success of this method depends on the level of interferences in the sample; results may vary due to the large variability and complicated matrices of solid waste samples.

1.1.1.5 Data Overview Prior to Validation

Before commencing validation, the reviewer must preview the associated Chain-of-Custody (COC) reports to determine:

- If the appropriate number of samples are present in the data package and if each sample was correctly analyzed for the parameters and methods specified.
- The identity of all associated field quality control blanks and field duplicate pairs.

Because many samples may have required dilutions, re-extractions and/or re-analyses, the validator should preview the data package contents to determine which analyses represent the better quality data.

Unless specifically directed by client protocol, never annotate the laboratory data package. Before beginning evaluation, prepare working copies (i.e., photocopies) of all Form I reports (including those for samples, laboratory method blanks and MS/MSD analyses), and all laboratory quality control summary forms (including all initial and continuing calibration summary statistics).

1.1.1.6 Technical Evaluation Summary

All data evaluations must be conducted in accordance with applicable USEPA Regional protocols and/or specific client contract requirements. The applicable documents must be referenced during the data evaluation process as this S.O.P. is only intended as a general procedure for the data validation tasks.

General parameters such as Data Completeness, Overall System Performance, Chromatographic Quality, Detection Limits and Compound Identification are evaluated concurrently with the parameters discussed in the following subsections.

1.1.1.6.1 Holding Times

Holding times are evaluated by reviewing the COC reports, the individual sample Form I reports, and the associated laboratory raw data. Holding times are calculated from date of collection to date of analysis.

For unpreserved aqueous samples, generally a 7-day maximum holding time allowance for aromatic compounds, along with a 14-day maximum holding time allowance for chlorinated hydrocarbons is used.

The technical maximum holding time allowance for aqueous samples preserved with hydrochloric acid (HCl) is 14 days.

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No technical holding times have been for solid matrices promulgated; a 14-day maximum holding time allowance is currently being used.

Positive results in affected samples are generally qualified as estimated (J); nondetects (UJ). These results are biased low. Some USEPA Regions apply the bias qualifiers, L and UL, instead. If the holding times are exceeded by a factor of 2 or more, the holding time exceedance is considered to be gross, and positive results are generally qualified as estimated (J); nondetects are generally considered to be unreliable and are qualified (R). Results for which the holding time was grossly exceeded are biased very low.

1.1.1.6.2 Calibration

Check that an initial calibration was performed for each instrument used for analysis and that all calibrations were performed at all appropriate concentration levels within 12 hours of the associated instrument tuning.

Review the data package Form Vs (tuning) using the applicable USEPA Regional Functional Guidelines, and qualify the data as appropriate.

Review initial calibration Form VIs and the associated laboratory raw data. Determine which compounds have average Relative Response Factors (RRFs) <0.050 and which compounds have Percent Relative Standard Deviations (%RSDs) >50 and between 30%-50%. Circle these noncompliances on your working copies of these Forms. Spot-check (i.e., recalculate) a few of the RRFs and %RSDs to verify the laboratory's computation.

Determine which samples are affected by reviewing the continuing calibration Form VIIs. Check the initial calibration date(s) noted in the headings of the Form VIIs to determine which continuing calibrations are associated with which initial calibrations. Next, review the sample listings given on the data package Form Vs. Match the indicated continuing calibration run with the appropriate Form VII by matching the laboratory file ID numbers. Write the affected samples (those listed on the matched Form V) on your working copies of the appropriate Form VI and VII.

Review the continuing calibration Form VIIs and the associated laboratory raw data. Determine which compounds have RRFs <0.050 and which compounds have Percent Differences (%Ds) >50, and between 25%-50%; circle the noncompliances on your working copies of these Forms. Spot-check (i.e., recalculate) a few of the RRFs and %Ds to verify the laboratory's computation.

Generally, affected positive results for compounds for which RRFs are <0.050 are qualified as estimated (J); nondetects are rejected (R). In accordance with some USEPA Regional protocol, the (L) qualifier may be used instead of (J) when qualifying positive results. Bias for these results is very low.

Generally, positive results for compounds for which %RSD exceeds 50% or %D exceeds 25% are qualified as estimated (J); nondetects (UJ). Check the specific applicable data validation protocol for further guidance as there are some protocols which reject nondetects if the %RSD or %D is excessive. Bias for these results cannot be determined.

Generally, positive results for compounds for which %RSD is between 30%-50% are qualified as estimated, (J). Qualification of nondetects is protocol-specific. Follow the rules given in the appropriate validation protocol.

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1.1.1.6.3 Blank Contamination

When using the information given below and in the appropriate USEPA Regional Functional Guidelines, keep in mind that the validation action levels derived are sample specific and must be adjusted for dilution, sample aliquot used for analysis, and sample moisture content (when applicable).

The rules for qualifying data based on the occurrence of blank contamination vary based on regional protocols; The guidelines provided in the appropriate protocol should be followed.

Generally the blank contamination review process is completed by first considering the maximum amount of a particular contaminant occurring in the laboratory method blanks. (Do not consider lab blanks run after high concentration samples for purposes of determining carryover as laboratory method blanks!) Then repeat the process for contaminants occurring in the associated field quality control blanks. Action levels for qualification (10X or 5X depending upon whether or not the contaminant is a common contaminant) are then set. The list of common contaminants may vary among protocols. Additionally, some hierarchy among the field quality control blanks apply, and the manner in which the qualifiers are applied vary [i.e. use of (U) or (B); replacement by CRQL, etc.]. Refer to appropriate protocol for specific guidance.

1.1.1.6.4 Surrogates

Surrogates are evaluated by reviewing the laboratory data package Form II reports and the laboratory raw data. The quality control ranges are given on the laboratory data package Form IIs; circle any noncompliances on your working copies of these Forms.

Results for all compounds in an affected sample are qualified if any one of the surrogate spike compounds fail to meet the quality control criteria provided. Generally, for samples having a surrogate recovery < 10%, positive results are qualified as estimated (J), nondetects are rejected (R). These results are biased low. For samples having a surrogate recovery which is low but > 10%, positive results are generally qualified as estimated (J); nondetects (UJ). The bias qualifiers (L, UL) may be used instead, depending upon the specific USEPA Regional guidance. For samples having a surrogate recovery which is high, positive results are generally qualified as estimated (J, K) based on regional guidance; nondetects are not qualified based on high surrogate recoveries.

1.1.1.6.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

Generally, no data are qualified based upon MS/MSD results alone. If qualification does occur, generally only the result for that particular noncompliant compound is qualified in the original unspiked sample. Refer to the applicable data validation protocol for specific procedures for appropriately evaluating MS/MSD analyses.

1.1.1.6.6 Internal Standards

Internal standards are evaluated by reviewing the data package Form VIIIs and the laboratory raw data. The quality control ranges are given on the Form VIIIs. Circle any noncompliances on your working copies of these forms; evaluate and qualify as stipulated in the appropriate data validation protocol.

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1.1.1.6.7 Tentatively Identified Compounds (TICs)

TICs are evaluated using the laboratory data package Form I VOA-TIC reports and the laboratory raw data. The guidance given in the March 1990 National Functional Guidelines for USEPA Region III is very concise; use the information in this document to evaluate and qualify accordingly.

1.1.1.6.8 Other Considerations

Laboratory precision can be evaluated by comparing the unspiked sample results with MS/MSD analyses results for unspiked compounds. Consider nondetects and results reported at concentrations less than the Contract Required Quantitation Limit (CRQL) to be in agreement. Use professional judgment in determining whether to qualify sample results based on the comparison.

Likewise, compare the positive compound results for field duplicate samples. Generally, the Relative Percent Difference (RPD) between field duplicate results for the aqueous matrix should be <35%; for soil matrix results, <50%. Qualification of the sample data is limited to the specific field duplicate pair. Positive results for compounds showing imprecision are qualified as estimated (J); nondetects (UJ). Bias for these results cannot be determined.

In some USEPA Regions, a "Percent Solids" rule applies. For example, if a sediment sample contains <50% solids in USEPA Region II, all associated data are considered to be estimated and are qualified accordingly. Follow the appropriate protocol guidance when applicable.

1.1.1.6.9 Quantitation

Verify and record the quantitation of at least one compound per analytical fraction. If no positive results are reported, use the MS/MSD data to confirm proper computation by the laboratory. Validator and laboratory quantitations must agree within 10 percent.

1.1.1.7 Deliverables Guidance

In addition to any specific USEPA Regional requirements (e.g. data validation memorandum, data summary spreadsheets, Regional worksheets), all laboratory data package quality control summary forms, sample Form I reports, method blank Form Is, and the Chain-of-Custody report must be given to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct (in accordance with the appropriate USEPA Regional or client requirements) and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

1.1.2 Semivolatiles (USEPA CLP Statement of Work (SOW) 3/90)

1.1.2.1 Applicability

CLP 3/90 semivolatile methodology is applicable to nearly all types of samples, regardless of water content, including groundwater, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. Method 8250 can be used to analyze groundwater samples as well.

The semivolatile TCL includes the following compounds:

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Acenaphthene	1,2-Dichlorobenzene	Indeno(1,2,3-cd)pyrene
Acenaphthylene	1,3-Dichlorobenzene	Isophorone
Anthracene	1,4-Dichlorobenzene	2-Methylnaphthalene
Benzo(a)anthracene	3,3'-Dichlorobenzidine	2-Methylphenol
Benzo(b)fluoranthene	2,4-Dichlorophenol	4-Methylphenol
Benzo(k)fluoranthene	Diethylphthalate	Naphthalene
Benzo(g,h,i)perylene	2,4-Dimethylphenol	2-Nitroaniline
Benzo(a)pyrene	Dimethylphthalate	3-Nitroaniline
4-Bromophenyl-phenylether	Di-n-butylphthalate	4-Nitroaniline
Butylbenzylphthalate	4,6-Dinitro-2-methylphenol	Nitrobenzene
Carbazole	2,4-Dinitrophenol	2-Nitrophenol
4-Chloroaniline	2,4-Dinitrotoluene	4-Nitrophenol
bis(2-Chloroethoxy)methane	2,6-Dinitrotoluene	N-Nitroso-di-n-propylamine
bis(2-Chloroethyl)ether	Di-n-octylphthalate	N-Nitroso-diphenylamine
4-Chloro-3-methylphenol	bis(2-Ethylhexyl)phthalate	Pentachlorophenol
2-Chloronaphthalene	Fluoranthene	Phenanthrene
2-Chlorophenol	Fluorene	Phenol
4-Chlorophenyl-phenylether	Hexachlorobenzene	Pyrene
2,2'-oxybis(1-Chloropropane)	Hexachlorobutadiene	1,2,4-Trichlorobenzene
Chrysene	Hexachlorocyclopentadiene	2,4,5-Trichlorophenol
Dibenzo(a,h)anthracene	Hexachloroethane	2,4,6-Trichlorophenol
Dibenzofuran		

The preceding method is based upon solvent extractions followed by gas chromatographic/mass spectrometric (GC/MS) procedures.

1.1.2.2 Interferences

Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of chromatograms. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. The use of high purity reagents and solvents helps to minimize interference problems; purification of solvents by distillation in all-glass systems may be required.

Interferences co-extracted from the samples will vary considerably from source to source depending upon the diversity of the industrial complex or waste being sampled.

1.1.2.3 General Laboratory Practices

An extraction blank should be prepared with each batch of samples extracted.

Matrix Spike/Matrix Spike Duplicate (MS/MSD) analyses should be conducted to determine the effects of sample matrix upon the compounds of interest.

1.1.2.4 Sample Preparation

Prior to GC/MS analysis, aqueous samples are acidified to pH 2 and extracted with methylene chloride using a continuous liquid-liquid extractor. Both neat and diluted organic liquids may be analyzed by direct injection. Solid samples are extracted with 1:1 methylene chloride/acetone using a sonication procedure. Cleanup by Gel Permeation Chromatography (GPC) is required for solid sample extracts.

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1.1.2.5 Data Overview to Validation

Before commencing validation, the reviewer must preview the associated Chain-of-Custody (COC) reports to determine:

- If the appropriate number of samples are present in the data package and if each sample was correctly analyzed for the parameters and methods specified.
- The identity of all associated field quality control blanks and field duplicate pairs.

Because many samples may have required dilutions, re-extraction and/or reanalyses, the data validator should preview the data package contents to determine which analyses represent the better quality data.

The data package should never be annotated unless specifically directed by client protocol. All Form I reports (including those for samples, laboratory method blanks, and MS/MSD analyses) and all laboratory quality control summary forms (including all initial and continuing calibration summary statistics) should be photocopied for use as working copies.

1.1.2.6 Technical Evaluation Summary

All data evaluations must be conducted in accordance with the appropriate USEPA Regional protocols (when applicable) and/or specified client contract requirements. The applicable documents must be referenced during the data validation process as this S.O.P. is only intended as a general procedure for all data validation tasks.

General parameters such as Data Completeness, Overall System Performance, Chromatographic Quality, Detection Limits and Compound Identification are evaluated concurrently with the parameters discussed in the following subsections.

1.1.2.6.1 Holding Times

Holding times are evaluated by reviewing the COC reports, the individual sample Form I reports, and the associated laboratory raw data. Holding times for extraction are calculated from date of collection to date of extraction.

The technical holding times for aqueous and solid matrices are as follows:

- Extraction: 7 days
- Analysis: 40 days from date of extraction

Affected positive results are generally qualified as estimated (J), nondetects (UJ). Alternately, the L or UL bias qualifiers may be used dependent upon the applicable USEPA Regional Guidance. If the sample was extracted beyond 14 days from collection, the holding time exceedance is considered to be gross and positive results are qualified as estimated (J) or (L); nondetects are rejected (R). Generally, if the holding time until extraction is exceeded, the affected sample results are considered to be biased low. If the holding time until analysis is exceeded (and potentially, some of the extract may have evaporated), the affected sample results may be considered to be biased high. Follow the qualification guidance given in the appropriate data validation protocol.

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1.1.2.6.2 Calibration

Check that an initial calibration was performed for each instrument used for analysis and that all calibrations were performed at all appropriate concentration levels within 12 hours of the associated instrument tuning.

Review the data package Form Vs (tuning) using the applicable USEPA Regional Functional Guidelines, and qualify the data as appropriate.

Review initial calibration Form VIs and the associated laboratory raw data. Determine which compounds have average Relative Response Factors (RRFs) < 0.050 and which compounds have Percent Relative Standard Deviations (%RSDs) > 50 and between 30%-50%. Circle these noncompliances on your working copies of these Forms. Spot-check (i.e., recalculate) a few of the RRFs and %RSDs to verify the laboratory's computation.

Determine which samples are affected by reviewing the continuing calibration Form VIIs. Check the initial calibration date(s) noted in the headings of the Form VIIs to determine which continuing calibrations are associated with which initial calibrations. Next, review the sample listings given on the data package Form Vs. Match the indicated continuing calibration run with the appropriate Form VII by matching the laboratory file ID numbers. Write the affected samples (those listed on the matched Form V) on your working copies of the appropriate Form VI and VII.

Review the continuing calibration Form VIIs and the associated laboratory raw data. Determine which compounds have RRFs < 0.050 and which compounds have Percent Differences (%Ds) > 50 , and between 25%-50%; circle the noncompliances on your working copies of these Forms. Spot-check (i.e., recalculate) a few of the RRFs and %Ds to verify the laboratory's computation.

Generally, affected positive results for compounds for which RRFs are < 0.050 are qualified as estimated (J); nondetects are rejected (R). In accordance with some USEPA Regional protocol, the (L) qualifier may be used instead of (J) when qualifying positive results. Bias for these results is low.

Generally, positive results for compounds for which %RSD or %D exceeds 50% are qualified as estimated (J); nondetects (UJ). Check the specific applicable data validation protocol for further guidance as there are some protocol which reject nondetects if the %RSD or %D is excessive. Bias for these results cannot be determined.

Generally, positive results for compounds for which %RSD is between 30%-50% or %D is between 25%-50% are qualified as estimated (J). Qualification of nondetects is protocol-specific. Follow the rules given in the appropriate validation protocol.

1.1.2.6.3 Blank Contamination

Note that unlike VOA fraction analyses, a laboratory method blank does not have to be analyzed after every continuing calibration standard. Be very sure, however, that one semivolatle method blank was extracted for each day that associated samples were extracted (with a maximum of 20 samples per batch).

The action levels for qualification are 10X the maximum amount of phthalates found in the blanks (phthalates are common contaminants) and 5X the maximum amount of other contaminants found in the blanks. The actual action level applied is sample-specific and must be adjusted for dilution, sample aliquot used for analysis, and moisture content. The type and manner in which the qualifiers are applied

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vary with protocol [i.e., use of (U) or (B); replacement by CRQL, etc.]. Refer to appropriate data validation protocol for specific guidance.

1.1.2.6.4 Surrogates

Surrogates are evaluated by reviewing the laboratory data package Form II reports and the associated laboratory raw data. The quality control ranges are given on the laboratory data package Form IIs; circle any noncompliances on your working copies of these Forms.

Semivolatile compounds are divided into two classes, base-neutral compounds and acid-extractable compounds. Each class of compounds has its own associated surrogates. If the recovery is <10% for any one surrogate, positive results for all compounds in that class in the affected sample are qualified as estimated, (J) or (L), and nondetects are rejected, (R). These results are biased low.

No qualification actions are taken for samples having any one surrogate recovery which is noncompliant but > 10%.

If the recoveries for any two surrogates of the same class are noncompliant but above 10%, all sample results for that class of compounds in the affected sample are qualified. If the recoveries are low, positive results are generally qualified as estimated (J); nondetects (UJ). In some Regions, the bias qualifiers, L and UL, may be used instead. If the recoveries for any two surrogates of the same class are high, positive results for all compounds in that class in the affected sample are qualified, J or K, depending upon the appropriate USEPA Regional guidance; nondetects are not qualified based on high surrogate recoveries.

1.1.2.6.5 Matrix Spike/Matrix Spike Duplicates

Generally, no data are qualified based upon MS/MSD results alone. If qualification does occur, generally only the result for that particular noncompliant compound is qualified in the original unspiked sample. Refer to the appropriate validation guidelines for specific procedures for evaluating MS/MSD analyses.

1.1.2.6.6 Internal Standards

Internal standards are evaluated by reviewing the data package Form VIIIs and the laboratory raw data. The quality control ranges are given on the Form VIIIs. Circle any noncompliances on your working copies of these forms; evaluate and qualify as stipulated in the appropriate protocol.

1.1.2.6.7 Tentatively Identified Compounds (TICs)

TICs are evaluated using the laboratory data package Form I BNA-TIC reports, and the laboratory raw data. The guidance given in the 3/90 National Functional Guidelines for USEPA Region III is very concise; evaluate and qualify accordingly.

1.1.2.6.8 Other Considerations

Laboratory precision can be evaluated by comparing MS/MSD sample results for unspiked compounds with the unspiked sample results. Consider nondetects and results reported at concentration levels less than the Contract Required Quantitation Limit (CRQL) to be in agreement. Use professional judgment in determining whether to qualify sample results based on the comparison.

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Likewise, compare the positive compound results for field duplicate samples. Generally the Relative Percent Difference (RPD) between field duplicate results for the aqueous matrix should be less than 35%; for soil matrix results, less than 50%. Qualification of sample data is limited to that specific field duplicate pair. Positive results for compounds showing imprecision are qualified as estimated (J); and nondetects (UJ). Bias for these results cannot be determined.

In some USEPA regions a "Percent Solids" rule applies. For example, if a sediment contains less than 50% solids in USEPA Region II, all associated data are considered to be estimated and are qualified accordingly. Follow the appropriate protocol guidance when applicable.

1.1.2.6.9 Quantitation

Verify and record quantitation of at least one compound per analytical fraction. If no positive results are reported, use the MS/MSD data to confirm proper computation by the laboratory. Validator and laboratory quantitations must agree within 10 percent.

1.1.2.7 Deliverables Guidance

In addition to any specific USEPA Regional requirements (e.g., data validation memorandum, data summary spreadsheets, USEPA Regional worksheets), all laboratory data package quality control summary forms, sample Form I reports, method blank Form Is, and the Chain-of-Custody report must be given to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct (in accordance with the appropriate USEPA Regional or client requirements) and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

1.2 CLP Organics by GC

1.2.1 **Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs) (USEPA CLP Statement of Work (SOW) 3/90)**

1.2.1.1 Applicability

CLP 3/90 methodology is used to determine the concentration of certain organochlorine pesticides and polychlorinated biphenyls (PCBs) in groundwater, liquid, and solid sample matrices. Specifically, the CLP 3/90 TCL includes the following substances:

Aldrin	Dieldrin	Methoxychlor
alpha-BHC	Endosulfan I	Toxaphene
beta-BHC	Endosulfan II	Aroclor-1016
delta-BHC	Endosulfan sulfate	Aroclor-1221
gamma-BHC (Lindane)	Endrin	Aroclor-1232
Chlordane	Endrin aldehyde	Aroclor-1242
4,4'-DDD	Endrin ketone	Aroclor-1248
4,4'-DDE	Heptachlor	Aroclor-1254
4,4'-DDT	Heptachlor epoxide	Aroclor-1260

CLP 3/90 methodology for organochlorine pesticides and PCBs is a Gas Chromatographic (GC) procedure in which samples are first extracted and then analyzed by direct injection. The compounds

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of interest are analyzed via GC/ECD (Electron Capture Detector; an equivalent Halogen-Specific Detector may also be used).

1.2.1.2 Interferences

The sensitivity of these methods usually depends on the level of interferences rather than on instrumental limitations. Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. The use of high purity reagents and solvents helps to minimize these interference problems. Extraction blanks are analyzed as method blanks in order to monitor the occurrences of interferences.

Interferences co-extracted from the sample will vary considerably and will dictate the nature and extent of clean-up procedures used. Phthalate esters are a common interference to organochlorine pesticide analyses; phenols and organic acids may act as interferents when analyzing for chlorinated herbicides.

1.2.1.3 General Laboratory Practices

An extraction blank should be prepared with each batch of samples extracted.

Matrix Spike/Matrix Spike Duplicate (MS/MSD) analyses should be conducted to determine the effects of sample matrix upon the compounds of interest.

Standard quality assurance practices such as the analyses of field replicates should also be employed.

1.2.1.4 Sample Preparation

Prior to GC analysis, aqueous samples are extracted at a neutral pH with methylene chloride as a solvent using a separatory funnel or a continuous liquid-liquid extractor. Solid samples are extracted with hexane:acetone (1:1) using sonication procedures.

1.2.1.5 Data Overview Prior to Validation

Before commencing validation, the reviewer must preview the associated Chain-of-Custody (COC) reports to determine:

- If the appropriate number of samples are present in the data package and if each sample was correctly analyzed for the parameters and methods specified.
- The identity of all associated field quality control blanks and field duplicate pairs.

Because many samples may have required dilutions, re-extractions and/or re-analyses, the validator should preview the data package contents to determine which analyses represent the better quality data.

Unless specifically directed by client protocol, never annotate the laboratory data package. Before beginning evaluation, prepare working copies (i.e., photocopies) of all Form I reports (including those for samples, laboratory method blanks and MS/MSD analyses) and all laboratory quality control summary forms.

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1.2.1.6 Technical Evaluation Summary

All data evaluations must be conducted in accordance with applicable USEPA Regional protocols (when applicable) and/or specific client contract requirements. The applicable documents must be referenced during the data evaluation process as this S.O.P. is only intended as a general procedure for the data validation tasks.

General parameters such as Data Completeness, Overall System Performance, Chromatographic Quality, Detection Limits, and Compound Identification are evaluated concurrently with the parameters discussed in the following subsections.

1.2.1.6.1 Holding Times

Holding times are evaluated by reviewing the COC reports, the individual sample Form I reports, and the associated laboratory raw data. Holding times are calculated from date of collection to date of extraction/analysis.

All samples to be analyzed for pesticides, PCBs and/or herbicides must be extracted within 7 days of collection regardless of matrix and analyzed within 40 days of extraction.

When the holding time criteria are not met, positive results in affected samples are generally qualified as estimated (J); nondetects (UJ). These results are biased low. Some USEPA Regions apply the bias qualifiers, L and UL, instead. If the holding times are exceeded by a factor of 2 or more, the holding time exceedance is considered to be gross, and positive results are generally qualified as estimated (J); nondetects are generally considered to be unreliable and are rejected (R). These results are biased low.

1.2.1.6.2 Calibration

Data pertaining to the initial calibration (i.e., evaluation check for linearity) is found on the data package Form VIs. Check that the initial calibration was performed for each instrument used and at all appropriate concentration levels.

Generally, positive results for compounds whose Percent Relative Standard Deviation (%RSD) exceeds 20% are qualified as estimated (J). Check the pesticide analytical sequence (Form VIII) to determine which samples are affected. Check the specific applicable data validation protocol for further guidance as there are some protocol which reject nondetects if the %RSD or %D is excessive. Bias for these results cannot be determined. Follow the rules given in the appropriate data validation protocol.

Verify that a resolution check mixture, Performance Evaluation Mixture (PEM), Individual Standard Mixtures A and B, and multicomponent target compounds were analyzed at the proper frequency (see Form VIII) on each GC analytical column. Retention times for PEM target compounds and Individual Standard Mixtures A and B target compounds should be within the established retention time windows. If a compound is outside of the retention time window, further evaluation of the sample chromatograms is necessary. In addition, check that the Relative Percent Difference (RPD) (recorded on Forms VII-D and VII-E) between the calculated amount and true amount for each pesticide is $\leq 25\%$. If this criterion is not met, positive results and nondetects for the affected compounds are qualified as estimated, (J) and (UJ), respectively.

The DDT/Endrin Breakdown for each PEM should not exceed 20% (recorded on Form VII-D). Generally, if % breakdown for DDT exceeds 20%, estimate (J) all positive results for DDT, DDE and DDD following the last in-control standard until the next acceptable PEM (see analytical sequence); acceptability of the

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next individual A/B mix may also be considered when qualifying data for DDT breakdown. If there are no positive results for DDT but there are positive results for DDD or DDE then reject (R) nondetects for DDT in associated samples. Generally, if Endrin % Breakdown exceeds 20%, estimate (J) positive results for Endrin, Endrin Aldehyde, and Endrin Ketone in all samples following the last in-control standard until the next acceptable PEM; acceptability of the next individual A/B mix may also be considered when qualifying data for Endrin breakdown. If there are positive results for Endrin Aldehyde or Endrin Ketone but none for Endrin, reject (R) nondetect Endrin results.

1.2.1.6.3 Blank Contamination

When using the information provided below and in the appropriate data validation guidelines, keep in mind that the validation action levels derived are sample-specific and must be adjusted for dilution, sample aliquot used for analysis, and sample moisture content (when applicable).

The rules for qualifying data based on the occurrence of blank contamination vary based on regional protocols; Guidelines provided in the appropriate data validation protocol should be followed.

An action level of 5X the maximum amount of contaminant found is used to evaluate the sample data. The manner in which the qualifiers are applied vary [i.e. use of (U) or (B); replacement by CRQL, etc.]. Refer to appropriate validation protocol for specific guidance.

1.2.1.6.4 Surrogates

Surrogates are evaluated by reviewing the laboratory data package Form II reports and the associated laboratory raw data. The advisory limits are given on the laboratory data package Form IIs; circle any recoveries outside these limits on your working copies of these Forms.

No qualifications are made for surrogates which show zero recoveries because they were "diluted out." Generally, positive results affected by low surrogate recovery are qualified as estimated (J), or the (L) bias qualifier is used when applicable; nondetects are qualified (UJ) or (UL), accordingly. If a positive sample result is affected by high surrogate recovery, the result is qualified as estimated (J) or the (K) bias qualifier is used when applicable; nondetects are not qualified based on high surrogate recovery. Because the surrogate recovery limits for this fraction are advisory, generally no results are rejected.

The decachlorobiphenyl (DCB) and tetrachloro-m-xylene (TCX) retention times found on data package Form VIII must be ± 0.10 for DCB and ± 0.05 for TCX. If DCB and TCX retention time criteria are not met, the raw data must be checked for misidentified GC peaks. The validator's professional judgment for qualifications should be used.

1.2.1.6.5 Matrix Spike/Matrix Spike Duplicates

Generally, no data are qualified based upon MS/MSD results alone. If qualification does occur, generally only the result for that particular noncompliant compound is qualified in the original unspiked sample. Refer to the appropriate data validation guidelines for the specific procedures for evaluating MS/MSD analyses.

1.2.1.6.6 Other Considerations

Laboratory precision can be evaluated by comparing the unspiked sample results with MS/MSD analyses results for unspiked compounds. Consider nondetect results and results reported at concentrations less

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than the Contract Required Quantitation Limit (CRQL) to be in agreement. Use professional judgment in determining whether to qualify sample results based on the comparison.

Likewise, compare the positive compound results for field duplicate samples. Generally, the Relative Percent Difference (RPD) between field duplicate results for the aqueous matrix should be <35%; for soil matrix results, <50%. Qualification of the sample data is limited to the specific field duplicate pair. Positive results for compounds showing imprecision are qualified as estimated (J); nondetects (UJ). Bias for these results cannot be determined.

In some USEPA Regions, a "Percent Solids" rule applies. For example, if a sediment sample contains <50% solids in USEPA Region II, all associated data are considered to be estimated, and are qualified accordingly. Follow the appropriate protocol guidance when applicable.

1.2.1.6.7 Quantitation

Verify and record the quantitation of at least one compound per analytical fraction. If no positive results are reported, use the MS/MSD data to confirm proper computation by the laboratory. Validator and laboratory quantitations must agree within 10%.

1.2.1.7 Deliverables Guidance

In addition to any specific USEPA Regional requirements (e.g., data validation memorandum, data summary spreadsheets, USEPA Regional worksheets), all laboratory data package quality control summary forms, sample Form I reports, method blank Form Is, and the Chain-of-Custody report must be given to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct (in accordance with the appropriate USEPA Regional or client requirements) and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

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2.0 NON-CLP ORGANICS FOR SOLID MATRICES

2.1 SW-846 Organics by GC/MS

2.1.1 Volatiles (Method 8240B, 8260A)

2.1.1.1 Applicability

Method 8240 is used to determine volatile organic compounds in most waste matrices including groundwater, sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

Method 8240 analyte list includes of the volatile CLP 3/90 Target Compound List (TCL) (Section 1.1.1) plus the following compounds* :

Acetonitrile	trans-1,2-Dichloroethene
Acrolein	Ethyl methacrylate
Acrylonitrile	Iodomethane
Allyl chloride	Methacrylonitrile
Chloropropene	Methyl methacrylate
1,2-Dibromo-3-chloropropane	2-Picoline
1,2-Dibromoethane	Pyridine
Dibromomethane	Trichlorofluoromethane
trans-1,4-Dichloro-2-butene	1,2,3-Trichloropropane
Dichlorodifluoromethane	Vinyl acetate

* Appendix IX target compounds

Method 8240 is based upon a purge-and-trap, gas chromatographic/mass spectrometric (GC/MS) procedure. Prior to analysis, samples must be prepared by Method 5030.

2.1.1.2 Interferences

Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. Associated field quality control blanks are analyzed in order to monitor this.

Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe or purging device is rinsed out between samples with reagent water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination.

If sample or matrix interferences are encountered, a secondary or alternate analytical column may be used to resolve the compounds of interest.

2.1.1.3 General Laboratory Practices

A method blank consisting of organic free water spiked with surrogates and internal standards should be analyzed immediately following each daily calibration and also after the analysis of every high concentration sample.

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Matrix Spike/Matrix Spike Duplicate (MS/MSD) analyses should be conducted to determine the effects of sample matrix upon the compounds of interest.

2.1.1.4 Sample Preparation

Method 5030 is a purge-and-trap procedure performed to prepare and extract volatile compounds from samples and introduce those compounds into the GC/MS.

For highly volatile matrices, direct injection preceded by dilution should be used to prevent gross contamination of the instrumentation. For pastes, dilution of the sample until it becomes free-flowing is used to ensure adequate interfacial area. The success of this method depends on the level of interferences in the sample; results may vary due to the large variability and complicated matrices of solid waste samples.

2.1.1.5 Data Overview Prior to Validation

Before commencing validation, the reviewer must preview the associated Chain-of-Custody (COC) reports to determine:

- If the appropriate number of samples are present in the data package and if each sample was correctly analyzed for the parameters and methods specified.
- The identity of all associated field quality control blanks and field duplicate pairs.

Because many samples may have required dilutions, re-extractions and/or re-analyses, the validator should preview the data package contents to determine which analyses represent the better quality data.

Unless specifically directed by client protocol, never annotate the laboratory data package. Before beginning evaluation, prepare working copies (i.e., photocopies) of all Form I reports (including those for samples, laboratory method blanks and MS/MSD analyses) and all laboratory quality control summary forms (including all initial and continuing calibration summary statistics).

2.1.1.6 Technical Evaluation Summary

All data evaluations must be conducted in accordance with applicable USEPA Regional protocols and/or specific client contract requirements. The applicable documents must be referenced during the data evaluation process as this S.O.P. is only intended as a general procedure for the data validation tasks.

General parameters such as Data Completeness, Overall System Performance, Chromatographic Quality, Detection Limits and Compound Identification are evaluated concurrently with the parameters discussed in the following subsections.

2.1.1.6.1 Holding Times

Holding times are evaluated by reviewing the COC reports, the individual sample Form I reports, and the associated laboratory raw data. Holding times are calculated from date of collection to date of analysis.

The technical maximum holding time allowance for aqueous samples preserved with hydrochloric acid (HCL) is 14 days.

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No technical holding times for solid matrices have been promulgated: a 14-day maximum holding time allowance is currently being used.

For unpreserved aqueous samples, generally a 7-day maximum holding time allowance for aromatic compounds, along with a 14-day maximum holding time allowance for chlorinated hydrocarbons is used.

Positive results in affected samples are generally qualified as estimated (J); nondetects (UJ). These results are biased low. Some USEPA Regions apply the bias qualifiers, L and UL, instead. If the holding times are exceeded by a factor of 2 or more, the holding time exceedance is considered to be gross and positive results are generally qualified as estimated (J); nondetects are generally considered to be unreliable and are qualified (R). Results for which the holding time was grossly exceeded are biased low.

2.1.1.6.2 Calibration

Check that an initial calibration was performed for each instrument used for analysis and that all calibrations were performed at all appropriate concentration levels within 12 hours of the associated instrument tuning.

Review the data package Form Vs (tuning) using the applicable USEPA Regional Functional Guidelines, and qualify the data as appropriate.

Review initial calibration Form VIs and the associated laboratory raw data. Determine which compounds have average Relative Response Factors (RRFs) <0.050 and which compounds have Percent Relative Standard Deviations (%RSDs) >50% and between 30% and 50%. Circle these noncompliances on your working copies of these Forms. Spot-check (i.e., recalculate) a few of the RRFs and %RSDs to verify the laboratory's computation.

Determine which samples are affected by reviewing the continuing calibration Form VIIs. Check the initial calibration date(s) noted in the headings of the Form VIIs to determine which continuing calibrations are associated with which initial calibrations. Next, review the sample listings given on the data package Form Vs. Match the indicated continuing calibration run with the appropriate Form VII by matching the laboratory file ID numbers. Write the affected samples (those listed on the matched Form V) on your working copies of the appropriate Form VI and VII. Spot-check (i.e., recalculate) a few of the RRFs and %Ds to verify the laboratory's computation.

Review the continuing calibration Form VIIs and the associated laboratory raw data. Determine which compounds have RRFs <0.050 and which compounds have Percent Differences (%Ds) >25%; circle the noncompliances on your working copies of these Forms.

Generally, affected positive results for compounds whose RRFs are <0.050 are qualified as estimated (J); nondetects are rejected (R). In accordance with some USEPA Regional protocol, the (L) qualifier may be used instead of (J), when qualifying positive results. Bias for these results is low.

Generally, positive results for compounds for which %RSD exceeds 50% or %D exceeds 25% are qualified as estimated (J); nondetects (UJ). Check the specific applicable data validation protocol for further guidance as there are some protocol which reject nondetects if the %RSD or %D is excessive. Bias for these results cannot be determined.

Generally, positive results for compounds for which %RSD is between 30%-50% are qualified as estimated (J). Qualification of nondetects is protocol-specific. Follow the rules given in the appropriate validation protocol.

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2.1.1.6.3 Blank Contamination

When using the information given below and in the appropriate USEPA Regional Functional Guidelines, keep in mind that the validation action levels derived are sample-specific and must be adjusted for dilution, sample aliquot used for analysis, and sample moisture content (when applicable).

The rules for qualifying data based on the occurrence of blank contamination vary based on regional protocols. The guidelines provided in the appropriate protocol should be followed.

Generally the blank contamination review process is completed by first considering the maximum amount of a particular contaminant occurring in the laboratory method blanks. (Do not consider lab blanks run after high concentration samples for purposes of determining carryover as laboratory method blanks!) Then repeat the process for contaminants occurring in the associated field quality control blanks. Action levels for qualification (10X or 5X depending upon whether or not the contaminant is a common contaminant) are then set. The list of common contaminants may vary among protocols. Additionally, some hierarchy among the field quality control blanks apply, and the manner in which the qualifiers are applied vary [i.e. use of (U) or (B); replacement by CRQL, etc.]. Refer to appropriate protocol for specific guidance.

2.1.1.6.4 Surrogates

Surrogates are evaluated by reviewing the laboratory data package Form II reports and the laboratory raw data. The quality control ranges are given on the laboratory data package Form IIs; circle any noncompliances on your working copies of these Forms.

Results for all compounds in an affected sample are qualified if any one of the surrogate spike compounds fail to meet the quality control criteria provided. Generally, for samples having a surrogate recovery < 10%, positive results are qualified as estimated (J), nondetects are rejected (R). These results are biased low. For samples having a surrogate recovery which is low but > 10%, positive results are generally qualified as estimated (J); nondetects (UJ). The bias qualifiers (L, UL) may be used instead, depending upon the specific USEPA Regional guidance. For samples having a surrogate recovery which is high, positive results are generally qualified as estimated (J, K) based on regional guidance, nondetects are not qualified based on high surrogate recovery.

2.1.1.6.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

Generally, no data are qualified based upon MS/MSD results alone. If qualification does occur, generally only the result for that particular noncompliant compound is qualified in the original unspiked sample. Refer to the applicable data validation protocol for specific procedures for appropriately evaluating MS/MSD analyses.

2.1.1.6.6 Internal Standards

Internal standards are evaluated by reviewing the data package Form VIIIs and the laboratory raw data. The quality control ranges are given on the Form VIIIs. Circle any noncompliances on your working copies of these forms; evaluate and qualify as stipulated in the appropriate data validation protocol.

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2.1.1.6.7 Tentatively Identified Compounds (TICs)

TICs are evaluated using the laboratory data package Form I VOA-TIC reports and the laboratory raw data. The guidance given in the March 1990 National Functional Guidelines for USEPA Region III is very concise; use the information in this document to evaluate and qualify accordingly.

2.1.1.6.8 Other Considerations

Laboratory precision can be evaluated by comparing the unspiked sample results with MS/MSD analyses results for unspiked compounds. Consider nondetects and results reported at concentrations less than the Contract Required Quantitation Limit (CRQL) to be in agreement. Use professional judgment in determining whether to qualify sample results based on the comparison.

Likewise, compare the positive compound results for field duplicate samples. Generally, the Relative Percent Difference (RPD) between field duplicate results for the aqueous matrix should be <35%; for soil matrix results, <50%. Qualification of the sample data is limited to the specific field duplicate pair. Positive results for compounds showing imprecision are qualified as estimated (J); nondetects (UJ). Bias for these results cannot be determined.

In some USEPA Regions, a "Percent Solids" rule applies. For example, if a sediment sample contains <50% solids in USEPA Region II, all associated data are considered to be estimated and are qualified accordingly. Follow the appropriate protocol guidance when applicable.

2.1.1.6.9 Quantitation

Verify and record the quantitation of at least one compound per analytical fraction. If no positive results are reported, use the MS/MSD data to confirm proper computation by the laboratory. Validator and laboratory quantitations must agree within 10 percent.

2.1.1.7 Deliverables Guidance

In addition to any specific USEPA Regional requirements (e.g. data validation memorandum, data summary spreadsheets, Regional worksheets), all laboratory data package quality control summary forms, sample Form I reports, method blank Form Is, and the Chain-of-Custody report must be given to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct (in accordance with the appropriate USEPA Regional or client requirements) and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

2.1.2 Semivolatiles (Method SW8250A, 8270B)

2.1.2.1 Applicability

Methods 8250 and 8270 are applicable to most types of samples, regardless of water content, including groundwater, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. Method 8250 can be used to analyze groundwater samples as well.

These methods can be used to quantify most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of elution without derivatization as sharp peaks from a gas

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chromatographic column. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols.

The above methods specifically analyze for the semivolatile CLP 3/90 Target Compound List (TCL) (Section 1.1.2) plus the following compounds*:

Acetophenone	Hexachlorophene	N-nitrosodimethylethylamine
Aniline	Hexachloropropene	N-nitroso-di-n-butylamine
Benzyl alcohol	Isodrin	N-nitrosomorpholine
Bis(2-chloroisopropyl)ether	Isosafrole	N-nitrosopiperidine
Chlorobenzilate	Kepone	Pentachlorobenzene
Diallate	Methapyrilene	Pentachloronitrobenzene
2,6-Dichlorophenol	3-Methylcholanthrene	Phenacetin
Dimethoate	Methyl methanesulfonate	p-Phenylenediamine
p-Dimethylaminoazobenzene	3-Methylphenol	Phorate
7,12-Dimethylbenz(a)anthracene	1,4-Naphthoquinone	2-Picoline
3,3'-Dimethylbenzidine	4-Nitroquinoline-1-oxide	Pronamide
a,a-Dimethylphenylamine	1-Naphthylamine	Safrole
1,3-Dinitrobenzene	2-Naphthylamine	1,2,4,5-Tetrachlorobenzene
Diphenylamine	5-Nitro-o-toluidine	Thionazin
Ethyl methanesulfonate	N-nitrosodiethylamine	o,o,o-Triethylphosphorothioate
Famphur	N-nitrosodimethylamine	1,3,5-Trinitrobenzene

* Appendix IX target compounds

The preceding methods are based upon solvent extractions followed by gas chromatographic/mass spectrometric (GC/MS) procedures, Method 8250 being a GC/MS method using the packed column technique, and Method 8270 using GC/MS capillary column technique.

2.1.2.2 Interferences

Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of chromatograms. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. The use of high purity reagents and solvents helps to minimize interference problems; purification of solvents by distillation in all-glass systems may be required.

Interferences co-extracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or waste being sampled.

2.1.2.3 General Laboratory Practices

An extraction blank should be prepared with each batch of samples extracted.

Matrix Spike/Matrix Spike Duplicate (MS/MSD) analyses should be conducted to determine the effects of sample matrix upon the compounds of interest.

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2.1.2.4 Sample Preparation

Prior to analysis, the samples must be extracted using the appropriate techniques. Aqueous samples are extracted at the appropriate pH with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Both neat and diluted organic liquids may be analyzed by direct injection. Solid samples are extracted at the appropriate pH with methylene chloride using either Soxhlet Extraction (Method 3540) or sonication (Method 3550) procedures.

2.1.2.5 Data Overview to Validation

Before commencing validation, the reviewer must preview the associated Chain-of-Custody (COC) reports to determine:

- If the appropriate number of samples are present in the data package and if each sample was correctly analyzed for the parameters and methods specified.
- The identity of all associated field quality control blanks and field duplicate pairs.

Because many samples may have required dilutions, re-extraction and/or reanalyses, the data validator should preview the data package contents to determine which analyses represent the better quality data.

The data package should never be annotated unless specifically directed by client protocol. All Form I reports (including those for samples, laboratory method blanks, and MS/MSD analyses) and all laboratory quality control summary forms (including all initial and continuing calibration summary statistics) should be photocopied for use as working copies.

2.1.2.6 Technical Evaluation Summary

All data evaluations must be conducted in accordance with the appropriate USEPA Regional protocols and/or specified client contract requirements. The applicable documents must be referenced during the data validation process as this S.O.P. is only intended as a general procedure for all data validation tasks.

General parameters such as Data Completeness, Overall System Performance, Chromatographic Quality, Detection Limits and Compound Identification are evaluated concurrently with the parameters discussed in the following subsections.

2.1.2.6.1 Holding Times

Holding times are evaluated by reviewing the COC reports, the individual sample Form I reports, and the associated laboratory raw data. Holding times for extraction are calculated from date of collection to date of extraction.

The technical holding times for aqueous and solid matrices are as follows:

- **Extraction:**
 - Water samples: 7 days
 - Solid samples: 14 days
- **Analysis:** 40 days from date of extraction

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Affected positive results are generally qualified as estimated (J), nondetects (UJ). Alternately, the L or UL bias qualifiers may be used dependent upon the applicable USEPA Regional Guidance. If the sample was extracted beyond 14 days from collection (28 days for solid samples), the holding time exceedance is considered to be gross and positive results are qualified as estimated (J) or (L); nondetects are rejected (R). Generally, if the holding time until extraction is exceeded, the affected sample results are considered to be biased low. If the holding time until analysis has been exceeded (and potentially, some of the extract may have evaporated), the affected sample results may be considered to be biased high. Follow the qualification guidance given in the appropriate data validation protocol.

2.1.2.6.2 Calibration

Check that an initial calibration was performed for each instrument used for analysis and that all calibrations were performed at all appropriate concentration levels within 12 hours of the associated instrument tuning.

Review the data package Form Vs (tuning) using the applicable USEPA Regional Functional Guidelines, and qualify the data as appropriate.

Review initial calibration Form VIs and the associated laboratory raw data. Determine which compounds have average Relative Response Factors (RRFs) < 0.050 and which compounds have Percent Relative Standard Deviations (%RSDs) $> 50\%$ and between 30% and 50% . Circle these noncompliances on your working copies of these Forms. Spot-check (i.e., recalculate) a few of the RRFs and %RSDs to verify the laboratory's computation.

Determine which samples are affected by reviewing the continuing calibration Form VIIs. Check the initial calibration date(s) noted in the headings of the Form VIIs to determine which continuing calibrations are associated with which initial calibrations. Next, review the sample listings given on the data package Form Vs. Match the indicated continuing calibration run with the appropriate Form VII by matching the laboratory file ID numbers. Write the affected samples (those listed on the matched Form V) on your working copies of the appropriate Form VI and VII. Spot-check (i.e., recalculate) a few of the RRFs and %Ds to verify the laboratory's computation.

Review the continuing calibration Form VIIs, and the associated laboratory raw data. Determine which compounds have RRFs < 0.050 and which compounds have Percent Differences (%Ds) $> 30\%$; circle the noncompliances on your working copies of these Forms.

Generally, affected positive results for compounds for which RRFs are < 0.050 are qualified as estimated (J); nondetects are rejected (R). In accordance with some USEPA Regional protocol, the (L) qualifier may be used instead of (J) when qualifying positive results. Bias for these results is low.

Generally, positive results for compounds for which %RSD exceeds 50% or %D exceeds 30% , are qualified as estimated (J); nondetects (UJ). Check the specific applicable data validation protocol for further guidance as there are some protocol which reject nondetects if the %RSD or %D is excessive. Bias for these results cannot be determined.

Generally, positive results for compounds for which %RSD is between 30% - 50% are qualified as estimated (J). Qualification of nondetects is protocol-specific. Follow the rules given in the appropriate validation protocol.

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2.1.2.6.3 Blank Contamination

Note that unlike VOA fraction analyses, a laboratory method blank does not have to be analyzed after every continuing calibration standard. Be very sure, however, that one semivolatile method blank was extracted for each day that associated samples were extracted (with a maximum of 20 samples per batch).

The action levels for qualification are 10X the maximum amount of phthalates found in the blanks (phthalates are common contaminants) and 5X the maximum amount of other contaminants found in the blanks. The actual action level applied is sample-specific and must be adjusted for dilution, sample aliquot used for analysis, and moisture content. The type and manner in which the qualifiers are applied vary with protocol [i.e., use of (U) or (B); replacement by CRQL, etc.]. Refer to appropriate data validation protocol for specific guidance.

2.1.2.6.4 Surrogates

- Surrogates are evaluated by reviewing the laboratory data package Form II reports and the associated laboratory raw data. The quality control ranges are given on the laboratory data package Form IIs; circle any noncompliances on your working copies of these Forms.

Semivolatile compounds are divided into two classes, base-neutral compounds and acid-extractable compounds. Each class of compounds has its own associated surrogates. If the recovery is <10% for any one surrogate, positive results for all compounds in that class in the affected sample are qualified as estimated, (J) or (L), and nondetects are rejected, (R). These results are biased low.

No qualification actions are taken for samples having any one surrogate recovery which is noncompliant but >10%.

If the recoveries for any two surrogates of the same class are noncompliant but above 10%, all sample results for that class of compounds in the affected sample are qualified. If the recoveries are low, positive results are generally qualified as estimated (J); nondetects (JJ). In some Regions, the bias qualifiers, L and UL, may be used instead. If the recoveries for any two surrogates of the same class are high, positive results for all compounds in that class in the affected sample are qualified, J or K, depending upon the appropriate USEPA Regional guidance; nondetects are not qualified based on high surrogate recoveries.

2.1.2.6.5 Matrix Spike/Matrix Spike Duplicates

Generally, no data are qualified based upon MS/MSD results alone. If qualification does occur, generally only the result for that particular noncompliant compound is qualified in the original unspiked sample analysis. Refer to the appropriate validation guidelines for specific procedures for evaluating MS/MSD analyses.

2.1.2.6.6 Internal Standards

Internal standards are evaluated by reviewing the data package Form VIIIs and the laboratory raw data. The quality control ranges are given on the Form VIIIs. Circle any noncompliances on your working copies of these forms; evaluate and qualify as stipulated in the appropriate protocol.

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2.1.2.6.7 Tentatively Identified Compounds (TICs)

TICs are evaluated using the laboratory data package Form I BNA-TIC reports and the laboratory raw data. The guidance given in the 3/90 National Functional Guidelines for USEPA Region III is very concise; evaluate and qualify accordingly.

2.1.2.6.8 Other Considerations

Laboratory precision can be evaluated by comparing MS/MSD sample results for unspiked compounds with the unspiked sample results. Consider nondetects and results reported at concentration levels less than the Contract Required Quantitation Limit (CRQL) to be in agreement. Use professional judgment in determining whether to qualify sample results based on the comparison.

Likewise, compare the positive compound results for field duplicate samples. Generally the Relative Percent Difference (RPD) between field duplicate results for the aqueous matrix should be less than 35%; for soil matrix results, less than 50%. Qualification of sample data is limited to that specific field duplicate pair. Positive results for compounds showing imprecision are qualified as estimated (J); and nondetects (UJ). Bias for these results cannot be determined.

In some USEPA regions a "Percent Solids" rule applies. For example, if a sediment contains less than 50% solids in USEPA Region II, all associated data are considered to be estimated and are qualified accordingly. Follow the appropriate protocol guidance when applicable.

2.1.2.6.9 Quantitation

Verify and record quantitation of at least one compound per analytical fraction. If no positive results are reported, use the MS/MSD data to confirm proper computation by the laboratory. Validator and laboratory quantitations must agree within 10 percent.

2.1.2.7 Deliverables Guidance

In addition to any specific USEPA Regional requirements (e.g., data validation memorandum, data summary spreadsheets, USEPA Regional worksheets), all laboratory data package quality control summary forms, sample Form I reports, method blank Form Is, and the Chain-of-Custody report, must be given to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct (in accordance with the appropriate USEPA Regional or client requirements) and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

2.2 SW846 Non-CLP Organics by Gas Chromatography

2.2.1 Volatiles (SW 5030/SW 8010B, 8015A, 8020A, 8030A)

2.2.1.1 Applicability

Method 8010B is used to determine the concentration of the following halogenated volatile organic compounds in groundwater, liquid, and solid matrices:

Allyl chloride
Benzyl chloride

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Bis (2-chloroethoxy)methane
 Bis (2-chloroisopropyl)ether
 Bromoacetone
 Bromobenzene
 Bromodichloromethane
 Bromoform
 Bromomethane
 Carbon tetrachloride
 Chlorobenzene
 Chloroethane
 2-Chloroethanol
 Chloroform
 1-Chlorohexane
 2-Chloroethyl vinyl ether
 Chloromethane
 Chloromethyl methyl ether
 Chloroprene
 4-Chlorotoluene
 Dibromochloromethane
 1,2-Dibromo-3-chloropropane
 Dibromomethane
 1,2-Dichlorobenzene
 1,3-Dichlorobenzene
 1,4-Dichlorobenzene
 Dichlorodifluoromethane
 1,1-Dichloroethane
 1,2-Dichloroethane
 1,1-Dichloroethylene (Vinylidene chloride)
 trans-1,2-Dichloroethylene
 Dichloromethane
 1,2-Dichloropropane
 1,3-Dichloro-2-propanol
 cis-1,3-Dichloropropene
 trans-1,3-Dichloropropene
 Epichlorhydrin
 Ethylene dibromide
 Methyl iodide
 1,1,2,2-Tetrachloroethane
 1,1,1,2-Tetrachloroethane
 Tetrachloroethylene
 1,1,1-Trichloroethane
 1,1,2-Trichloroethane
 Trichloroethylene
 Trichlorofluoromethane
 1,2,3-Trichloropropane
 Vinyl chloride

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Method 8015A is used to determine the concentration of the following nonhalogenated volatile organic compounds in groundwater, liquid, and solid matrices:

Diethyl ether
Ethanol
Methyl ethyl ketone (MEK)
Methyl isobutyl ketone (MIBK)

Method 8020A is used to determine the concentration of the following aromatic volatile organic compounds in groundwater, liquid, and solid matrices:

Benzene
Chlorobenzene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Toluene
Ethyl benzene
Xylenes (Dimethyl benzenes)

Method 8030A is used to determine the concentration of the following volatile organic compounds in groundwater, liquid, and solid matrices:

Acrolein (Propenal)
Acrylonitrile

All of the above Methods are gas chromatographic (GC) only (i.e., no mass spectrometer detector is employed). Method 8010B analyzes for halogenated volatile organics via GC/HSD (Halide-Specific Detector), Method 8015A analyzes for nonhalogenated volatile organics via GC/FID (Flame Ionization Detector), Method 8020A analyzes for aromatic Volatile organics via GC/PID (Photo-ionization Detector), and Method 8030A analyzes for the compounds acrolein and acrylonitrile using GC/FID. Samples can be analyzed by these methods using direct injection, the headspace method (Method 5020) or the purge-and-trap method (Method 5030). Groundwater samples should be determined using Method 5030.

2.2.1.2 Interferences

Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. Associated field quality control blanks are analyzed in order to monitor this.

Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe or purging device is rinsed with reagent water between samples. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination.

If sample or matrix interferences are encountered, a secondary or alternate analytical column may be used to resolve the compounds of interest.

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2.2.1.3 General Laboratory Practices

A method blank consisting of organic free water spiked with surrogates and internal standards should be analyzed immediately following each daily calibration, and also after the analysis of every high concentration sample.

Matrix Spike/Matrix Spike Duplicate (MS/MSD) analyses should be conducted to determine the effects of sample matrix upon the compounds of interest.

2.2.1.4 Sample Preparation

Method 5020 is a static headspace technique for extracting volatile organic compounds in pastes, solids, and liquids. Because of the large variability and complicated matrices of waste samples detection limits for this method may vary widely among samples.

Method 5030 is a purge-and-trap method applicable to nearly all types of samples, regardless of water content, including aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, groundwater, mounds, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

For highly volatile matrices, direct injection preceded by dilution should be used to prevent gross contamination of the instrumentation. For pastes, dilution of the sample until it becomes free-flowing is used to ensure adequate interfacial area. The success of this method depends on the level of interferences in the sample; results may vary due to the large variability and complicated matrices of solid waste samples.

2.2.1.5 Data Overview Prior to Validation

Before commencing validation, the reviewer must preview the associated Chain-of-Custody (COC) reports to determine:

- If the appropriate number of samples are present in the data package and if each sample was correctly analyzed for the parameters and methods specified.
- The identity of all associated field quality control blanks and field duplicate pairs.

Because many samples may have required dilutions, re-extractions and/or re-analyses, the validator should preview the data package contents to determine which analyses represent the better quality data.

Unless specifically directed by client protocol, never annotate the laboratory data package. Before beginning evaluation, prepare working copies (i.e. photocopies) of all Form I reports (including those for samples, laboratory method blanks and MS/MSD analyses) and all laboratory quality control summary forms (including all initial and continuing calibration summary statistics).

2.2.1.6 Technical Evaluation Summary

All data evaluations must be conducted in accordance with applicable USEPA Regional protocols and/or specific client contract requirements. The applicable documents must be referenced during the data evaluation process as this S.O.P. is only intended as a general procedure for the data validation tasks.

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General parameters such as Data Completeness, Overall System Performance, Chromatographic Quality, Detection Limits and Compound Identification are evaluated concurrently with the parameters discussed in the following subsections.

2.2.1.6.1 Holding Times

Holding times are evaluated by reviewing the COC reports, the individual sample Form I reports, and the associated laboratory raw data. Holding times are calculated from date of collection to date of analysis.

The technical maximum holding time allowance for aqueous samples preserved with hydrochloric acid (HCL) is 14 days.

No technical holding times for solid matrices have been promulgated; a 14-day maximum holding time allowance is currently being used.

For unpreserved aqueous samples, generally a 7-day maximum holding time allowance for aromatic compounds, along with a 14-day maximum holding time allowance for chlorinated hydrocarbons is used.

Positive results in affected samples are generally qualified as estimated (J); nondetects (UJ). These results are biased low. Some USEPA Regions apply the bias qualifiers, L and UL, instead. If the holding times are exceeded by a factor of 2 or more, the holding time exceedance is considered to be gross and positive results are generally qualified as estimated (J); nondetects are generally considered to be unreliable and are qualified (R). Results for which the holding time was grossly exceeded are biased low.

2.2.1.6.2 Calibration

Check that an initial calibration was performed for each instrument used for analysis and that all calibrations were performed at all appropriate concentration levels.

In general, either the correlation coefficient (R) or the Percent Relative Standard Deviation (%RSD) is evaluated in the data validation. If the correlation coefficient is chosen by the laboratory, the calibration curve should be checked for linearity. Generally, associated sample data are qualified as estimated (J, UJ) if the calibration curve correlation coefficient is <0.995. Professional judgment should be used to qualify sample data in cases when sample results fall outside the linear portion of the calibration curve. If the %RSD is used, determine which compounds have Percent Relative Standard Deviations (%RSDs) >40% and between 20%-40%. Circle these noncompliances on your working copies of these Forms. Spot-check (i.e., recalculate) a few of the %RSDs to verify the laboratory's computation.

Determine which samples are affected by reviewing the continuing calibration forms. Determine which continuing calibrations are associated with which initial calibrations. Write the affected samples on your working copies of the appropriate continuing calibration forms. Spot-check (i.e., recalculate) a few of the %Ds to verify the laboratory's computation.

Review the continuing calibration form and the associated laboratory raw data. Determine which compounds have Percent Differences (%Ds) >30% and between 15%-30%; circle the noncompliances on your working copies of these forms.

Generally, positive results for compounds for which %RSD or %D exceeds 40% or 30%, respectively, are qualified as estimated (J); nondetects (UJ). Check the specific applicable data validation protocol for further guidance as there are some protocol which reject nondetects if the %RSD or %D is excessive. Bias for these results cannot be determined.

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Generally, positive results for compounds for which %RSD is between 20%-40% or %D is between 15%-30% are qualified as estimated (J). Qualification of nondetects is protocol-specific. Follow the rules provided in the appropriate validation protocol.

2.2.1.6.3 Blank Contamination

When using the information given below and in the appropriate USEPA Regional Functional Guidelines, keep in mind that the validation action levels derived are sample-specific and must be adjusted for dilution, sample aliquot used for analysis, and sample moisture content (when applicable).

The rules for qualifying data based on the occurrence of blank contamination vary based on regional protocols; the guidelines provided in the appropriate protocol should be followed.

Generally the blank contamination review process is completed by first considering the maximum amount of a particular contaminant occurring in the laboratory method blanks. (Do not consider lab blanks run after high concentration samples for purposes of determining carryover as laboratory method blanks!). Then repeat the process for contaminants occurring in the associated field quality control blanks. Action levels for qualification (10X or 5X depending upon whether or not the contaminant is a common contaminant) are then set. The list of common contaminants may vary among protocols. Additionally, some hierarchy among the field quality control blanks apply and the manner in which the qualifiers are applied vary [i.e. use of (U) or (B); replacement by CRQL, etc.]. Refer to appropriate protocol for specific guidance.

2.2.1.6.4 Surrogates

Surrogates are evaluated by reviewing the laboratory data package Form II reports and the laboratory raw data. The quality control ranges are given on the laboratory data package Form IIs; circle any noncompliances on your working copies of these Forms.

All results for all compounds in an affected sample are qualified if any one of the surrogate spike compounds fails to meet the quality control criteria provided. Generally, for samples having a surrogate recovery <10%, positive results are qualified as estimated (J), nondetects are rejected (R). These results are biased low. For samples having a surrogate recovery which is low but >10%, positive results are generally qualified as estimated (J); nondetects (JJ). The bias qualifiers (L, UL) may be used instead, depending upon the specific USEPA Regional guidance. For samples having a surrogate recovery which is high, positive results are generally qualified as estimated (J, K) based on regional guidance; these results are biased high. Nondetects are not qualified based on high surrogate recoveries.

2.2.1.6.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

Generally, no data are qualified based upon MS/MSD results alone. If qualification does occur, generally only the result for that particular noncompliant compound is qualified in the original unspiked sample analysis. Refer to the applicable data validation protocol for specific procedures for evaluating MS/MSD analyses.

2.2.1.6.6 Other Considerations

Laboratory precision can be evaluated by comparing the unspiked sample results with MS/MSD analyses results for unspiked compounds. Consider nondetects and results reported at concentrations less than

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the Contract Required Quantitation Limit (CRQL) to be in agreement. Use professional judgment in determining whether to qualify sample results based on the comparison.

Likewise, compare the positive compound results for field duplicate samples. Generally, the Relative Percent Difference (RPD) between field duplicate results for the aqueous matrix should be <35%; for soil matrix results, <50%. Qualification of the sample data is limited to the specific field duplicate pair. Positive results for compounds showing imprecision are qualified as estimated (J); nondetects (UJ). Bias for these results cannot be determined.

In some USEPA Regions, a "Percent Solids" rule applies. For example, if a sediment sample contains <50% solids in USEPA Region II, all associated data are considered to be estimated and are qualified accordingly. Follow the appropriate protocol guidance when applicable.

2.2.1.6.7 Quantitation

Verify and record the quantitation of at least one compound per analytical fraction. If no positive results are reported, use the MS/MSD data to confirm proper computation by the laboratory. Validator and laboratory quantitations must agree within 10 percent.

2.2.1.7 Deliverables Guidance

In addition to any specific USEPA Regional requirements (e.g. data validation memorandum, data summary spreadsheets, Regional worksheets), all laboratory data package quality control summary forms, sample Form I reports, method blank Form Is, and the Chain-of-Custody report must be given to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct (in accordance with the appropriate USEPA Regional or client requirements) and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

2.2.2 Semivolatiles (SW8040A, 8060, 8090, 8100)

2.2.2.1 Applicability

Method 8040A is used to determine the concentration of the following phenolic compounds in groundwater, liquid, and solid matrices:

- Phenol
- 2-Chlorophenol
- 2,4-Dichlorophenol
- 2,6-Dichlorophenol
- Trichlorophenols
- Tetrachlorophenols
- Pentachlorophenol
- Cresols (methyl phenols)
- 4-Chloro-3-methylphenol
- 2,4-Dimethylphenol
- 2-Nitrophenol
- 4-Nitrophenol
- 2,4-Dinitrophenol
- 2-sec-Butyl-4,6-dinitrophenol (DNBP)

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2-Cyclohexyl-4,6-dinitrophenol
2-Methyl-4,6-dinitrophenol

Method 8060 is used to determine the concentration of the following phthalate esters in groundwater, liquid, and solid sample matrices:

Benzyi butyl phthalate
Bis(2-ethylhexyl)phthalate
Di-n-butyl phthalate
Di-n-octyl phthalate
Diethyl phthalate
Dimethyl phthalate

Method 8090 is used to determine the concentration of the following nitroaromatic and cyclic ketone compounds in groundwater, liquid, and solid sample matrices:

Nitrobenzene
Dinitrobenzene
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Isophorone
Naphthoquinone

Method 8100 is used to determine the concentration of the following polynuclear aromatic hydrocarbons (PAHs) in liquid and solid sample matrices:

Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(ghi)perylene
Benzo(j)fluoranthene
Benzo(k)fluoranthene
Chrysene
Dibenzo(a,h)anthracene
Dibenz(a,h)acridine
Dibenz(a,i)acridine
7H-Dibenzo(c,g)carbazole
Dibenzo(a,e)pyrene
Dibenzo(a,h)pyrene
Dibenzo(a,i)pyrene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
3-Methylcholanthrene
Naphthalene
Phenanthrene
Pyrene

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All of the above methods are gas chromatographic (GC) only (i.e., no mass spectrometer detector is employed). These methods use either an electron capture detector (ECD) or a flame ionization detector (FID).

2.2.2.2 Interferences

Solvents, reagents, glassware, and other sample-processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

Interferences co-extracted from samples will vary considerably from source to source depending upon the waste being sampled. While general cleanup techniques such as Method 3530 are provided as part of these methods, unique samples may require additional cleanup.

If sample or matrix interferences occur, a secondary column may be employed in addition to the primary column so as to resolve any questionable compound results.

2.2.2.3 General Laboratory Practices

An extraction blank should be prepared with each batch of samples extracted.

Matrix Spike/Matrix Spike Duplicate (MS/MSD) analyses should be conducted to determine the effects of sample matrix upon the compounds of interest.

2.2.2.4 Sample Preparation

Prior to analysis, the samples must be extracted using the appropriate techniques. Aqueous samples are extracted at the appropriate pH with methylene chloride as a solvent using Method 3510 (separatory funnel extraction) or Method 3520 (continuous liquid-liquid extraction). Both neat and diluted organic liquids may be analyzed by direct injection. Solid samples are extracted at the appropriate pH with methylene chloride using either Soxhlet Extraction (Method 3540) or Sonication (Method 3550) procedures.

2.2.2.5 Data Overview Prior to Validation

Before commencing validation the reviewer must preview the associated Chain-of-Custody (COC) reports to determine:

- If the appropriate number of samples are present in the data package and if each sample was correctly analyzed for the parameters and methods specified.
- The identity of all associated field quality control blanks and field duplicate pairs.

Because many samples may have required dilutions, re-extractions and/or reanalyses, the data validator should preview the data package contents to determine which analyses represent the better quality data.

The data package should never be annotated unless specifically directed by client protocol. All Form I reports (including those for samples, laboratory method blanks, and MS/MSD analyses) and all

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laboratory quality control summary forms (including all initial and continuing calibration summary statistics) should be photocopied for use as working copies.

2.2.2.6 Technical Evaluation Summary

All data evaluations must be conducted in accordance with the appropriate USEPA Regional protocols and/or specified client contract requirements. The applicable documents must be referenced during the data validation process as this S.O.P. is only intended as a general procedure for the data validation tasks.

General parameters such as Data Completeness, Overall System Performance, Chromatographic Quality, Detection Limits and Compound Identification are evaluated concurrently with the parameters discussed in the following subsections.

2.2.2.6.1 Holding Times

Holding times are evaluated by reviewing the COC reports, the individual sample Form I reports, and the associated laboratory raw data. Holding times for extraction are calculated from date of collection to date of extraction.

The technical holding times for aqueous and solid matrices are as follows:

- Extraction:
 - Water samples: 7 days
 - Solid samples: 14 days
- Analysis: 40 days from date of extraction

Generally, positive results affected by noncompliances are qualified as estimated (J); nondetects (UJ). These results are considered to be biased low. Alternately, the bias qualifiers L and UL may be used. Nondetects may be rejected (R) when the sample was extracted after 14 days (28 days for solid samples). If the holding time until analysis has been exceeded (and potentially, some of the extract may have evaporated), the affected sample results may be considered to be biased high. Refer to the appropriate data validation protocol for specific guidance.

2.2.2.6.2 Calibration

Check that an initial calibration was performed for each instrument used for analysis and that all calibrations were performed at all appropriate concentration levels.

In general, either the correlation coefficient (R) or the Percent Relative Standard Deviation (%RSD) is evaluated in the data validation. If the correlation coefficient is chosen by the laboratory, the calibration curve should be checked for linearity. Generally, associated sample data are qualified as estimated (J, UJ) if the calibration curve correlation coefficient is <0.995. Professional judgment should be used to qualify sample data in cases when sample results fall outside the linear portion of the calibration curve. If the %RSD is used, determine which compounds have Percent Relative Standard Deviations (%RSDs) >40% and between 20%-40%. Circle these noncompliances on your working copies of these Forms. Spot-check (i.e., recalculate) a few of the %RSDs to verify the laboratory's computation.

Determine which samples are affected by reviewing the continuing calibration forms. Determine which continuing calibrations are associated with which initial calibrations. Write the affected samples on your

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working copies of the appropriate continuing calibration forms. Spot-check (i.e., recalculate) a few of the %Ds to verify the laboratory's computation.

Review the continuing calibration form and the associated laboratory raw data. Determine which compounds have Percent Differences (%Ds) >30%, and between 15%-30%; circle the noncompliances on your working copies of these forms.

Generally, positive results for compounds for which %RSD or %D exceeds 40% or 30%, respectively, are qualified as estimated (J); nondetects (UJ). Check the specific applicable data validation protocol for further guidance as there are some protocol which reject nondetects if the %RSD or %D is excessive. Bias for these results cannot be determined.

Generally, positive results for compounds for which %RSD is between 20%-40% or whose %D is between 15%-30% are qualified as estimated (J). Qualification of nondetects is protocol-specific. Follow the rules provided in the appropriate validation protocol.

2.2.2.6.3 Blank Contamination

When using the information given below and in the appropriate USEPA Regional Functional Guidelines, keep in mind that the validation action levels derived are sample-specific and must be adjusted for dilution, sample aliquot used for analysis, and sample moisture content (when applicable).

The rules for qualifying data based on the occurrence of blank contamination vary based on regional protocols; the guidelines provided in the appropriate protocol should be followed.

Generally the blank contamination review process is completed by first considering the maximum amount of a particular contaminant occurring in the laboratory method blanks. (Do not consider lab blanks run after high concentration samples for purposes of determining carryover as laboratory method blanks!) Then repeat the process for contaminants occurring in the associated field quality control blanks. Action levels for qualification (10X or 5X depending upon whether or not the contaminant is a common contaminant) are then set. The list of common contaminants may vary among protocols. Additionally, some hierarchy among the field quality control blanks apply and the manner in which the qualifiers are applied vary [i.e. use of (U) or (B); replacement by CRQL, etc.]. Refer to appropriate protocol for specific guidance.

2.2.2.6.4 Surrogates

Surrogates are evaluated by reviewing the laboratory data package Form II reports and the laboratory raw data. The quality control ranges are given on the laboratory data package Form IIs; circle any noncompliances on your working copies of these Forms.

All results for all compounds in an affected sample are qualified if any one of the surrogate spike compounds fails to meet the quality control criteria provided. Generally, for samples having a surrogate recovery < 10%, positive results are qualified as estimated (J), nondetects are rejected (R). These results are biased low. For samples having a surrogate recovery which is low but > 10%, positive results are generally qualified as estimated (J); nondetects (UJ). The bias qualifiers (L, UL) may be used instead, depending upon the specific USEPA Regional guidance. For samples having a surrogate recovery which is high, positive results are generally qualified as estimated (J, K) based on regional guidance; these results are biased high. Nondetects are not qualified based on high surrogate recovery.

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2.2.2.6.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

Generally, no data are qualified based upon MS/MSD results alone. If qualification does occur, generally only the result for that particular noncompliant compound is qualified in the original unspiked sample. Refer to the applicable data validation protocol for specific procedures for evaluating MS/MSD analyses.

2.2.2.6.6 Other Considerations

Laboratory precision can be evaluated by comparing the unspiked sample results with MS/MSD analyses results for unspiked compounds. Consider nondetects and results reported at concentrations less than the Contract Required Quantitation Limit (CRQL) to be in agreement. Use professional judgment in determining whether to qualify sample results based on the comparison.

Likewise, compare the positive compound results for field duplicate samples. Generally, the Relative Percent Difference (RPD) between field duplicate results for the aqueous matrix should be <35%; for soil matrix results, <50%. Qualification of the sample data is limited to the specific field duplicate pair. Positive results for compounds showing imprecision are qualified as estimated (J); nondetects (UJ). Bias for these results cannot be determined.

In some USEPA Regions, a "Percent Solids" rule applies. For example, if a sediment sample contains <50% solids in USEPA Region II, all associated data are considered to be estimated, and are qualified accordingly. Follow the appropriate protocol guidance when applicable.

2.2.2.6.7 Quantitation

Verify and record the quantitation of at least one compound per analytical fraction. If no positive results are reported, use the MS/MSD data to confirm proper computation by the laboratory. Validator and laboratory quantitations must agree within 10 percent.

2.2.2.7 Deliverables Guidance

In addition to any specific USEPA Regional requirements (e.g. data validation memorandum, data summary spreadsheets, Regional worksheets), all laboratory data package quality control summary forms, sample Form I reports, method blank Form Is, and the Chain-of-Custody report, must be given to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct (in accordance with the appropriate USEPA Regional or client requirements), and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

2.2.3 **Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs), Organophosphorous Pesticides, Chlorinated Herbicides (SW 8080B, 8140, 8150B)**

2.2.3.1 Applicability

Method 8080B is used to determine the concentration of the following organochlorine pesticides and polychlorinated biphenyls (PCBs) in groundwater, liquid, and solid sample matrices:

Aldrin
alpha-BHC
beta-BHC

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delta-BHC
 gamma-BHC (Lindane)
 Chlordane
 4,4'-DDD
 4,4'-DDE
 4,4'-DDT
 Dieldrin
 Endosulfan I
 Endosulfan II
 Endosulfan sulfate
 Endrin
 Endrin aldehyde
 Heptachlor
 Heptachlor epoxide
 Methoxychlor
 Toxaphene
 Aroclor-1016
 Aroclor-1221
 Aroclor-1232
 Aroclor-1242
 Aroclor-1248
 Aroclor-1254
 Aroclor-1260

Similarly, Method 8140 is used to determine the following pesticides in groundwater and waste samples:

Azinphos methyl
 Bolstar (Sulprofos)
 Chlorpyrifos
 Coumaphos
 Demeton-O
 Demeton-S
 Diazinon
 Dichlorvos
 Disulfoton
 Ethoprop
 Fensulfothion
 Fenthion
 Merphos
 Mevinphos
 Naled
 Parathion methyl
 Phorate
 Ronnel
 Stirophos (Tetrachlorvinphos)
 Tokuthion (Prothiofos)
 Trichloronate

Note that when Method 8140 is used to analyze unfamiliar samples, compound identifications should be supported by at least one additional qualitative technique if mass spectroscopy is not employed.

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Method 8150B is used to determine the following chlorinated acid herbicides in groundwater and waste samples:

2,4-D
2,4-DB
2,4,5-T
2,4,5-TP (Silvex)
Dalapon
Dicamba
Dichloroprop
Dinoseb
MCPA
MCPP

Since these compounds are produced and used in various forms (i.e., acid, salt, ester, etc.), Method 8150 includes a hydrolysis step to convert the herbicide to the acid form prior to analysis. When Method 8150 is used to analyze unfamiliar samples, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column; alternately, the compounds of interest can be confirmed by detection via a mass spectrometer.

All of the above Methods are Gas Chromatographic (GC) in which sample extracts are analyzed by direct injection. Method 8080 analyzes for organochlorine pesticide compounds and PCBs via GC/ECD (Electron Capture Detector; an equivalent Halogen-Specific Detector may also be used). Method 8140 analyzes for organophosphorous pesticide compounds via GC/FID (Flame Ionization Detector), and Method 8150 analyzes for chlorinated herbicide compounds via GC/ECD (alternately, a Microcoulometric Detector or Hall Electrolytic Conductivity Detector may be used).

2.2.3.2 Interferences

The sensitivity of these methods usually depends on the level of interferences rather than on instrumental limitations. Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. The use of high purity reagents and solvents helps to minimize these interference problems. Extraction blanks are analyzed as method blanks in order to monitor the occurrences of interferences.

Interferences co-extracted from the sample will vary considerably, and will dictate the nature and extent of clean-up procedures used. Phthalate esters are a common interference to organochlorine pesticide analyses; phenols and organic acids may act as interferents when analyzing for chlorinated herbicides.

2.2.3.3 General Laboratory Practices

Matrix Spike/Matrix Spike Duplicate (MS/MSD) analyses should be conducted to determine the effects of sample matrix upon the compounds of interest.

Standard quality assurance practices such as the analyses of field replicate and laboratory duplicates should also be employed.

Note that herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, when performing Method 8150, glassware and glass wool must be acid-rinsed and sodium sulfate must be acidified with sulfuric acid prior to use to avoid this possibility.

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2.2.3.4 Sample Preparation

Prior to the use of Method 8080 and 8140, aqueous samples are extracted at a neutral pH with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid- liquid extractor (Method 3520). Solid samples are extracted with hexane:acetone (1:1) using either the Soxhlet extraction (Method 3540) or sonication (Method 3550) procedures.

Method 8150 provides its own specific preparation procedures for aqueous and solid samples which include extraction with acetone and diethyl ether followed by esterification using diazomethane as a derivatizing agent.

2.2.3.5 Data Overview Prior to Validation

Before commencing validation, the reviewer must preview the associated Chain-of-Custody (COC) reports to determine:

- If the appropriate number of samples are present in the data package and if each sample was correctly analyzed for the parameters and methods specified.
- The identity of all associated field quality control blanks and field duplicate pairs.

Because many samples may have required dilutions, re-extractions and/or re-analyses, the validator should preview the data package contents to determine which analyses represent the better quality data.

Unless specifically directed by client protocol, never annotate the laboratory data package. Before beginning evaluation, prepare working copies (i.e., photocopies) of all Form I reports (including those for samples, laboratory method blanks and MS/MSD analyses) and all laboratory quality control summary forms.

2.2.3.6 Technical Evaluation Summary

All data evaluations must be conducted in accordance with applicable USEPA Regional protocols and/or specific client contract requirements. The applicable documents must be referenced during the data evaluation process as this S.O.P. is only intended as a general procedure for the data validation tasks.

General parameters such as Data Completeness, Overall System Performance, Chromatographic Quality, Detection Limits, and Compound Identification are evaluated concurrently with the parameters discussed in the following subsections.

2.2.3.6.1 Holding Times

Holding times are evaluated by reviewing the COC reports, the individual sample Form I reports, and the associated laboratory raw data. Holding times for extraction are calculated from date of collection to date of extraction.

The technical holding times for aqueous and solid matrices are as follows:

- Extraction:
 - Water samples: 7 days
 - Solid samples: 14 days
- Analysis: 40 days from date of extraction

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When the holding time criteria are not met, positive results in affected samples are generally qualified as estimated (J); nondetects (UJ). These results are biased low. Some USEPA Regions apply the bias qualifiers, L and UL, instead. If the holding times are exceeded by a factor of 2 or more, the holding time exceedance is considered to be gross and positive results are generally qualified as estimated (J); nondetects are generally considered to be unreliable and are rejected (R). These results are biased very low.

2.2.3.6.2 Calibration

Data pertaining to the initial calibration (i.e., evaluation check for linearity) is found on the data package Form VIs or equivalent. Check that an initial calibration was performed for each instrument used and at all appropriate concentration levels.

In general, either the correlation coefficient (R) or the Percent Relative Standard Deviation (%RSD) is evaluated in the data validation. If the correlation coefficient is chosen by the laboratory, the calibration curve should be checked for linearity. Generally, associated sample data are qualified as estimated (J, UJ) if the calibration curve correlation coefficient is < 0.995 . Professional judgment should be used to qualify sample data in cases when sample results fall outside the linear portion of the calibration curve. If the %RSD is used, determine which compounds have Percent Relative Standard Deviations (%RSDs) $> 40\%$ and between 20% - 40% . Circle these noncompliances on your working copies of these Forms. Spot-check (i.e., recalculate) a few of the %RSDs to verify the laboratory's computation.

Determine which samples are affected by reviewing the continuing calibration forms. Determine which continuing calibrations are associated with which initial calibrations. Write the affected samples on your working copies of the appropriate continuing calibration forms. Spot-check (i.e., recalculate) a few of the %Ds to verify the laboratory's computation.

Review the continuing calibration form and the associated laboratory raw data. Determine which compounds have Percent Differences (%Ds) $> 30\%$ and between 15% - 30% ; circle the noncompliances on your working copies of these forms.

Generally, positive results for compounds for which %RSD or %D exceeds 40% or 30% , respectively, are qualified as estimated (J); nondetects (UJ). Check the specific applicable data validation protocol for further guidance as there are some protocol which reject nondetects if the %RSD or %D is excessive. Bias for these results cannot be determined.

Generally, positive results for compounds for which %RSD is between 20% - 40% or %D is between 15% - 30% are qualified as estimated (J). Qualification of nondetects is protocol-specific. Follow the rules provided in the appropriate validation protocol.

Method 8080A requires analysis of a DDT/Endrin breakdown check standard. The DDT/Endrin Breakdown should not exceed 20% . Generally, if % breakdown for DDT exceeds 20% , estimate (J) all positive results for DDT, DDE and DDD following the in-last control standard until the next in-control standard (see analytical sequence). If there are no positive results for DDT but there are positive results for DDD or DDE then reject (R) nondetects for DDT in associated samples. Generally, if Endrin % Breakdown exceeds 20% , estimate (J) positive results for Endrin, Endrin Aldehyde, and Endrin Ketone in all samples following the last in-control standard until the next acceptable standard. If there are positive results for Endrin Aldehyde or Endrin Ketone but none for Endrin, reject (R) nondetect Endrin results.

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2.2.3.6.3 Blank Contamination

When using the information provided below and in the appropriate USEPA Regional Functional Guidelines, keep in mind that the validation action levels derived are sample-specific, and must be adjusted for dilution, sample aliquot used for analysis, and sample moisture content (when applicable).

The rules for qualifying data based on the occurrence of blank contamination vary based on regional protocols; guidelines provided in the appropriate data validation protocol should be followed.

An action level of 5X the maximum amount of contaminant found is used to evaluate the sample data. The manner in which the qualifiers are applied vary [i.e. use of (U) or (B); replacement by CRQL, etc.]. Refer to appropriate validation protocol for specific guidance.

2.2.3.6.4 Surrogates

Surrogates are evaluated by reviewing the laboratory data package Form II reports and the associated laboratory raw data. The advisory limits are given on the laboratory data package Form IIs; circle any recoveries outside these limits on your working copies of these Forms.

No qualifications are made for surrogates which show zero recoveries because they were "diluted out." Generally, positive results affected by low surrogate recovery are qualified as estimated (J) or the (L) bias qualifier is used when applicable; nondetects are qualified (UJ) or (UL), accordingly. If a positive sample result is affected by high surrogate recovery, the result is qualified as estimated (J) or the (K) bias qualifier is used when applicable; nondetects are not qualified based on high surrogate recovery. Because the surrogate recovery limits for these fractions are advisory, generally no results are rejected.

The pesticide/PCB surrogates decachlorobiphenyl (DCB) and tetrachloro-m-xylene (TCX) retention times found on data package Form VIII or equivalent must be ± 0.10 for DCB and ± 0.05 for TCX. If DCB and TCX retention time criteria are not met, the raw data must be checked for misidentified GC peak. The validator's professional judgment for qualifications should be used.

2.2.3.6.5 Matrix Spike/Matrix Spike Duplicates

Generally, no data are qualified based upon MS/MSD results alone. If qualification does occur, generally only the result for that particular noncompliant compound is qualified in the original unspiked sample analysis. Refer to the appropriate data validation guidelines for specific procedures for evaluating MS/MSD analyses.

2.2.3.6.6 Other Considerations

Laboratory precision can be evaluated by comparing the unspiked sample results with MS/MSD analyses results for unspiked compounds. Consider nondetects and results reported at concentrations less than the Contract Required Quantitation Limit (CRQL) to be in agreement. Use professional judgment in determining whether to qualify sample results based on the comparison.

Likewise, compare the positive compound results for field duplicate samples. Generally, the Relative Percent Difference (RPD) between field duplicate results for the aqueous matrix should be <35%; for soil matrix results, <50%. Qualification of the sample data is limited to the specific field duplicate pair. Positive results for compounds showing imprecision are qualified as estimated (J); nondetects (UJ). Bias for these results cannot be determined.

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In some USEPA Regions, a "Percent Solids" rule applies. For example, if a sediment sample contains <50% solids in USEPA Region II, all associated data are considered to be estimated and are qualified accordingly. Follow the appropriate protocol guidance when applicable.

2.2.3.6.7 Quantitation

Verify and record the quantitation of at least one compound per analytical fraction. If no positive results are reported, use the MS/MSD data to confirm proper computation by the laboratory. Validator and laboratory quantitations must agree within 10%.

2.2.3.7 Deliverables Guidance

In addition to any specific USEPA Regional requirements (e.g. data validation memorandum, data summary spreadsheets, USEPA Regional worksheets), all laboratory data package quality control summary forms, sample Form I reports, method blank Form Is, and the Chain-of-Custody report, must be given to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct (in accordance with the appropriate USEPA Regional or client requirements), and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

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3.0 CLP INORGANICS FOR SOLID AND AQUEOUS MATRICES

3.1 Inorganics (CLP Statement of Work (SOW) ILM03.0)

Inductively Coupled Plasma Emission Spectroscopy (ICP) - Analytes commonly analyzed using ICP include: aluminum, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, magnesium, manganese, nickel, potassium, silver, sodium, vanadium, and zinc.

Graphite Furnace Atomic Absorption Spectroscopy (GFAA) - Analytes commonly analyzed using GFAA include: antimony, arsenic, lead, selenium, and thallium

Cold Vapor Methodology - Mercury is commonly analyzed using cold vapor methodology.

Automated Colorimetric Technique - Cyanide is commonly analyzed using automated colorimetric methodology.

3.1.1 **Applicability**

This method is applicable to a large number of matrices including EP extracts, TCLP extracts, industrial wastes, soils, groundwater, aqueous samples, sludges, sediments, and other solid wastes. All matrices require digestion prior to analysis.

3.1.2 **Data Overview Prior to Validation Process**

3.1.2.1 Data Completeness

The data reviewer must initially verify that all CLP Forms are present and complete (i.e., Forms 1 through 14 must be provided). Areas of special attention when accounting for required CLP Forms will include:

- Verify at least one Initial and Continuing Calibration Verification (ICV/CCV) Percent Recovery (%R) calculation as noted on the Form 2A.
- When reviewing Form 2B, verify that all atomic absorption (GFAA) analytes are present in the CRDL standard at concentrations at the CRDL. Verify that all ICP analytes (with the exceptions of Al, Ba, Ca, Fe, Mg, Na and K) are present in the CRDL standard at concentrations of 2X CRDL.
- Verify that a matrix-specific laboratory generated preparation blank has been analyzed for each respective matrix as noted on the Form 3 (note that filtered and unfiltered aqueous matrices are to be treated as distinctly different matrices).
- Verify that all ICP analytes are present in both ICSA and ICSAB solutions. (Note that 3/90 SOW ILM03.0 does not require that antimony, sodium, and potassium be present in these solutions). Also verify from the raw data that the laboratory reported all analytes present in solution A to the nearest whole number. It is not uncommon for laboratories to incorrectly report "zeros" or simply leave blank the appropriate solution A columns. Furthermore, %Rs for solution AB are to be reported to one decimal place on the Form 4.
- Check that one matrix spike was analyzed for each particular matrix per analytical batch. Laboratories typically will not include an aqueous matrix for waters if the only aqueous samples contained in the SDG are field quality control blanks (i.e., equipment rinsate blanks

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and/or field blanks). This is generally accepted without data validation letter text comment. Additionally, the data reviewer may want to verify spiking levels as noted on pg. E-20 of ILM03.0 3/90 Inorganic SOW.

- Verify that laboratory duplicate analyses were performed for each matrix. **NOTE:** Field quality control blanks are never to be designated for quality control analyses.
- Check that one Laboratory Control Sample (LCS) was analyzed for each batch of samples per matrix within an SDG. **NOTE:** An aqueous LCS is not required for mercury and cyanide analysis.
- The Method of Standard Additions (MSA) Form 8 may or may not be present as dictated by Post Digestion Spike (PDS) %Rs. See Section 3.1.3.11 for further details.
- Verify that at least one ICP serial dilution analysis was performed for each matrix within an SDG. **NOTE:** Typically one serial dilution will serve to monitor a given set of samples within an SDG. However, special contractual requirements may necessitate one serial dilution analysis per sample. Ascertain atypical serial dilution frequency requirements through the project manager.
- Simply check that the Form 11 ICP Interelement Correction Factors (Annually) is present.
- Verify that all ICP analytical results fall within the ICP Quarterly Linear Ranges provided on the Form 12. Verify that no GFAA analytical results exceed the highest standard used in the associated GFAA calibration.
- Verify that the Form 13 Preparation Log accounts for aqueous/soil ICP, AA, mercury, and cyanide digestions/distillations as applicable.
- Examine the Form 14s to verify that one and only one "X" flag has been used to signify each reported field sample result or quality control sample result. Laboratories are often careless when entering the "X" flag. An incorrectly entered "X" flag can lead to reporting errors for the sample and its associated QC. The validator must verify reported results in instances of discrepancies, amend appropriate forms, and mention in letter text.

Actions - Notify the appropriate laboratory contact of required resubmittals when discrepancies are noted on the forms discussed above.

3.1.3 Technical Evaluation Summary

All data evaluations must be conducted in accordance with current and applicable USEPA Regional protocols and/or specific client contractual requirements and obligations. The applicable documents must be referenced to during the data evaluation process as this Standard Operating Procedure (S.O.P) is intended as proprietary in-house guidance for general inorganic validation practices only.

General parameters such as Data Completeness, Overall System Performance, and Detection Limits must be evaluated concurrently with the parameters discussed below.

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3.1.3.1 Holding Times

Holding times are calculated from date of sample collection to date of sample analysis. The date of sample collection must be obtained from the Chain-of-Custody (COC) form. The date of sample analysis is best retrieved from the raw data but may also be obtained from the Form 14.

Sample preservation and holding time requirements are as follows:

- **Metals** - 6 months; pH <2
- **Mercury** - 28 days; pH <2
- **Cyanide** - 14 days; pH >12

Preservation requirements as noted above are applicable to aqueous samples only; solid samples do not receive preservative, but require maintenance at 4°C ($\pm 2^\circ\text{C}$) during shipment and storage.

Actions - Holding time exceedances result in potentially low-biased results; thus, positive results and nondetects shall be qualified as estimated, (J) and (UJ), respectively. **NOTE:** Gross holding time noncompliances are defined as holding times which are exceeded by a factor or 2X. In these extreme cases, it is practice to reject (R) nondetects while positive results are qualified based upon professional judgment regarding the reliability of the associated data.

3.1.3.2 Initial Calibration Requirements

Calibration must be initiated daily and prior to sample analysis. The following calibration standard requirements must be verified:

- **ICP analyses** - must employ a blank and at least one standard.
- **GFAA analyses** - must employ a blank and at least three standards. One of the standards must be at the CRDL. Additionally, the calibration correlation coefficient (r) must be checked for linearity for each GFAA analysis performed (i.e., $r = 0.995$ or greater).
- **Mercury analyses** - must employ a blank and at least four standards ($r = 0.995$ or greater).
- **Cyanide analyses** - must employ a blank and at least three standards ($r = 0.995$ or greater). **NOTE:** The midpoint standard for cyanide analyses must be distilled; verify this via distillation logs.

3.1.3.3 Initial and Continuing Calibration Verification (ICV/CCV)

Review Initial and Continuing Calibration Verification Form 2As and associated raw data. The ICV/CCV %R quality control limits are 90-110% for metals, 80-120% for mercury, and 85-115% for cyanide.

Actions - If ICV/CCV %Rs are low, qualify as estimated (J) positive results and (UJ) nondetects. If ICV/CCV %Rs are high, qualify as estimated (J) positive results; nondetects are not affected. Gross exceedance, as defined by applicable data validation protocol, may require rejection (R) of results. **NOTE:** Qualify results of only those samples associated with the noncompliant ICB or CCV (generally, those samples immediately preceding or following the noncompliant standard until the nearest in-control standard).

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3.1.3.4 CRDL Standard Analysis

Review CRDL Standard Form 2Bs and associated new data. The CRDL Standard analysis %R quality control limits are 80-120% for all metals.

Actions - If CRDL %Rs are low, qualify as estimated (J) positive results <3X CRDL and (UJ) nondetects. Generally, if CRDL %Rs are high, qualify as estimated (J) positive results <3X CRDL; nondetects remain unaffected. Note that when using EPA Region I validation guidelines, nondetects will receive qualification based upon high CRDL Standard analysis recovery. **NOTE:** The data reviewer need not specify affected samples; common practice is to apply data qualifications "across-the-board" based upon LOE time constraints.

3.1.3.5 Laboratory Method and Field Quality Control Blanks

Verify that a preparation blank was analyzed for each matrix and for each batch of 20 samples or each sample batch digested, whichever is more frequent. Continuing Calibration Blanks (CCBs) must be run at a frequency of 10% or every 2 hours whichever is more frequent.

The data reviewer will select the maximum contaminant level for each analyte in a particular matrix from which shall be calculated an "action level." The action level shall be established as 5X the maximum contaminant level but must be adjusted for dilution factor, moisture content, and sample weight prior to application.

ICB/CCB contamination shall be applied to all samples within an SDG. Preparation blank contamination shall be applied to samples of the same matrix only. Common practice shall be to qualify as nondetected (U) any contaminant present in sample which is considered a laboratory artifact (i.e., < the established action level). Professional judgment must be employed when discerning the validity of a concentration present in a field quality control blank. In many instances, contamination present in these blanks can be attributable to "dirty" laboratory practice and not actual field contaminant conditions.

Negative concentrations detected in the laboratory method blanks are indicative of instrumental problems and base-line drifting. Generally, any negative concentration > IDL shall warrant estimation [(J) positives and (UJ) nondetects] of the associated sample data regardless of matrix. Action levels shall not be established for negative concentration levels.

Actions - Qualify as nondetected (U) any positive result within the action level. Qualify as estimated (J) positive results and (UJ) nondetects for analytes for which negative concentrations were noted in the laboratory method blanks (i.e., ICBs, CCBs, and/or preparation blanks).

3.1.3.6 ICP Interference Check Sample (ICS) Results

Review ICP Interference Check Sample Form 4 and associated raw data. Verify that all recoveries for the ICP ICS solution fall within the 80-120% quality control window established for the ICS AB solution.

Actions - For ICS %Rs <80%, qualify as estimated (J) positive results and (UJ) nondetects in affected samples. For ICS %Rs > 120%, qualify as estimated (J) positive results in affected samples; nondetects are unaffected by high ICS solution AB recovery. **NOTE:** Affected samples include all samples analyzed between the initial and final solutions (or within the eight hour working shift, whichever occurs more frequently) which contain Al, Ca, Fe, or Mg at levels >50% of the respective concentration of Al, Ca, Fe, or Mg in the ICS True Solution A.

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Next, review concentrations of the four common interfering analytes (aluminum, calcium, iron, and magnesium) in the environmental samples. Any aforementioned interferant present in the environmental samples at concentrations which exceed 50% of those present in the ICS solution for that same analyte will require calculation of estimated elemental interference stemming from high interfering analyte concentration. If the previous condition is met; review the ICP/ICS Form 4 and note any analytes present in the ICS solution A at levels which exceed the IDL and which are not present in the ICS True solution A. Positive results in the ICS solution A indicate potentially elevated results for this analyte in the affected sample while negative results in the ICS solution A indicate potentially suppressed results for this analyte in the affected sample.

Next, an estimated elemental interference must be calculated for each analyte > IDL present in the ICS solution A which is not present in the ICS True solution A. The following equation shall be employed:

$$\text{Estimated elemental intf.} = \frac{[\text{Conc. affected analyte in ICS Soln A}] \times [\text{Interferent}] [\text{Conc. in Sample}]}{\text{Interferent Conc. in ICS Soln A}}$$

It is advisable, although not necessary, to routinely choose the lowest concentration for the interferant level in the ICS so as to calculate the highest estimated interference possible. This method lends itself to a more conservative overall data quality review.

Estimated interferences for each affected analyte > IDL in the ICSA solution must now be compared to the reported environmental sample result for that particular analyte.

Actions - For estimated interferences < 10% of the reported sample concentration for a particular affected analyte, take no action; interference is considered negligible. For estimated interferences > 10% of the reported sample concentration for a particular affected analyte, qualify (J) positive result and/or (UJ) nondetect for affected analyte in affected sample. (NOTE: Calculation of an estimated positive (potentially elevated) interference will have no effect on a reported nondetect; thus, no action is necessary).

3.1.3.7 Matrix Spike Sample Analysis (Pre-digestion)

Review Spike Sample Recovery Form 5A and associated raw data. Verify that at least one matrix spike was performed for each matrix for a given set of samples within an SDG. NOTE: Filtered and unfiltered samples are to be treated as distinctly different sample matrices and qualified accordingly. Refer to ILM03.0, 3/90 Inorganic SOW, Table 3, "SPIKING LEVELS FOR SPIKING SAMPLE ANALYSIS," page 20, Section E, for proper analyte spiking concentrations and requirements. Any deviations from the SOW shall be noted and require laboratory contact for correction.

Aqueous and soil Matrix Spike (MS) recoveries must be within the 75-125% quality control window in instances where the initial sample result is <4X amount spiked. If the initial sample result is >4X the amount spiked and the MS %R is noncompliant; no actions shall be taken.

Actions - For MS %Rs <30%, qualify as estimated (J) positive results and reject (R) nondetects in affected samples. For MS %Rs <75% but >30%, qualify as estimated (J) positive results and (UJ) nondetects in affected samples. For MS %Rs > 125%, qualify as estimated (J) positive results in affected samples; nondetects are not compromised by high MS recovery; thus, no actions are warranted.

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3.1.3.8 Laboratory Duplicate Precision

Review Duplicates Form 6 and associated raw data. Verify that one duplicate sample analysis was performed for each group of samples of a similar matrix within an SDG. Control criteria used to evaluate aqueous laboratory duplicates are as follows:

- a control limit of $\pm 20\%$ for relative percent difference when sample and duplicate results are $>5X$ CRDL
- a control limit of $\pm 1X$ CRDL for the difference between the sample values when sample and/or duplicate results are $<5X$ CRDL

Control criteria used to evaluate solid laboratory duplicates are as follows:

- a control limit of $\pm 35\%$ for relative percent difference when sample and duplicate results are $>5X$ CRDL
- a control limit of $\pm 2X$ CRDL for the difference between the sample values when sample and/or duplicate results are $<5X$ CRDL

NOTE: Review the CLP Form 6 carefully and verify that the laboratory has in fact reported a %RPD of 200% and not simply recorded the %RPD as noncalculable (in instances where the sample result is positive but the duplicate result is nondetect). Overlooking this minor point may result in incomplete sample data qualification in some instances.

Actions - For any situation involving laboratory duplicate imprecision, qualify as estimated (J) positive results and (JJ) nondetects in affected samples. **NOTE:** It is important to note in the letter text the cause of laboratory duplicate imprecision (i.e., noncompliant %RPD or noncompliant difference between sample and duplicate results).

3.1.3.9 Field Duplicate Precision

Field duplicates can be determined via Project Manager informational documents (i.e., sampling logs) or obtained from Chain-of-Custody (COC) forms. Field duplicates are generally identified as samples having identical sample collection times and dates. In instances where field duplicate samples are included with the sample data set, the following control criteria are generally used to evaluate aqueous field duplicates:

- a control limit of $\pm 30\%$ for relative percent difference when sample and duplicate results are $>5X$ CRDL
- a control limit of $\pm 2X$ CRDL for the difference between the sample values when sample and/or duplicate results are $<5X$ CRDL

Similarly, the following control criteria are generally used to evaluate solid field duplicates:

- a control limit of $\pm 50\%$ for the relative percent difference when sample and duplicate results are $>5X$ CRDL
- a control limit of $\pm 4X$ CRDL for the difference between the sample values when sample and/or duplicate results are $<5X$ CRDL

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NOTE: The %RPD should reflect a difference of 200% and should not simply be recorded as noncalculable in instances where the sample result is positive but the field duplicate result is nondetect. Overlooking this minor point may result in incomplete sample data qualification in some instances.

Actions - For any situation involving field duplicate imprecision, qualify as estimated (J) positive results and (UJ) nondetects in affected samples. **NOTE:** It is important to note in the letter text the cause of field duplicate imprecision (i.e., noncompliant %RPD or noncompliant difference between sample and duplicate results). Furthermore, laboratory duplicate data qualifications, as per Brown & Root Environmental convention, shall be matrix-specific but otherwise "across-the-board" for TAL inorganic analyses. However, field duplicate data validation qualifications shall be limited to the field duplicate pair only.

3.1.3.10 Laboratory Control Sample (LCS) Results

Review Laboratory Control Sample Form 7 and associated raw data. Verify that an LCS was analyzed for each matrix and for each batch of twenty samples or batch of samples digested (whichever is more frequent) within an SDG. The quality control criteria established for evaluation of aqueous LCS analyses are 80-120%. **NOTE:** An aqueous LCS is not required for mercury and cyanide analysis, and silver and antimony are not subject to quality control criteria. Verify that all solid "found values" fall within the EPA established control limits for soils.

Actions - Aqueous LCS: In instances where aqueous LCS %R < 80%, qualify as estimated (J) positive results and (UJ) nondetects. If aqueous LCS %R > 120, qualify as estimated (J) positive results. Solid LCS: In instances where solid found value is below lower quality control limit, qualify as estimated (J) positive results and (UJ) nondetects. If solid LCS found value exceeds EPA upper limit for soils, qualify as estimated (J) positive results.

3.1.3.11 Method of Standard Additions (MSA)

Review MSA Form 8 and verify instrument linearity by checking that all calibration correlation coefficients (r) are greater than or equal to 0.995. MSAs for a particular analyte in a particular sample may be run more than once. Check reanalyses in instances where initial MSA analysis yields (r) < 0.995. It is good practice to review one or two GFAA post-digestion spike (PDS) %Rs via reviewing unspiked and spiked sample concentrations and associated PDS recovery to verify that the Furnace Atomic Absorption Analysis Scheme has been followed as per directional guidance noted on page E-28, document ILM03.0.

Actions - If calibration correlation coefficient (r) < 0.995, qualify as estimated (J) positive result and/ or (UJ) nondetect in affected sample. **NOTE:** The "Q" column on the Form 1 of the affected sample should contain an "S" flag for that particular analyte to indicate that the result was obtained using MSA. A "+" flag should also be recorded when the MSA correlation coefficient (r) < 0.995. Review the appropriate Form 1 and amend if necessary.

3.1.3.12 ICP Serial Dilution Analysis

Review ICP Serial Dilutions Form 9 and associated raw data. Verify that a serial dilution was performed for each matrix and that all ICP analytes are included on the Form 9 with corresponding recovery calculations. Check the calculated Percent Difference (%D) column in instances where the diluted sample result is nondetected. In this situation, the laboratory should report a %D of 100% and not simply list the %D as noncalculable. Overlooking this minor point may result in incomplete sample data qualification in some instances. Amend the Form 9 if necessary. All %Ds for ICP serial dilution analyses

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should be <10% when concentrations of corresponding analytes in the original (undiluted) sample are minimally a factor of 50X IDL.

Actions - If %D >10% for an analyte, and the corresponding sample concentration is >50x IDL, qualify as estimated (J) positive results for that analyte in all samples of the same matrix. NOTE: The possibility of negative interference exists when the ICP serial dilution %D >10% and the diluted sample result is significantly > original (undiluted) sample result. Qualify as estimated (J) positive results and (UJ) nondetects in such instances.

3.1.3.13 EPA Analysis Run Logs Form 14s

The Form 14 serves several useful functions. It can be used to obtain sample analysis dates as noted in the heading of the page. Secondly, it is used to record any dilutions as applicable to ICP, GFAA, mercury, and cyanide analyses. And finally, it can be used to verify that GFAA PDS percent recoveries are within the 85-115% quality control limits. Additionally, the data reviewer should be careful to note that one and only one "X" flag has been used to indicate each reported field sample result or quality control sample result; this can be an area of frequent laboratory error.

Actions - If the PDS %R is <85%, qualify as estimated (J) the corresponding positive result and/or (UJ) nondetect in affected sample. If the PDS %R is >115%, qualify as estimated (J) the corresponding positive result in the affected sample; nondetects are not qualified based on high PDS %R.

3.1.3.14 Further GFAA Evaluations

It is necessary to review the raw data for GFAA analyses and verify that all Coefficients of Variation or Relative Standard Deviations (%RSDs) are <20% for reported sample results which exceed the CRDL.

Actions - If the CV or %RSD exceeds 20% and the reported sample result is > CRDL, qualify as estimated (J) positive result in affected sample.

3.1.4 **Deliverables Guidance**

In addition to any specific USEPA Regional requirements (e.g. data validation memorandum, data summary spreadsheets, USEPA Regional worksheets), all laboratory data package quality control summary forms, sample Form I reports, method blank Form Is, and the Chain-of-Custody report must be given to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct (in accordance with the appropriate USEPA Regional or client requirements) and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

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4.0 NON-CLP INORGANICS FOR SOLID AND AQUEOUS MATRICES

4.1 Inorganics (SW-846 6010/7470/9010)

Inductively Coupled Plasma Emission Spectroscopy (ICP) - Analytes commonly analyzed using ICP include: aluminum, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, magnesium, manganese, nickel, potassium, silver, sodium, vanadium, and zinc.

Graphite Furnace Atomic Absorption Spectroscopy (GFAA) - Analytes commonly analyzed using GFAA include: antimony, arsenic, lead, selenium, and thallium.

Cold Vapor Methodology - Mercury is commonly analyzed using cold vapor methodology.

Automated Colorimetric Technique - Cyanide is commonly analyzed using automated colorimetric methodology.

4.1.1 **Applicability**

These methods are applicable to a large number of matrices including EP extracts, TCLP extracts, industrial wastes, soils, groundwater, aqueous samples, sludges, sediments, and other solid wastes. All matrices require digestion prior to analysis.

Detection limits for analytes are established on a quarterly basis and are both laboratory and instrument specific.

4.1.2 **Data Overview Prior to Validation Process**

4.1.2.1 Data Completeness

The data reviewer must initially verify that all forms are present and complete (i.e., Forms 1 through 14 must be provided). Areas of special attention when accounting for required forms will include:

- Verify at least one Initial and Continuing Calibration Verification (ICV/CCV) Percent Recovery (%R) calculation as noted on the Calibration Summary (Form 2A or equivalent).
- Verify that a matrix-specific laboratory generated preparation blank has been analyzed for each respective matrix as noted on the blank summary (Form 3 or equivalent) (note, filtered and unfiltered aqueous matrices are to be treated as distinctly different matrices).
- Verify that all ICP analytes are present in both ICSA and ICSAB solutions. Also, verify from the raw data that the laboratory reported all analytes present in solution A to the nearest whole number. It is not uncommon for laboratories to incorrectly report "zeros" or simply leave blank the appropriate solution A columns.
- Check that one matrix spike was analyzed for each particular matrix per analytical batch. Laboratories typically will not include an aqueous matrix for waters if the only aqueous samples contained in the SDG are field quality control blanks (i.e., equipment rinsate blanks and/or field blanks). This is generally accepted without data validation letter text comment. Additionally, the data reviewer may want to verify spiking levels.

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- Verify that laboratory duplicate analyses were performed for each matrix. **NOTE:** Field quality control blanks are never to be designated for quality control analyses.
- Check that one Laboratory Control Sample (LCS) was analyzed for each batch of samples per matrix within an SDG. **NOTE:** An aqueous LCS is not required for mercury and cyanide analysis.
- The Method of Standard Additions (MSA) (Form 8 or equivalent) may or may not be present as dictated by Post Digestion Spike (PDS) %Rs. See Section 4.1.3.11 for further details.
- Verify that at least one ICP serial dilution analysis was performed for each matrix within an SDG. **NOTE:** Typically one serial dilution will serve to monitor a given set of samples within an SDG. However, special contractual requirements may necessitate one serial dilution analysis per sample. Ascertain atypical serial dilution frequency requirements through the project manager.
- Simply check that the Form 11 ICP Interelement Correction Factors (Annually) is present.
- Verify that all ICP analytical results fall within the ICP Quarterly Linear Ranges provided on the Form 12 (or equivalent). Verify that no GFAA analytical results exceed the highest standard in the associated GFAA calibration.
- Verify that the Preparation Log accounts for aqueous/soil ICP, AA, mercury, and cyanide digestions/distillation as applicable.
- Examine the Form 14s (or equivalent) to verify that one and only one "X" flag has been used to signify each reported field sample result or quality control sample result. Laboratories are often careless when entering the "X" flag. The validator must verify reported results in instances of discrepancies, amend appropriate forms, and mention in letter text.

Actions - Notify the appropriate laboratory contact of required resubmittals when discrepancies are noted on the forms discussed above.

4.1.3 Technical Evaluation Summary

All data evaluations must be conducted in accordance with current and applicable USEPA Regional protocols and/or specific client contractual requirements and obligations. The applicable documents must be referenced to during the data evaluation process as this Standard Operating Procedure (S.O.P) is intended as proprietary in-house guidance for general inorganic validation practices only.

General parameters such as Data Completeness, Overall System Performance, and Detection Limits must be evaluated concurrently with the parameters discussed below.

4.1.3.1 Holding Times

Holding times are calculated from date of sample collection to date of sample analysis. The date of sample collection must be obtained from the Chain-of-Custody (COC) form. The date of sample analysis is best retrieved from the raw data but may also be obtained from the Form 14.

Sample preservation and holding time requirements are as follows:

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- Metals - 6 months; pH <2
- Mercury - 28 days; pH <2
- Cyanide - 14 days; pH >12

Preservation requirements as noted above are applicable to aqueous samples only. Solid samples do not receive preservative but require maintenance at 4°C (±2°C) during shipment and storage.

The above holding times do not apply to leachate analyses. It is suggested that the data reviewer reference SW-846 Method 1311 for any questions regarding TCLP quality control requirements and analytical procedural requirements; these vary significantly from non-TCLP analyses.

Actions - Holding time exceedances result in potentially low-biased results; thus, positive results and nondetects shall be qualified as estimated, (J) and (UJ), respectively. **NOTE:** Gross holding time noncompliances are defined as holding times which are exceeded by a factor or 2X. In these extreme cases, it is practice to reject (R) nondetects while positive results are qualified based upon professional judgment regarding the reliability of the associated data.

4.1.3.2 Initial Calibration Requirements

Calibration must be initiated daily and prior to sample analysis. The following calibration standard requirements must be verified:

- **ICP analyses** - must employ a blank and at least one standard
- **GFAA analyses** - must employ a blank and at least three standards. Additionally, the calibration correlation coefficient (r) must be checked for linearity for each GFAA analysis performed (i.e. r = 0.995 or greater)
- **Mercury analyses** - must employ a blank and at least three standards (r = 0.995 or greater).
- **Cyanide analyses** - must employ a blank and at least three standards (r = 0.995 or greater). **NOTE:** At least two additional standards (a high or low) must be distilled and compared to similar values on the curve. Values of distilled standards should agree within ±10% of undistilled standards.

4.1.3.3 Initial and Continuing Calibration Verification (ICV/CCV)

The ICV/CCV %R quality control limits are 90-110% for ICP metals, 80-120% for GFAA metals and mercury, and 85-115% for cyanide.

Actions - If ICV/CCV %Rs are low, qualify as estimated, (J) positive results and (UJ) nondetects. If ICV/CCV %Rs are high, qualify as estimated (J) positive results; nondetects remain unaffected. **NOTE:** Qualify results of only those samples associated with the noncompliant ICV or CCV (generally, those samples immediately preceding or following the noncompliant standard until the nearest in-control standard).

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4.1.3.4 Laboratory Method and Field Quality Control Blanks

Verify that a preparation blank was analyzed for each matrix and for each batch of 20 samples or each sample batch digested, whichever is more frequent. Continuing Calibration Blanks (CCBs) must be run at a frequency of 10% or every 2 hours which ever is more frequent.

The data reviewer will select the maximum contaminant level for each analyte in a particular matrix from which shall be calculated an "action level." The action level shall be established as 5X the maximum contaminant level but must be adjusted for dilution factor, moisture content, and sample weight prior to application.

ICB/CCB contamination shall be applied to all samples within an SDG. Preparation blank contamination shall be applied to samples of the same matrix only. Common practice shall be to qualify as nondetected (U) any contaminant present in a sample which is considered a laboratory artifact (i.e., < the established action level). Professional judgment must be employed when discerning the validity of a concentration present in a field quality control blank. In many instances, contamination present in these blanks can be attributable to "dirty" laboratory practice and not actual field contaminant conditions.

Negative concentrations detected in the laboratory method blanks are indicative of instrumental problems and base-line drifting. Generally, any negative concentration > IDL shall warrant estimation [(J) positives and (UJ) nondetects] of the associated sample data regardless of matrix. Action levels shall not be established for negative concentration levels.

Actions - Qualify as nondetected (U) any positive result within the action level. Qualify as estimated (J) positive results and (UJ) nondetects for analytes for which negative concentrations were noted in the laboratory method blanks (i.e., ICBs, CCBs, and/or preparation blanks).

4.1.3.5 ICP Interference Check Sample Results

Verify that all recoveries for the ICP ICS solution fall within the 80-120% quality control window established for the ICS AB solution.

Actions - For ICS %Rs <80%, qualify as estimated (J) positive results and (UJ) nondetects in affected samples. For ICS %Rs >120%, qualify as estimated (J) positive results in affected samples; nondetects are unaffected by high ICS solution AB recovery. **NOTE:** Affected samples include all samples analyzed between the initial and final solutions or within the eight hour working shift whichever occurs more frequently) which contain Al, Ca, Fe, or Mg at levels >50% of the respective concentration of Al, Ca, Fe, or Mg in the ICS True Solution A.

Next, review concentrations of the four common interfering analytes (aluminum, calcium, iron, and magnesium) in the environmental samples. Any aforementioned interferant present in the environmental samples at concentrations which exceed those present in the ICS solution for that same analyte will require calculation of estimated elemental interference stemming from high interfering analyte concentration. If the previous condition is met; review the ICP/ICS Form 4 or equivalent and note any analytes present in the ICS solution A at levels which exceed the IDL and which are not present in the ICS True solution A. Positive results in the ICS solution A indicate potentially elevated results for this analyte in the affected sample, while negative results in the ICS solution A indicate potentially suppressed results for this analyte in the affected sample.

Next, an estimated elemental interference must be calculated for each analyte > IDL present in the ICS solution A which is not present in the ICS True solution A. The following equation shall be employed:

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$$\text{Estimated elemental intf.} = \frac{[\text{Conc. affected analyte in ICS Soln A}] \times [\text{Interferent}] [\text{Conc. Sample}]}{\text{Interferent Conc. in ICS Soln A}}$$

It is advisable, although not necessary, to routinely choose the lowest concentration for the interferant level in the ICS so as to calculate the highest estimated interference possible. This method lends itself to a more conservative overall data quality review.

Estimated interferences for each affected analyte > IDL in the ICSA solution must now be compared to the reported environmental sample result for that particular analyte.

Actions - For estimated interferences < 10% of the reported sample concentration for a particular affected analyte, take no action; interference is considered negligible. For estimated interferences > 10% of the reported sample concentration for a particular affected analyte, qualify (J) positive result and/or (UJ) nondetect for affected analyte in affected sample. (NOTE: Calculation of an estimated positive (potentially elevated) interference will have no effect on a reported nondetect; thus, no action is necessary).

4.1.3.6 Matrix Spike Sample Analysis (Pre-digestion)

Verify that at least one matrix spike was performed for each matrix for a given set of samples (maximum of 20 samples) within an SDG. NOTE: Filtered and unfiltered samples are to be treated as distinctly different sample matrices and qualified accordingly. Any deviations from the referenced method shall be noted and require laboratory contact for correction.

Aqueous and soil Matrix Spike (MS) recoveries must be within the 75-125% quality control window in instances where the initial sample result is < 4X amount spiked. If the initial sample result is > 4X the amount spiked and the MS %R is noncompliant, no actions shall be taken.

Actions - For MS %Rs < 30%, qualify as estimated (J) positive results and reject (R) nondetects in affected samples. For MS %Rs < 75% but > 30%, qualify as estimated (J) positive results and (UJ) nondetects in affected samples. For MS %Rs > 125%, qualify as estimated (J) positive results in affected samples; nondetects are not compromised by high MS recovery; thus, no actions are warranted.

4.1.3.7 Laboratory Duplicate Precision

Verify that one duplicate sample analysis was performed for each group of samples (maximum of 20 samples) of a similar matrix within an SDG. Control criteria used to evaluate the aqueous laboratory duplicates are as follows:

- a control limit of $\pm 20\%$ for relative percent difference when sample and duplicate results are > 5X CRDL
- a control limit of $\pm 1X$ CRDL for the difference between the sample values when sample and/or duplicate results are < 5X CRDL

Control criteria used to evaluate solid laboratory duplicates are as follows:

- a control limit of $\pm 35\%$ for relative percent difference when sample and duplicate results are > 5X CRDL

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- a control limit of $\pm 2X$ CRDL for the difference between the sample values when sample and/or duplicate results are $< 5X$ CRDL

NOTE: Review Duplicate Summary (Form 6 or equivalent) carefully and verify that the laboratory has in fact reported a %RPD of 200% and not simply recorded the %RPD as noncalculable (in instances where the sample result is positive but the duplicate result is nondetect). Overlooking this minor point may result in incomplete sample data qualification in some instances.

Actions - For any situation involving laboratory duplicate imprecision, qualify as estimated (J) positive results and (UJ) nondetects in affected samples. **NOTE:** It is important to note in the letter text the cause of laboratory duplicate imprecision (i.e., noncompliant %RPD or noncompliant difference between sample and duplicate results).

4.1.3.8 Field Duplicate Precision

Field duplicates can be determined via Project Manager informational documents (i.e., sampling logs) or obtained from Chain-of-Custody (COC) forms. Field duplicates are generally identified as samples having identical sample collection times and dates. In instances where field duplicate samples are included with the sample data set, the following control criteria are generally used to evaluate aqueous field duplicates:

- a control limit of $\pm 30\%$ for relative percent difference when sample and duplicate results are $> 5X$ CRDL
- a control limit of $\pm 2X$ CRDL for the difference between the sample values when sample and/or duplicate results are $< 5X$ CRDL

Similarly, the following control criteria are generally used to evaluate solid field duplicates:

- a control limit of $\pm 50\%$ for relative percent difference when sample and duplicate results are $> 5X$ CRDL
- a control limit of $\pm 4X$ CRDL for the difference between the sample values when sample and/or duplicate results are $< 5X$ CRDL

NOTE: The %RPD should reflect a difference of 200% and should not simply be recorded as noncalculable in instances where the sample result is positive but the field duplicate result is nondetect. Overlooking this minor point may result in incomplete sample data qualification in some instances.

Actions - For any situation involving field duplicate imprecision, qualify as estimated (J) positive results and (UJ) nondetects in affected samples. **NOTE:** It is important to note in the letter text the cause of field duplicate imprecision (i.e., noncompliant %RPD or noncompliant difference between sample and duplicate results). Furthermore, field duplicate data qualifications, as per Brown & Root Environmental convention, shall be matrix-specific but otherwise "across-the-board" for TAL inorganic analyses.

4.1.3.9 Laboratory Control Sample Results

Verify that an LCS was analyzed for each matrix and for each batch of twenty samples or batch of samples digested (whichever is more frequent) within an SDG. The quality control criteria established for evaluation of aqueous LCS analyses are 80-120%. **NOTE:** An aqueous LCS is not required for

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mercury and cyanide analysis. Verify that all solid "found values" fall within the EPA established control limits for soils.

Actions - Aqueous LCS: In instances where aqueous LCS %R < 80%, qualify as estimated (J) positive results and (UJ) nondetects. If aqueous LCS %R > 120, qualify as estimated (J) positive results. Solid LCS: In instances where solid found value is below lower quality control limit, qualify as estimated (J) positive results and (UJ) nondetects. If solid LCS found value exceeds EPA upper limit for soils, qualify as estimated (J) positive results.

4.1.3.10 Method of Standard Additions (MSA)

Review MSA Form 8 or equivalent and verify instrument linearity by checking that all calibration correlation coefficients (r) are greater than or equal to 0.995. MSAs for a particular analyte in a particular sample may be run more than once. Check reanalyses in instances where initial MSA analysis yields (r) < 0.995. It is good practice to review one or two GFAA post-digestion spike (PDS) %Rs via reviewing unspiked and spiked sample concentrations and associated PDS recovery to verify that the Furnace Atomic Absorption Analysis Scheme has been followed as per directional guidance in the method.

Actions - If calibration correlation coefficient (r) < 0.995, qualify as estimated (J) positive result and/ or (UJ) nondetect in affected sample.

4.1.3.11 ICP Serial Dilution Analysis

Verify that all ICP analytes are included on the Form 9 (or equivalent) with corresponding recovery calculations. Check the calculated Percent Difference (%D) column in instances where the diluted sample result is nondetected. In this situation, the laboratory should report a %D of 100% and not simply list the %D as noncalculable. Overlooking this minor point may result in incomplete sample data qualification in some instances. Amend the Form 9 if necessary. All %Ds for ICP serial dilution analyses should be < 10% when concentrations of corresponding analytes in the original (undiluted) sample are minimally a factor of 50X IDL.

Actions - If %D > 10% for an analyte, and the corresponding sample concentration is > 50 IDL, qualify as estimated (J) positive results for that analyte in all samples of the same matrix. NOTE: The possibility of suppressed results exists when the ICP serial dilution %D > 10% and the diluted sample result is significantly > original (undiluted) sample result. Qualify as estimated (J) positive results and (UJ) nondetects in such instances.

4.1.3.12 Analysis Run Logs Form 14

The Form 14 or equivalent serves several useful functions. It can be used to obtain sample analysis dates as noted in the heading of the page. Secondly, it is used to record any dilutions as applicable to ICP, GFAA, mercury, and cyanide analyses. And finally, it can be used to verify GFAA PDS percent recoveries within the 85-115% quality control limits. Additionally, the data reviewer should be careful to note that one and only one "X" flag has been used to indicate each reported sample result or quality control sample result; this can be an area of frequent laboratory error.

Actions - If the PDS %R is < 85%, qualify as estimated (J) the corresponding positive result and/or (UJ) nondetect in affected sample. If the PDS %R is > 115%, qualify as estimated (J) the corresponding positive result in the affected sample; nondetects are not qualified based on high PDS % R.

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4.1.3.13 Further GFAA Evaluations

It is necessary to review the raw data for GFAA analyses and verify that all Coefficients of Variation Relative Standard Deviations (%RSDs) are <20% for reported sample results which exceed the CRDL.

Actions - If the CV or %RSD exceeds 20% and the reported sample result is > CRDL, qualify as estimated (J) positive result in affected sample.

4.1.4 **Deliverables Guidance**

In addition to any specific USEPA Regional requirements (e.g., data validation memorandum, data summary spreadsheets, USEPA Regional worksheets), all laboratory data package quality control summary forms, sample Form I reports, method blank Form Is, and the Chain-of-Custody report must be given to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct (in accordance with the appropriate USEPA Regional or client requirements) and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

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5.0 TOXICITY CHARACTERISTIC LEACHING PROCEDURE

5.1 SW-846 Method 1311

5.1.1 **Applicability**

Method 1311, the Toxicity Characteristic Leaching Procedure (TCLP), is used to determine the mobility/leaching potential of inorganic and organic contaminants in liquid, solid and multi-phase wastes and identify and characterize the waste as hazardous or nonhazardous. Wastes are extracted using two different methods. One method is used prior to the determination of metals, pesticides, and semivolatiles, while another method, zero headspace extraction (ZHE), is used prior to volatile organic analysis.

5.2 Interferences

Besides interferences noted for the specific analytical procedures and extractions, the primary concern is the loss of volatiles via aeration prior to organic determinations.

5.3 Holding Times

Preservatives are not added to samples before extraction. Samples should be stored at 4°C unless refrigeration results in irreversible physical change to the samples. Teflon-lined septum capped vials should be used for samples for volatile analysis. After extraction and prior to analysis, the pH of a TCLP extract should be adjusted to <2 if metallic concentrations are to be measured. Extracts should be preserved for other analytes according to guidance given in the individual analysis methods.

The following holding times apply to TCLP analyses:

Parameter	From Sample Collection to TCLP Extraction	From TCLP Extraction to Preparative Extraction	From Extraction to Analysis
Volatiles (VOAs)	14	Not applicable	14
Semivolatiles (BNAs)	14	7	40
Mercury (Hg)	28	Not applicable	28
All other Metals	180	Not applicable	180

Chain of Custodies (COCs) and raw data are reviewed to determine if holding times were met for all samples. If holding times were not met, all sample data will be qualified as estimated, (J) and (UJ). Nondetects in affected samples will be qualified as rejected, (R), if the holding time was exceeded by a factor of 2 or more.

5.4 Sample Preparation

The selection of extraction reagents is critical to the efficiency of the leaching potential of inorganic and organic chemicals. The extraction fluids must be prepared at pH 4.93 ±0.05 and 2.88 ±0.05 in order to properly leach contaminants in waste samples.

The determination of sample aliquot size for extraction is specified in Method 1311. The determination of percent solids must also be considered in the preparation stage.

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5.5 Quality Control

The data package will be reviewed to ensure that the following TCLP quality control (QC) requirements plus the requirements dictated by the specific analytical method have been met.

5.5.1 Blanks

At a minimum, one TCLP extraction blank should be performed for every 20 extractions that have been conducted in an extraction vessel. TCLP extraction blanks should be subjected to the same analytical equipment and preparation reagents used to extract all associated samples. Contamination observed in extraction blanks should be considered when evaluating the sample data for introduced contamination.

5.5.2 Spikes

A minimum of one matrix spike per analytical batch (maximum 20 samples) must be performed for each waste type (e.g., wastewater treatment sludge, contaminated soil, etc.) unless it is already known that the constituents of the waste exceed regulatory levels. In most cases, matrix spikes should be added at a concentration equivalent to the corresponding regulatory level, following the matrix spike addition guidance provided in the analytical method as a minimum.

Internal calibration quantitation methods (such as the method of standard additions) must be employed for a metallic contaminant when the spike %R is <50% and the concentration does not exceed the regulatory level or when the detected concentration is within 20% of the regulatory level. Associated sample results will be qualified as estimated, (J) and (UJ), if internal calibration quantitation methods were not performed when required.

Inorganic contaminant concentrations for TCLP extracts must be quantitated by the method of standard additions (MSA) if analytical methods are determined to be inadequate. MSA curves should be checked for linearity. Positive sample results will be qualified as estimated, (J), if the MSA correlation coefficient is <0.995.

5.5.3 Deliverables Guidance

In addition to any work-request requirements (e.g., data validation memorandum), all laboratory data package quality control summary forms, laboratory summaries of sample results and laboratory method blanks, and COCs must be provided for the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

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6.0 POLYCHLORINATED DIOXINS AND FURANS FOR SOLID AND AQUEOUS MATRICES

6.1 CLP/SW-846 Method 8280

6.1.1 Applicability

Method 8280 and CLP SOW DFLM1.1 are applicable for the determination of the tetra-, penta-, hexa-, hepta-, and octachlorinated congeners of dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) (by Gas Chromatography/Mass Spectrometry (GC/MS) via selective ion monitoring) in chemical wastes including fuel oils, sludges, fly ash, still bottoms, reactor residues, soil, and water.

6.1.2 Dioxin Data Package Deliverable Minimum Requirements

The following information must be present in data package prior to the validation effort:

- Appropriate Chain-of-Custody (COC) Form(s)
- Laboratory Case Narrative documenting any particular analytical anomalies encountered and sample description information (i.e., sample cross-reference identifications)
- Calibration Summaries
- Laboratory Control Sample and Duplicate forms
- Single Control Samples and Method Blank Results
- Matrix Spike/Matrix Spike Duplicates
- Retention Time Marker Solutions
- Internal and Recovery Standard Area Summaries

The appropriate laboratory liaison must be contacted immediately if any of the above items have been omitted from the data package.

6.1.3 Technical Data Evaluation

NOTE: Analysis of a fortified standard and blank may be submitted as evidence of compliant Performance Evaluation (PE) analyses as per region-specific requirements. The fortified standard will contain 2,3,7,8-TCDD at a known quantity while the fortified blank will contain 1,2,3,4-TCDD plus other known interferences. The recovery for 2,3,7,8-TCDD recognition must be within the EPA's 99% confidence interval.

6.1.4 Quality Control

6.1.4.1 Holding Times and Sample Preservation

All samples are to be extracted within 30 days of sample collection, and all subsequent analyses are to be conducted within 45 days from the date of collection. **NOTE:** Data qualification based upon holding time noncompliances is rare due to the minor effect of extended storage time on PCDD/PCDF quantitation resulting from the inherent persistence and known stability of these compounds. However, estimation of associated sample data based on holding time shall be subject to the professional judgment of the data validator.

Sample preservation shall be checked by referencing the appropriate Chain-of-Custody (COC) form(s) and verifying that all samples receiving PCDD/PCDF analysis were cooled to and stored at 4°C.

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6.1.4.2 Initial Calibration Verification

Review the average Relative Response Factors (RRFs) for all dioxin congeners by recalculating approximately 10% of the reported RRFs while also verifying proper use of quantitation ions. The following ions are specified for selective ion monitoring for PCDDs and PCDFs:

Analyte		Quantitation Ion	Confirmation Ions
PCDDs	Tetra	322	320
	Penta	356	354; 358
	Hexa	390	388; 392
	Hepta	424	422; 426
	Octa	460	458
PCDFs	Tetra	306	304
	Penta	340	338; 342
	Hexa	374	372; 376
	Hepta	408	406; 410
	Octa	444	442

Internal Standards

Analyte	Quantitation Ion	Confirmation Ion
¹³ C ₁₂ -2,3,7,8-TCDD	334	332
¹³ C ₁₂ -1,2,3,6,7,8-H _x CDD	404	402
¹³ C ₁₂ -OCDD	472	470
¹³ C ₁₂ -2,3,7,8-TCDF	318	316
¹³ C ₁₂ -1,2,3,4,6,7,8-H _p CDF	420	422

Recovery Standards

Analyte	Quantitation Ion	Confirmation Ion
¹³ C ₁₂ -1,2,3,4-TCDD	334	332
¹³ C ₁₂ -1,2,3,7,8,9-H _x CDD	404	402

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Next verify the acceptability of isotopic ratios as outlined in the following table:

Analyte		Selected Ions	Relative m/z
PCDDs	Tetra	320/322	0.65-0.89
	Penta	356/358	1.24-1.86
	Hexa	390/392	1.05-1.43
	Hepta	424/426	0.88-1.20
	Octa	458/460	0.76-1.02
PCDFs	Tetra	304/306	0.65-0.89
	Penta	340/342	1.24-1.86
	Hexa	374/376	1.05-1.43
	Hepta	408/410	0.88-1.20
	Octa	442/444	0.76-1.02

Internal Standards

Analyte	Selected Ions	Relative m/z
¹³ C12-2,3,7,8-TCDD	332/334	0.65-0.89
¹³ C12-1,2,3,6,7,8-H _x CDD	402/404	1.05-1.43
¹³ C12-OCDD	470/472	0.76-1.02
¹³ C12-2,3,7,8-TCDF	316/318	0.65-0.89
¹³ C12-1,2,3,4,6,7,8-H _p CDF	420/422	0.88-1.20

Recovery Standards

Analyte	Selected Ions	Relative m/z
¹³ C12-1,2,3,4-TCDD	332/334	0.65-0.89
¹³ C12-1,2,3,7,8,9-H _x CDD	402/404	1.05-1.43

Typically, the data reviewer can expect to associate the following congeners with their associated internal standards as follows:

Internal Standard #1 (¹³ C12-2,3,7,8-TCDD)	TCDD, PeCDD
Internal Standard #2 (¹³ C12-1,2,3,6,7,8-H _x CDD)	HxCDD, HpCDD
Internal Standard #3 (¹³ C-OCDD)	OCDD, OCDF
Internal Standard #4 (¹³ C12-TCDF)	TCDF, PeCDF
Internal Standard #5 (¹³ C12-HpCDF)	HxCDF, HpCDF

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Additionally, verify that the Relative Standard Deviation (%RSD) for all target compounds and internal standards is $\leq 15\%$.

Actions - Qualify as estimated, (J) positive results and (UJ) nondetects in affected samples if RSD is $> 15\%$.

Window Defining Mix

This is a retention time check which must be run prior to the continuing calibration. The composition of the window defining mix may or may not be known. Review the following criteria:

- Peak separation must be $\leq 25\%$ valley criterion for TCDD isomers
- Peak separation must be \leq the 50% valley criterion for HxCDD isomers
- Multiple ion detection mass chromatograms and reconstructed ion chromatograms should be present for the window defining mix

Actions - Professional judgment (weighted primarily upon chromatographic expertise) must be employed when assigning data qualifications.

6.1.4.3 Continuing Calibration Verification

Evaluation of the CCV involves evaluating the Daily Standard (which is a standard that contains the required target compounds plus internal standards), versus the initial standard.

Verify that a Continuing Calibration Verification (CCV) was analyzed prior to sample analysis and at the beginning of each subsequent 12-hour period. A CCV must also be analyzed at the end of the final analysis period.

The Signal-to-Noise ratio (S/N) for all internal standards must be $> 10:1$. No quality control criteria exist to govern internal standard recovery; however, internal standard advisory recovery limits of 40-120% were established in earlier EPA validation protocol.

Verify that the internal standard area count in the sample is -50% to +100% of the internal standard area count in the associated daily standard.

Complete one Percent Recovery ($\%R_{is}$) calculation for an internal standard as outlined in **equation A** below:

Equation A:
$$\%R_{is} = \frac{(A_{is}) (Q_{rs})}{(A_{rs}) (RRF_{is}) (Q_{is})} \times 100$$

where:

A_{is}	=	area of the quantitation ion of the internal standard
A_{rs}	=	area of the quantitation ion of the recovery standard
Q_{is}	=	ng of internal standard
Q_{rs}	=	ng of recovery standard
RRF_{is}	=	Relative Response Factor for the internal standard as determined from the associated continuing calibration

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An RRF shall be calculated for each congener in the CCV solution. A Percent Difference (%D) of 30% from the average RRF must be accomplished for the CCV. **NOTE:** Recalculate some (approximately 10%) of the continuing calibration RRFs for thoroughness.

Actions - Qualify associated sample data as estimated, i.e., (J) positive results and (UJ) nondetects in affected samples in instances where CCV %D >30%. Qualify as rejected (R) all associated sample data in instances where the internal standard S/N ratio <10:1.

6.1.4.4 Laboratory Method Blank Evaluations

Verify that a laboratory generated method blank was analyzed prior to sample analysis and for each matrix and extraction batch for all samples within an SDG. The laboratory method blanks should be free from contamination and/or interferences stemming from glassware involved in sample preparation and subsequent analytical procedures, associated reagents and solvents, etc. The following criteria shall be employed for evaluation of contaminant levels present in laboratory method blanks:

- The signal of any confirmed analyte present in a method blank must be <2% of the signal of the associated internal standard (based on peak height or peak area). Comparison of contaminants present in the blanks at levels below the calibration range (i.e., contaminants present at levels which constitute <2% of the respective internal standard) shall not require reanalyses as stipulated by the method.
- An action level of 5X the maximum contaminant level shall be used in instances of positive detections.
- The data reviewer should complete a detection limit verification calculation.
- Detection limits are sample-specific dependent upon the concentration of a given analyte to produce a signal with a peak height $\geq 2.5 X$ the background signal.
- The data reviewer shall consider all applicable sample weight, moisture content, and dilution factors prior to application of the aforementioned action level.
- The data reviewer shall recalculate at least one Detection Limit (DL) using **equation B** as follows:

Equation B:

$$DL = \frac{(2.5) (H_x) (Q_{is})}{(A_{is}) (RRF_A) (W)}$$

where:

A_{is}	=	area of the quantitation ion of the internal standard
Q_{is}	=	ng of internal standard
H_x	=	peak height of noise for the analyte's quantitation ion
RRF_{is}	=	Relative Response Factor for the analyte as determined from the associated continuing calibration
W	=	dry weight of the sample (g)

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Actions - Effects on sample data and subsequent data qualifications shall be upon the professional judgment of the data reviewer, but the following general qualifying guidance shall be employed; Qualify as nondetected (U) any positive result less than the corresponding action level.

6.1.4.5 Duplicate Control Samples

The Duplicate Control Sample (DCS) is a well-characterized matrix which is spiked and analyzed at approximately 10% of the sample load in order to establish method-specific quality control limits. The DCS spike recovery quality control limits of 60-140% shall be employed. Additionally, the RPDs between control sample and duplicate shall be below 50%.

Actions - Qualify as estimated (J) positive results in affected samples when DCS spike recoveries are >140%. Qualify as estimated (J) positive results and (UJ) nondetects in affected samples when DCS spike recoveries are <60%. Qualify as estimated (J) positive results and (UJ) nondetects in affected samples when %RPD between control and duplicate sample exceeds 50%.

6.1.4.6 Matrix Spike/Matrix Spike Duplicate Review

Verify that a matrix spike has been analyzed for each matrix and batch of samples within an SDG.

Verify that the %RSD between matrix spike and duplicate injections is $\leq 50\%$. Additionally, the following recovery limits shall be employed for the respective congeners:

Congener	Recovery Limits
TCDD	50-150%
PCDD	50-150%
HxCDD	50-150%
HpCDD	50-150%
OCDD	50-150%
TCDF	50-150%
PeCDF	50-150%
HxCDF	50-150%
HpCDF	50-150%
OCDF	50-150%

Actions - Qualify as estimated (J) only positive results in affected samples when the recovery exceeds the upper quality control limit. Qualify as estimated, (J) positive results and (UJ) nondetects in affected samples when the recovery is below the lower quality control limit.

6.1.4.7 Chromatographic Performance and Evaluation

Verify that the recovery standard area counts are within -50% to +100% of the area counts in the respective daily check standard.

Examine chromatographic acceptability by checking the chromatographic base-line for fluctuation (i.e., raising or lowering), peak shape and resolution. Proper peak resolution between 13C-2,3,7,8-TCDD and

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13C-1,2,3,4-TCDD (or 13C-2,3,7,8-TCDD and its closest eluting isomer), shall be attained at a threshold acceptability level of <25%.

Actions - Data qualification shall be based upon the professional judgment of the data reviewer.

6.1.4.8 Sample Quantitation

Confirm the quantitation of at least one Estimated Maximum Positive Concentration (EMPC). The laboratory will report an EMPC as opposed to a confirmed, definite positive hit in instances where the S/N ≥ 2.5 for both the quantitation ion and confirmation ion for a given target isomer/analyte. The following equation shall be used to verify at least one EMPC calculation:

$$EMPC = \frac{(A_x) (Q_{is})}{(A_{is}) (RRF_A) (W)}$$

where: A_x = area of the quantitation or confirmation ion, whichever is lower
 Q_{is} , A_{is} , RRF_A , and W are defined in the previous equation.

The data reviewer will also confirm at least one positive detection using the following equation:

$$C_A = \frac{(A_A) (Q_{is})}{(A_{is}) (RRF_A) (W)}$$

where: A_{is} , Q_{is} , RRF_A , and W are defined in previous equations
 C_A = analyte concentration (ng/g or ug/kg)
 A_A = analyte quantitation ion area

NOTE: EMPC values are estimates by definition. If these values are used for risk assessment, it must be understood that an EMPC value is "less certain" than positive results which are qualified (J), since the qualified results meet identification criteria while EMPCs do not.

6.1.5 **Deliverables**

In addition to any work-request requirements (e.g., data validation memorandum), all laboratory data package quality control summary forms, laboratory summaries of sample results and laboratory method blanks, and COCs must be provided to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct, and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

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7.0 MISCELLANEOUS ORGANICS

7.1 Biochemical Oxygen Demand (SM 5210B, EPA 405.1)

7.1.1 **Applicability**

This method determines oxygen requirements of municipal and industrial wastewaters by measuring the oxygen required for the biochemical degradation of organic material and the oxygen used to oxidize inorganic material such as sulfides and ferrous ion. It may also measure the oxygen used to oxidize forms of nitrogen unless their oxidation is prevented by an inhibitor. Results from this test may be used for the development of engineering criteria for the design of wastewater treatment plants.

7.1.2 **Interferences**

BOD results can be affected by contamination of the dilution water used in the analysis, the presence of toxicants, or by use of a poor seeding material. Insuring the purity of the dilution water will reduce misleading BOD results. Samples containing toxic substances may require special treatment before analysis.

7.1.3 **Holding Times**

Samples designated for BOD analysis are collected in high-density polyethylene bottles and stored at 4°C until analysis (unless samples are analyzed within 2 hours of collection). A 24 hour holding time is recommended for this method, however, the maximum holding time for BOD analyzed via EPA method 405.1 is 48 hours. If the holding time is exceeded the sample results are qualified as estimated, (J) and (UJ). Gross exceedance (>2X holding time) may warrant the rejection, (R), of nondetects.

7.1.4 **Quality Control**

7.1.4.1 Blanks

At a minimum, one laboratory method blank should be analyzed per sample batch (maximum 20 samples). The COCs should be consulted to determine if any field quality control blanks (field, rinsate, equipment, etc.) are associated with the samples. If contamination is noted in the associated blanks, positive sample results < the maximum amount detected in the blanks will be qualified as undetected, (U).

7.1.4.2 Glucose-glutamic Acid Check Standard

BOD is determined from a check standard containing a seed, and a glucose-glutamic acid solution. If the BOD value for this check standard is outside the range of 200 ±37 mg/L, BOD determinations made with the seed and diluted water are rejected.

7.1.5 **Deliverables Guidance**

The content and format of the data package generated for BOD analysis may vary significantly depending upon the work request.

In addition to any work-request requirements (e.g., data validation memorandum), all laboratory data package quality control summary forms, laboratory summaries of sample results and laboratory method

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blanks, and COCs must be provided to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

7.2 Chemical Oxygen Demand (EPA Method 410.1/410.2)

7.2.1 **Applicability**

Methods 410.1 and 410.2 determine the quantity of oxygen required to oxidize organic matter in a domestic or industrial waste sample under specific conditions of oxidizing agent, temperature, and time. Method 410.1 is applicable to samples containing an organic carbon concentration greater than 50 mg/L, which Method 410.2 is applied to samples containing an organic carbon concentration in the range of 5 to 50 mg/L.

7.2.2 **Interferences**

Traces of organic material, rise in temperature, or high concentrations of chloride may cause error in determination of COD. Glassware used in the procedure would be conditioned by running blank procedures to eliminate traces of organic material, and contamination of the distilled water used in the procedure must be avoided. Loss of volatile substances may be minimized by cooling the flask used in the analysis during the addition of the sulfuric acid solution. Positive interferences caused by chlorides are eliminated with the addition of mercuric sulfate.

7.2.3 **Holding Times**

Glass bottles are recommended for sample collection, although plastic may be permissible if the containers are free of organic material contamination. Samples are preserved with sulfuric acid to a pH <2 and stored at 4°C until analysis. The maximum holding time specified (from sample collection to analysis) is 28 days. (The method does recommend that biologically active samples be tested as soon as possible.) Sample results will be qualified as estimated, (J) and (UJ), if this holding time is exceeded. Gross holding time exceedances (>2X holding time) will warrant rejection (R); of nondetects.

7.2.4 **Quality Control**

7.2.4.1 Blanks

A low COD water blank must be run simultaneously with the environmental sample to quantitate the amount of COD present in the environmental sample. Additionally, one laboratory method blank should be analyzed per sample batch. The COCs should be consulted to determine if any field quality control blanks (field, rinsate, equipment, etc.) are associated with the samples. If contamination is noted in the associated blanks, positive sample results < the maximum amount detected in the blanks will be qualified as undetected, (U).

7.2.5 **Deliverables Guidance**

The content and format of the data package generated for COD analysis may vary significantly depending upon the work request.

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In addition to any work-request requirements (e.g., data validation memorandum), all laboratory data package quality control summary forms, laboratory summaries of sample results and laboratory method blanks, and COCs must be provided to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

7.3 Total Recoverable Petroleum Hydrocarbons (EPA 418.1)

7.3.1 **Applicability**

EPA Method 418.1 is used to measure the amount of fluorocarbon-113 extractable petroleum hydrocarbons from aqueous matrices. With modification, solid waste petroleum hydrocarbons can also be measured. Infrared analysis of a waste sample extract is performed by direct comparison with a calibration standard plot.

7.3.2 **Interferences**

The measurement of petroleum hydrocarbons by infrared analysis is subject to interference. The addition of silica gel to the sample reduces the effects of interference.

7.3.3 **Holding Times**

Samples are collected in glass bottles. Aqueous samples are preserved with hydrochloric acid to a pH <2 and are cooled to 4°C. Solid samples are stored at 4°C until analysis.

A 28-day holding time is used to evaluate the samples. Chain of Custodies (COCs) and raw data are reviewed to determine if holding times were met for all samples. Samples results will be qualified as estimated, (J) and (UJ), if holding times are exceeded. Gross holding time violations (>2X holding time) will warrant rejection. (R), of nondetects.

7.3.4 **Quality Control**

Quality control criteria are not specified in Method 418.1. However, if quality control analyses are performed by the laboratory, the following criteria will be used to evaluate the associated data.

7.3.4.1 Calibration

The calibration curve of absorbance versus concentration of petroleum hydrocarbons in known standards should be checked for linearity. Generally, associated sample data are qualified as estimated, (J) and (UJ), if the calibration curve correlation coefficient is <0.995. Professional judgment should be used to qualify sample data in cases when sample results fall outside the linear portion of the calibration curve.

If analyzed, the percent recovery (%R) of a continuing calibration verification (CCV) standard will be evaluated using an 85-115% quality control range. Associated sample data will be qualified as estimated, (J) and (UJ), if the CCV %R is <85%. Only positive results in the affected samples will be qualified as estimated, (J), if the CCV %R is >115%.

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7.3.4.2 Blanks

Laboratory method blanks, if analyzed, should be evaluated for contamination. The COCs should be consulted to determine if any field quality control blanks (field, rinsate, equipment, etc.) are associated with the samples. If contamination is noted in any of the associated blanks, positive sample results < the maximum amount detected in the blanks will be qualified as undetected, (U). Sample aliquot and moisture content factors will be taken into consideration when qualifying the associated sample data.

7.3.4.3 Spikes/Duplicates

If a spiked sample is analyzed, a 75-125% quality control range will be used to evaluate the spike %R. Associated sample data will be qualified as estimated, (J) and (UJ), when the spiked sample %R is < 75%. When the %R is > 125%, only positive results are impacted and qualified as estimated, (J). If a spike %R is < 30%, associated nondetects will be qualified as rejected, (R), and positive results will be qualified as estimated, (J).

7.3.4.4 Duplicates

Qualification of sample data based on duplicate precision is left to the professional judgment of the validator. Generally, a $\pm 20\%$ aqueous quality control limit and a $\pm 30\%$ solid quality control limit are used to evaluate the Relative Percent Difference (RPD) between the sample and laboratory duplicate results; a $\pm 30\%$ aqueous quality control limit and a $\pm 50\%$ solid quality control limit are generally used to evaluate the RPD between field duplicate results; qualification based on field duplicate imprecision is applied only to the field duplicate pair for general chemistry parameters.

7.3.4.5 Sample Quantitation

All reported sample concentrations should fall within the range of the calibration curve. If samples containing concentrations > the highest calibration standard were not diluted and reanalyzed, the associated sample data will be qualified as estimated, (J).

Verify that sample results were properly quantitated.

7.3.5 **Deliverables Guidance**

The content and format of the data package generated for petroleum hydrocarbon analysis may vary significantly depending upon the work request.

In addition to any work-request requirements (e.g., data validation memorandum), all laboratory data package quality control summary forms, laboratory summaries of sample results and laboratory method blanks, and COCs must be provided to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

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7.4 Total Organic Carbon (EPA SW846 Method 9060)

7.4.1 Applicability

Method 9060 is used to measure concentrations of total organic carbon (TOC) in excess of 1 mg/L in domestic and industrial wastes, groundwater, and surface and saline waters. The organic carbon is first converted to carbon dioxide; the CO₂ is then measured directly using an infrared detector or converted to methane and measured by a flame ionization detector.

7.4.2 Interferences

The presence of inorganic carbon (i.e., carbonate and bicarbonate) must be considered. These substances can be accounted for in the sample calculation or eliminated by acidification and degassing before analysis. If degassing is utilized, volatilization of organic carbon can occur.

7.4.3 Holding Times

Although it is preferable that samples are collected in glass bottles, plastic containers may be used if it is established that the containers do not contribute contaminating organics to the samples. Samples are preserved with hydrochloric or sulfuric acid to a pH < 2 and are cooled to 4°C. Protection from light is important for TOC analysis.

Although a precise holding time (elapsed time period from sample collection to analysis) is not stated in the method, a 28-day holding time will be used to evaluate the samples. Chain of Custodies (COCs) and raw data are reviewed to determine if holding times were met for all samples. Samples results will be qualified as estimated, (J) and (UJ), if holding times are exceeded. Gross holding time violations (>2X holding time) will warrant rejection, (R), of nondetects.

7.4.4 Quality Control

7.4.4.1 Calibration

A calibration curve should be prepared comparing concentrations of known standards to actual TOC readings. (Samples should be analyzed in quadruplicate; the average value and the range of readings should be reported.) The calibration curve should be checked for linearity. Generally, associated sample data are qualified as estimated, (J) and (UJ), if the calibration curve correlation coefficient is < 0.995. Professional judgment should be used to qualify sample data in cases when sample results fall outside the linear portion of the calibration curve.

The method requires that a continuing calibration verification (CCV) standard be analyzed every 15 samples. An 85-115% quality control range will be used to evaluate the percent recovery (%R) of the CCV. Associated sample data will be qualified as estimated, (J) and (UJ), if the CCV %R is < 85%. Only positive results in the affected samples will be qualified as estimated, (J), if the CCV %R is > 115%.

7.4.4.2 Blanks

At a minimum, one laboratory method blank (other than the blank used for the calibration curve) should be analyzed per sample batch (maximum of 20 samples). The COCs should be consulted to determine if any field quality control blanks (field, rinsate, equipment, etc.) are associated with the samples. If contamination is noted in the associated blanks, positive sample results < the maximum amount

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detected in the blanks will be qualified as undetected, (U). Sample digestion and moisture content factors will be taken into consideration when qualifying the associated sample data.

7.4.4.3 Spikes/Duplicates

A spiked sample and spiked duplicate sample should be analyzed for every 10 samples. If a spike or duplicate spike %R is <75%, the associated sample data will be qualified as estimated, (J) and (UJ). If the %R is >125%, only positive results are impacted and qualified as estimated, (J). If a spike %R is <30%, associated nondetects will be qualified as rejected, (R), and positive results will be qualified as estimated. (J).

Qualification of sample data based on duplicate precision is left to the professional judgment of the validator. Generally, a $\pm 20\%$ aqueous quality control limit and a $\pm 30\%$ solid quality control limit are used to evaluate the relative percent difference (RPD) between the spiked sample and spiked duplicate sample results. A $\pm 30\%$ aqueous control limit and a $\pm 50\%$ solid quality control limit are generally used to evaluate the RPD between field duplicate results; qualification based on field duplicate imprecision is applied only to the field duplicate pair for general chemistry parameters.

7.4.4.4 Sample Quantitation

All reported sample concentrations should fall within the range of the calibration curve. If samples having concentrations > the highest calibration standard were not diluted and reanalyzed, the associated sample data will be qualified as estimated, (J).

Verify that sample results were properly quantitated.

7.4.5 **Deliverables Guidance**

The content and format of the data package generated for TOC analysis may vary significantly depending upon the work request.

In addition to any work-request requirements (e.g., data validation memorandum), all laboratory data package quality control summary forms, laboratory summaries of sample results and laboratory method blanks, and COCs must be provided to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct, and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

7.5 **Total Organic Halides (EPA SW-846 Method 9020B)**

7.5.1 **Applicability**

Method 9020B uses carbon adsorption with a microcoulometric-titration detector to measure the concentration of total organic halides (TOX) as chloride in drinking and ground waters. This method detects all organic halides containing chlorine, bromine, and iodine.

- Organic halides containing fluorine cannot be measured.
- TOX adsorbed to undissolved solids cannot be measured.

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- The concentration of inorganic halides in the sample can not exceed the organic halide concentration by a factor >20,000.

7.5.2 Interferences

Interferences from contaminated reagents, glassware, activated carbon, and other laboratory devices must be minimized. Special care must be taken to clean, dry, and store materials used during analysis to protect against contamination from halogenated organic vapors and oily residue.

Suspended matter, which can clog adsorption columns, must be eliminated prior to sample analysis by decanting the aqueous phase or centrifuging to separate undissolved materials.

7.5.3 Holding Times

Samples should be collected in duplicate, preserved with sulfuric acid to a pH <2, and cooled to 4°C. Plastic or glass containers may be used. All samples must be protected from light.

Samples must be analyzed within 28 days of collection. Chain of Custodies (COCs) and raw data are reviewed to determine if holding times were met for all samples. Samples results will be qualified as estimated, (J) and (UJ), if holding times are exceeded. Gross holding time violations (>2X holding time) will warrant rejection (R), of nondetects.

7.5.4 Quality Control

7.5.4.1 Calibration

Pyrolyzation

The following requirements must be met during the pyrolysis stage:

- The adsorption efficiency of the activated carbon must be checked. The percent recovery (%R) of a standard should be within $\pm 10\%$.
- A nitrate-wash blank must be run after every 10 pyrolyzations.
- Pyrolysis instrument calibration standards, which should be run after every 10 determinations, must be analyzed in duplicate. The %R for these standards must be within $\pm 10\%$ of the true value.

If any of these requirements have not been met, associated sample data will be qualified as estimated, (J) and (UJ).

Microcoulometric Analysis

The method requires that a continuing calibration verification (CCV) standard be analyzed every 15 samples. Although the method does not specify criteria to evaluate the CCV, an 85-115% quality control range will be used for validation purposes. Affected sample data will be qualified as estimated, (J) and (UJ), if the CCV %R is <85%. Only positive results in the affected samples will be qualified as estimated, (J), if the CCV %R is >115%.

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7.5.4.2 Blanks

A minimum of two method blanks (other than the blanks used for the calibration and pyrolyzation) should be analyzed to establish the repeatability of the method background and the background should be monitored by analyzing method blanks after every eight samples. The COCs should be consulted to determine if any field quality control blanks (field, rinsate, equipment, etc.) are associated with the samples. If contamination is noted in the associated blanks, positive sample results < the maximum amount detected in the blanks will be qualified as undetected, (U). Dilution factors will be taken into consideration when qualifying the associated sample data. (Nitrate-wash blanks, which are considered to be laboratory method blanks, should not be used to qualify sample results since contamination in these blanks is already accounted for in the sample calculation.)

7.5.4.3 Spikes/Duplicates

A spiked sample should be analyzed between every 10 samples. If a spike or duplicate spike %R is not within 75-125%, the associated sample data will be qualified as estimated, (J) and (UJ). If the %R is >125%, only positive results are impacted and qualified as estimated, (J). If a spike %R is <30%, associated nondetects will be qualified as rejected, (R), and positive results will be qualified as estimated, (J).

The method requires that all samples be seen in duplicate. Qualification of sample data based on duplicate precision is left to the professional judgment of the validator. Generally, a ±20% aqueous quality control limit and a ±30% solid quality control limit are used to evaluate the relative percent difference (RPD) between the sample and laboratory duplicate sample results. A ±30% aqueous quality control limit and a ±50% solid quality control limit are generally used to evaluate the RPD between field duplicate results; qualification based on field duplicate results for general chemistry parameters are applied to the field duplicate pair only.

7.5.4.4 Breakthrough

Check the extent of organohalide breakthrough from the first column. The second column measurement should not exceed 10% of the sum of the measurements from both columns. Positive results will be estimated, (J), if the 10% quality control limit was exceeded.

7.5.4.5 Sample Quantitation

The following equation is used to calculate TOX:

$$TOX (\mu g/L) = \frac{(conc_1 - conc_{blank}) + (conc_2 - conc_{blank})}{vol_{sample}}$$

where:

conc ₁	=	concentration of chloride measured on first column (μg)
conc ₂	=	concentration of chloride measured on second column (μg)
conc _{blank}	=	average, daily concentration in nitrate-wash blanks (μg)
vol	=	volume of sample aliquot (L)

Verify that sample results were accurately quantitated.

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7.5.5 Deliverables Guidance

The content and format of the data package generated for TOX analysis may vary significantly depending upon the work request.

In addition to any work-request requirements (e.g., data validation memorandum), all laboratory data package quality control summary forms, laboratory summaries of sample results and laboratory method blanks, and COCs must be provided to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

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8.0 MISCELLANEOUS INORGANICS

8.1 Carbonate/Bicarbonate Alkalinity (EPA 600 Series Method 310.2)

8.1.1 Applicability

Method 310.2 is an automated method used to measure alkalinity (as CaCO_3) at concentrations ranging from 10 to 200 mg/L in domestic and industrial effluents, and drinking, surface and saline waters.

8.1.2 Interferences

Since the method of analysis is colorimetric, primary interferences for this method include turbidity and color. Samples can be filtered prior to analysis to reduce interferences from turbidity.

8.1.3 Holding Times

Samples should be collected in plastic or glass containers and cooled to 4°C. No preservative is needed.

Holding time is defined as the elapsed time period from sample collection to analysis. The holding time for this method is 14 days. Chain of Custodies (COCs) and raw data are reviewed to determine if holding times were met for all samples. Positive results and nondetects will be qualified as estimated, (J) and (UJ), respectively, if holding times were exceeded. Gross holding time violations (>2X holding time) will warrant rejection, (R), of nondetects.

8.1.4 Quality Control

Quality control analyses and criteria (i.e., calibrations, blanks, spikes, etc.) are not specified in Method 310.2. However, if these analyses were performed by the laboratory, the following criteria will be used to evaluate the associated sample data.

8.1.4.1 Calibration

According to the method, a calibration curve should be prepared by plotting peak heights of standards to known concentrations. This curve should be checked for linearity. Generally, associated sample data are qualified as estimated, (J) and (UJ), if the calibration curve correlation coefficient is <0.995. Professional judgment should be used to qualify sample data in cases when sample results fall outside the linear portion of the calibration curve.

If analyzed, the percent recovery (%R) of a continuing calibration verification (CCV) standard will be evaluated using an 85-115% quality control range. Associated sample data will be qualified as estimated, (J) and (UJ), if the CCV %R is <85%. Only positive results in the affected samples will be qualified as estimated, (J), if the CCV %R is >115%.

8.1.4.2 Blanks

Laboratory method and field quality control blanks, if analyzed, should be identified and assessed for introduced contamination. Field quality control blanks (field, rinsate, equipment, etc.) can be identified by consulting the COCs. If contamination is noted in the associated blanks, positive sample results < the maximum amount detected in the blanks will be qualified as undetected, (U). Sample digestion and moisture content factors will be taken into consideration when qualifying the associated sample data.

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8.1.4.3 Spikes

If a spiked sample is analyzed, a 75-125% quality control range will be used to evaluate the spike %R. Associated sample data will be qualified as estimated, (J) and (UJ), when the spiked sample %R is <75%. When the %R is > 125%, only positive results are impacted and qualified as estimated, (J). If a spike %R is <30%, associated nondetects will be qualified as rejected, (R), and positive results will be qualified as estimated. (J).

8.1.4.4 Duplicates

Qualification of sample data based on duplicate precision is left to the professional judgment of the validator. Generally, an aqueous quality control limit of $\pm 20\%$ and a solid quality control limit of $\pm 30\%$ is used to evaluate the relative percent difference (RPD) between the sample and laboratory duplicate results. An aqueous quality control limit of $\pm 30\%$ and a solid quality control limit of $\pm 50\%$ are generally used to evaluate the RPD between field duplicate results: qualification based on field duplicate imprecision for general chemistry parameters is applied to the field duplicate pair only.

8.1.4.5 Sample Quantitation

All reported sample concentrations should fall within the range of the calibration curve. If samples having detected concentrations > the highest calibration standard were not diluted and reanalyzed, associated sample data will be qualified as estimated, (J).

The validator should verify that sample results were properly quantitated.

8.1.5 **Deliverables Guidance**

The content and format of the data package generated for alkalinity analysis may vary significantly depending upon the work request.

In addition to any work-request requirements (e.g., data validation memorandum), all laboratory data package quality control summary forms, laboratory summaries of sample results and laboratory method blanks, and COCs must be provided to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

8.2 **Anions (EPA Method 300.0)**

The Determination of Inorganic Anions in Water by Ion Chromatography

8.2.1 **Applicability**

Method 300.0 is a Ion Chromatographic (IC) Procedure used to determine the inorganic anions chloride, fluoride, nitrate (as nitrogen), nitrite (as nitrogen), ortho-phosphate (as phosphorus), and sulfate in drinking water, surface water, and mixed domestic and industrial wastewater.

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8.2.2 Interferences

Interferences may be caused by particulates or other substances present in the sample that may have retention times similar to the particular anion of interest. Also, a large concentration of one anion may mask the resolution of an adjacent anion. Sample dilution and/or spiking (to generate a sample-specific calibration) may be employed to resolve these problems. Additionally, method interferences may be caused by contaminants in reagent water, reagents, glassware, and other elements of sample processing.

The fluoride peak, in particular, may be affected by a water dip (a negative peak) that elutes near it. This problem can be eliminated by the addition of 1 mL of concentrated sodium carbonate eluent solution to 100 mL of each standard and sample.

8.2.3 General Laboratory Practices

The laboratory should spike and analyze a minimum of 10% of all samples to monitor continuing laboratory performance. Field and laboratory duplicates should also be analyzed.

Validation: The validator should check the work request to ascertain what contracted quality control analyses are required. Likewise, the validator should check with the project manager to determine which samples (if any) are field duplicates or field quality control blanks.

Before any analyses are performed the laboratory must demonstrate the ability to generate acceptable accuracy and precision using a blank spike sample (laboratory control sample; LCS), which is a reagent water blank spiked with a known concentration of stock standard solutions at the concentrations stipulated in EPA Method 300.0, Sections 8.2.2 through 8.3.1.

Analysis of this blank spike sample will indicate the accuracy of the measurement via the calculation of Percent Recovery (%R). Upper and lower control limits for %Rs should be calculated. These control limits can then be used to construct control charts that may be useful in observing trends in performance. This blank spike sample should also be duplicated and analyzed to indicate precision of the measurements between identical samples through comparison of the recoveries generated via the blank spike and blank spike duplicate analyses. The blank spike/blank spike duplicate analyses should be performed with the same frequency as matrix spike/matrix spike duplicate analyses.

Validation: The data reviewer shall examine The %Rs to determine if they are within the laboratory generated control limits. If %Rs are below the control limits positive results will be qualified (J) and nondetected results will be qualified (UJ). If %Rs are above the control limits only positive results will be qualified (J). If %Rs are extremely low (less than 10%) the laboratory should reanalyze the blank spike and blank spike duplicate samples. If the laboratory does not reanalyze these samples then qualifications are necessary. Positive results will be qualified as estimated (J) and nondetects will be rejected (R), when %Rs are less than 10%.

The reviewer should also examine the Relative Percent Difference (RPD) between the calculated %Rs. If the RPD is above an acceptable level qualify positive results (J) and use professional judgment to determine if nondetects should be qualified (UJ).

8.2.4 Holding Times

The following table indicates sample preservation and holding time requirements:

Analyte	Preservation	Holding time
Chloride	None required	28 days
Fluoride	None require	28 days
Nitrate-N	Cool to 4°C	48 hours
Nitrite-N	Cool to 4°C	48 hours
o-Phosphate-P	Filter & cool to 4°C	48 hours
Sulfate	Cool to 4°C	28 days

Validation: Holding times are calculated from time of collection obtained from Chain-of-Custody (COC) forms to time of analysis. Positive results in samples analyzed past holding times are qualified as estimated (J); nondetects (UJ). If holding times are exceeded by a factor of 2 or more it is considered to be a gross exceedance; positive results are qualified as estimated, (J), and nondetects are rejected, (R). Results are considered to be biased low when holding times are exceeded.

8.2.5 Sample Preparation

Samples containing particles greater than 0.45 microns and reagent solutions containing particles greater than 0.20 microns require filtration to prevent damage to the instrument columns and flow systems.

8.2.6 Calibration and Testing

Per each analyte of interest, calibration standards at a minimum of 3 concentration levels should be prepared (generated from a stock solution and diluted appropriately) and analyzed along with a blank. One of the standard concentrations must be near but above the MDL. A sufficient number of standards should be analyzed to accurately define a calibration curve.

A consistent aliquot (injections of 0.1 to 1.0 mL) for samples and standards must be used. An automated constant volume injection system may be employed.

Calibration for each analyte should be verified daily, or whenever the anion eluent is changed, and after every 20 samples. Retention times must agree within $\pm 10\%$. If agreement is not met a new calibration curve should be generated for that analyte.

Validation: The validator will evaluate the 3-point calibration and verify that one of the points was at a concentration near the MDL. Next, the retention times will be examined to ensure that they agree within $\pm 10\%$. If the retention time is outside the $\pm 10\%$ window, the result for the affected analyte will be qualified as estimated; (J) positive results and (UJ) nondetects.

If peak response exceeds the linear calibration range of the instrument, the sample should be diluted with the appropriate amount of reagent water and reanalyzed. If the chromatogram does not produce adequate resolution or if identification of the chromatographic peaks are questionable, the sample should be spiked with the appropriate amount of standard and reanalyzed.

Validation: The validator will review chromatograms to verify the absence of a water dip (see Section 8.2.2) and to verify that peak responses are within the linear range and that adequate resolution was achieved. If any noncompliances exist they should be noted. Qualifications will be made per situation, based upon professional judgment.

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8.2.7 Blank Contamination

Method blanks (reagent water) should be analyzed at the beginning of each sample batch (maximum of 20 samples) to ensure that there is no carryover or contamination from glassware and/or reagents.

Validation: Blank results should be reported for each sample data set. If contamination is noted in the blanks, the maximum concentration of each contaminant should be used to set action. Action levels are set using professional judgment based upon comparability of the sample result with concentration of the blank contaminant. Results reported for contaminants found in samples that are greater than the detection limit and within the action level are qualified as undetected, (U). The same process is repeated for field quality control blanks.

8.2.8 Sample Quantitation

A standard curve should be generated by plotting anion peak size in area units against standard anion solution concentration values. Sample concentration can then be calculated by comparing sample peak response with the standard curve. Sample data results should be reported in mg/L.

Validation: The validator shall compare sample results against standard results to confirm that the samples were properly quantitated.

8.2.9 Deliverables Guidance

The content and format of the data package generated for anion analysis may vary significantly dependent upon the work request.

In addition to any work-request requirements (e.g., data validation memorandum, data spread sheet), all laboratory data package quality control summary forms, laboratory summaries of sample data results and method blank analyses and the chain-of-custody report must be given to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

8.3 Bromide (EPA 600 Series Method 320.1)

8.3.1 Applicability

Method 320.1 is a titrimetric method used to determine the concentration of bromide in domestic and industrial effluents, and drinking, surface and saline waters. Bromide concentrations ranging from 2 to 20 mg/L can be measured by this method.

8.3.2 Interferences

Interferences can be caused by the presence of organic matter, iron, and manganese. Pretreatment of samples with calcium oxide removes or reduces these interferences to insignificant concentrations.

Color interferes with the observation of indicator and bromine-water color changes. Steps can be taken during analysis to eliminate this interference (e.g., the use of a pH meter instead of a pH indicator).

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8.3.3 Holding Times

Samples should be collected in plastic or glass bottles and cooled to 4°C. No preservative is needed.

Holding time is defined as the elapsed time period from sample collection to analysis. A 28-day holding time is specified for analysis. Chain of Custodies (COCs) and raw data are reviewed to determine if holding times were met for all samples. Positive results and nondetects will be qualified as estimated, (J) and (UJ), respectively, if holding times were exceeded. Gross holding time violations (>2X holding time) will warrant rejection, (R), of nondetects.

8.3.4 Quality Control

Quality control analyses (i.e., blanks, spikes, etc.) are not specified in Method 320.1. However, if these analyses were performed by the laboratory, the following criteria will be used to evaluate the associated sample data.

8.3.4.1 Verification Standard

The percent recovery (%R) of a verification standard, if analyzed, will be evaluated using an 85-115% quality control criteria. Associated sample data will be qualified as estimated, (J) and (UJ), if the %R is <85%. Only positive results in the affected samples will be qualified as estimated, (J), if the %R is >115%.

8.3.4.2 Blanks

Laboratory method and field quality control blanks, if analyzed, should be evaluated for contamination. Field quality control blanks (field, rinsate, equipment, etc.) can be identified by consulting the COCs. If contamination is noted in the associated blanks, positive sample results < the maximum amount detected in the blanks will be qualified as undetected, (U). Sample digestion and moisture content factors will be taken into consideration when qualifying the associated sample data.

8.3.4.3 Spikes

If a spiked sample is analyzed, a 75-125% quality control range will be used to evaluate the spike %R. Associated sample data will be qualified as estimated, (J) and (UJ), when the spiked sample %R is <75%. When the %R is >125%, only positive results are impacted and qualified as estimated, (J). If a spike %R is <30%, associated nondetects will be qualified as rejected, (R), and positive results will be qualified as estimated, (J).

8.3.4.4 Duplicates

Qualification of sample data based on duplicate precision is left to the professional judgment of the validator. Generally, an aqueous quality control limit of $\pm 20\%$ and a solid quality control limit of $\pm 30\%$ is used to evaluate the relative percent difference (RPD) between the sample and laboratory duplicate results. An aqueous quality control limit of $\pm 30\%$ and a solid quality control limit of $\pm 50\%$ are generally used to evaluate the RPD between field duplicate results; qualification based on field duplicate imprecision for general chemistry parameters is applied to the field duplicate pair only.

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8.3.4.5 Sample Quantitation

All reported sample concentrations should fall within the range of 2 to 20 mg/L. If samples having detected concentrations >20 mg/L were not diluted and reanalyzed, the associated sample data will be qualified as estimated, (J).

The validator should verify that sample results were properly quantitated.

8.3.5 **Deliverables Guidance**

The content and format of the data package generated for bromide analysis may vary significantly depending upon the work request.

In addition to any work-request requirements (e.g., data validation memorandum), all laboratory data package quality control summary forms, laboratory summaries of sample results and laboratory method blanks, and COCs must be provided to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

8.4 Fluoride (EPA 600 Series Method 340.2)

8.4.1 **Applicability**

Method 340.2 is a potentiometric method which uses an ion selective electrode to measure concentrations of fluoride in domestic and industrial effluents, and drinking, surface and saline waters. The practical range of determination is 0.1 to 1,000 mg/L.

8.4.2 **Interferences**

The pH of samples can cause significant interferences. The ideal pH range of a sample is between 5 and 9.

Complexing cations, such as Si^{+4} , Fe^{+3} , and Al^{+3} , can produce additional interferences during fluoride determinations. Samples can be treated with a pH 5.0 buffer containing a strong chelating agent to eliminate these interferences.

8.4.3 **Holding Times**

Samples are to be collected in plastic bottles. No preservative is required.

A 28-day holding time (elapsed time period from sample collection to analysis) is specified for analysis. Chain of Custodies (COCs) and raw data are reviewed to determine if holding times were met for all samples. Sample data will be qualified as estimated, (J) and (UJ), if holding times were exceeded. Gross holding time violations (>2X holding time) will warrant rejection, (R), of nondetects.

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8.4.4 Quality Control

Quality control analyses (i.e., calibrations, blanks, spikes, etc.) are not specified in Method 340.2. However, if these analyses were performed by the laboratory, the following criteria will be used to evaluate the associated sample data.

8.4.4.1 Calibration

According to the method, the calibration curve should consist of standards ranging in concentration from 0 to 2 mg/L. Semi-logarithmic graph paper should be used to plot the known concentration of the standard versus the electrode potential.

If a continuing calibration verification (CCV) standard is analyzed, the percent recovery of the standard will be evaluated using 85-115% quality control limits. Associated sample data will be qualified as estimated, (J) and (UJ), if the CCV %R is <85%. Only positive results in the affected samples will be qualified as estimated, (J), if the CCV %R is >115%.

8.4.4.2 Blanks

Laboratory method and field quality control blanks, if analyzed, should be assessed for introduced contamination. Field quality control blanks (field, rinsate, equipment, etc.) can be identified by consulting the COCs. If contamination is noted in the associated blanks, positive sample results < the maximum amount detected in the blanks will be qualified as undetected, (U). Sample digestion and moisture content factors will be taken into consideration when qualifying the associated sample data.

8.4.4.3 Spikes

If a spiked sample is analyzed, a 75-125% quality control range will be used to evaluate the spike %R. Associated sample data will be qualified as estimated, (J) and (UJ), when the spiked sample %R is <75%. If the %R is >125%, only positive results are impacted and qualified as estimated, (J). If a spike %R is <30%, associated nondetects will be qualified as rejected, (R), and positive results will be qualified as estimated, (J).

8.4.4.4 Duplicates

Qualification of sample data based on duplicate precision is left to the professional judgment of the validator. Generally, an aqueous quality control limit of $\pm 20\%$ and a solid quality control limit of $\pm 30\%$ is used to evaluate the relative percent difference (RPD) between the sample and laboratory duplicate results. An aqueous quality control limit of $\pm 30\%$ and a solid quality control limit of $\pm 50\%$ is used to evaluate the RPD between field duplicate results; qualification based on field duplicate imprecision for general chemistry parameters is applied to the field duplicate pair only.

8.4.4.5 Sample Quantitation

All reported sample concentrations should fall in the range of the calibration curve. If samples having detected concentrations > the highest calibration standard were not diluted and reanalyzed, associated sample data will be qualified as estimated, (J).

The validator should verify that sample results were properly quantitated.

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8.4.5 Deliverables Guidance

The content and format of the data package generated for fluoride analysis may vary significantly depending upon the work request.

In addition to any work-request requirements (e.g., data validation memorandum), all laboratory data package quality control summary forms, laboratory summaries of sample results and laboratory method blanks, and COCs must be provided to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

8.5 Nitrogen (Various)

8.5.1 Nitrate-Nitrogen (EPA 300 Series Method 352.1)

8.5.1.1 Applicability

Method 352.1 is a brucine, colorimetric method used to measure nitrate-nitrogen at concentrations ranging from 0.1 to 2 mg/L in domestic and industrial effluents, and drinking, surface and saline waters.

8.5.1.2 Interferences

The following is a list of interferences observed for this method:

- Uniform temperature control is extremely critical during the color development stage. Erratic heating can produce inconsistent results.
- Strong oxidizing or reducing agents, residual chloride, ferrous and ferric iron, quadrivalent manganese, and salinity in samples can create interferences.
- Interferences from naturally colored samples and dissolved organic matter can affect color during heating and produce erroneous results.

8.5.1.3 Holding Times

Samples should be collected in plastic or glass containers and cooled to 4°C.

The holding time, elapsed time period from sample collection to analysis, for this method is 48 hours. Chain of Custodies (COCs) and raw data are reviewed to determine if holding times were met for all samples. Positive results and nondetects will be qualified as estimated, (J) and (UJ), respectively, if holding times were exceeded. Gross holding time violations (>2X holding time) will warrant rejection, (R), of nondetects.

8.5.1.4 Quality Control

Quality control analyses (i.e., calibrations, blanks, spikes, etc.) are not specified in this method. However, if these analyses were performed by the laboratory, the following criteria will be used to evaluate the associated sample data.

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Calibration

A calibration curve should be prepared by plotting absorbances of standards against known concentrations. Because the color reaction does not always obey Beer's Law, qualification of sample data based on nonlinear calibration curves may be inappropriate. Professional judgment should be used to qualify sample data when nonlinearity (calibration curve correlation coefficient <0.995) is encountered.

The percent recovery (%R) of a continuing calibration verification (CCV) standard, if analyzed, will be evaluated using an 85-115% quality control criteria. If the %R is <85%, associated sample data will be qualified as estimated, (J) and (UJ). Only positive results in the affected samples will be qualified as estimated, (J), if the CCV %R is >115%.

Blanks

If analyzed, laboratory method and field quality control blanks should be assessed for contamination. Field quality control blanks (field, rinsate, equipment, etc.) can be identified by consulting the COCs. If contamination is noted in the associated blanks, positive sample results < the maximum amount detected in the blanks will be qualified as undetected, "U." Sample digestion and moisture content factors will be taken into consideration when qualifying the associated sample data.

Spikes

A 75-125% quality control range will be used to evaluate %Rs if a spiked sample was analyzed. Associated sample results will be qualified as estimated, (J) and (UJ), when the spiked sample %R is <75%. If the %R is >125%, only positive results are impacted and qualified as estimated, (J). Associated nondetects will be qualified as rejected, (R), and positive results will be qualified as estimated, (J), if the spike %R is <30%.

Duplicates

Qualification of sample data based on duplicate precision is left to the professional judgment of the validator. Generally, an aqueous quality control limit of $\pm 20\%$ and a solid quality control limit of $\pm 30\%$ is used to evaluate the relative percent difference (RPD) between the sample and laboratory duplicate results. An aqueous quality control limit of $\pm 30\%$ and a solid quality control limit of $\pm 50\%$ is used to evaluate the RPD between field duplicate results; qualification based on field duplicate imprecision for general parameters is applied to the field duplicate pair only.

Sample Quantitation

All reported sample concentrations should fall within the range of the calibration curve. If samples having detected concentrations > the highest calibration standard were not diluted and reanalyzed, associated sample data will be qualified as estimated, (J).

The validator should verify that sample results were properly quantitated.

8.5.1.5 Deliverables Guidance

The content and format of the data package generated for this method of analysis may vary significantly depending upon the work request.

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In addition to any work-request requirements (e.g., data validation memorandum), all laboratory data package quality control summary forms, laboratory summaries of sample results and laboratory method blanks, and COCs must be provided to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

8.5.2 Nitrate-Nitrite or Nitrite (EPA 300 Series Method 353.2)

8.5.2.1 Applicability

Method 353.2 is a cadmium reduction, automated colorimetric method used to determine the concentration of either nitrite or combined nitrate and nitrite in domestic and industrial effluents, and surface and saline waters. The applicable range of this method is 0.05 to 10 mg/L.

8.5.2.2 Interferences

The presence of suspended matter and high concentrations of oil and grease and some metals (i.e., iron, copper) can create interferences with this method. Samples can be filtered before analysis to minimize the problem of restricted sample flow caused by suspended matter. An organic solvent extraction and the addition of EDTA to samples can eliminate interferences from oil and grease and problematic metals, respectively.

8.5.2.3 Holding Times

Samples should be collected in plastic or glass bottles, preserved with sulfuric acid to a pH <2, and cooled to 4°C.

A 28-day holding time (elapsed time period from sample collection to analysis) is specified for analysis. Chain of Custodies (COCs) and raw data are reviewed to determine if holding times were met for all samples. Positive results and nondetects will be qualified as estimated, (J) and (UJ), respectively, if holding times were exceeded. Gross holding time violations (>2X holding time) will warrant rejection, (R), of nondetects.

8.5.2.4 Quality Control

The method does not specify the analysis of quality control measures (i.e., calibrations, blanks, spikes, etc.). However, if these analyses were performed by the laboratory, the following criteria will be used to evaluate the associated sample data.

Calibration

The calibration curve should be checked for linearity (correlation coefficient curve >0.995). In general, associated sample data are qualified as estimated, (J) and (UJ), when calibration curves are not linear. However, professional judgment should be used to qualify sample data when a nonlinear curve is encountered.

If analyzed, the percent recovery (%R) of a continuing calibration verification (CCV) standard will be evaluated using an 85-115% quality control criteria. If the %R is <85%, associated sample data will be

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qualified as estimated, (J) and (UJ). Only positive results in the affected samples will be qualified as estimated, (J), if the CCV %R is >115%.

Blanks

Laboratory method and field quality control blanks, if analyzed, should be evaluated for contamination. Field quality control blanks (field, rinsate, equipment, etc.) can be identified by consulting the COCs. If contamination is noted in the associated blanks, positive sample results < the maximum amount detected in the blanks will be qualified as undetected, (U). Sample digestion and moisture content factors will be taken into consideration when qualifying the associated sample data.

Spikes

If a spiked sample was analyzed, a 75-125% quality control range will be used to evaluate %Rs. Associated sample results will be qualified as estimated, (J) and (UJ), when the spiked sample %R is <75%. If the %R is >125%, only positive results are impacted and qualified as estimated, (J). Associated nondetects will be qualified as rejected, (R), and positive results will be qualified as estimated, (J), if the spike %R is <30%.

Duplicates

Qualification of sample data based on duplicate precision is left to the professional judgment of the validator. Generally, an aqueous quality control limit of $\pm 20\%$ and a solid quality control limit of $\pm 30\%$ is used to evaluate the relative percent difference (RPD) between the sample and laboratory duplicate results. An aqueous quality control limit of $\pm 30\%$ and a solid quality control limit of $\pm 50\%$ is used to evaluate the RPD between field duplicate results; qualification based on field duplicate imprecision for general chemistry parameters is applied to the field duplicate pair only.

Sample Quantitation

All reported sample concentrations should fall within the range of the calibration curve. If samples having detected concentrations the calibration range were not diluted and reanalyzed, associated sample data will be qualified as estimated, (J).

The validator should verify that sample results were properly quantitated.

8.5.2.5 Deliverables Guidance

The content and format of the data package generated for this method of analysis may vary significantly depending upon the work request.

In addition to any work-request requirements (e.g., data validation memorandum), all laboratory data package quality control summary forms, laboratory summaries of sample results and laboratory method blanks, and COCs must be provided to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

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8.6 Phosphorus (EPA 600 Series Method 365.4)

8.6.1 Applicability

Method 365.4 is a colorimetric method used to measure the concentration of total phosphorus in domestic and industrial effluents, and drinking and surface waters. The practical range of determination is 0.01 to 20 mg/L.

8.6.2 Interferences

No interferences noted in the method.

8.6.3 Holding Times

Samples are to be collected in plastic or glass containers, preserved to a pH < 2 with sulfuric acid, and cooled to 4°C.

A 28-day holding time between sample collection and analysis is specified. Chain of Custodies (COCs) and raw data are reviewed to determine if holding times were met for all samples. Sample data will be qualified as estimated, (J) and (UJ), if holding times were exceeded. Gross holding time violations (>2X holding time) will warrant rejection, (R), of nondetects.

8.6.4 Quality Control

Quality control analyses (i.e., calibrations, blanks, spikes, etc.) are not specified in Method 365.4. However, if these analyses were performed by the laboratory, the following criteria will be used to evaluate the associated sample data.

8.6.4.1 Calibration

The calibration curve should be checked for linearity (correlation coefficient >0.995). In general, associated sample data are qualified as estimated, (J) and (UJ), when calibration curves are not linear.

If a continuing calibration verification (CCV) standard is analyzed, the percent recovery (%R) of the CCV will be evaluated using 85-115% quality control limits. Associated sample data will be qualified as estimated, (J) and (UJ), if the CCV %R is <85%. Only positive results in the affected samples will be qualified as estimated, (J), if the CCV %R is >115%.

8.6.4.2 Blanks

Laboratory method and field quality control blanks, if analyzed, should be evaluated for contamination. Field quality control blanks (field, rinsate, equipment, etc.) can be identified by consulting the COCs. If contamination is noted in the associated blanks, positive sample results < the maximum amount detected in the blanks will be qualified as undetected, (U). Sample digestion and moisture content factors will be taken into consideration when qualifying the associated sample data.

8.6.4.3 Spikes

If a spiked sample is analyzed, a 75-125% quality control range will be used to evaluate the spike %R. Associated sample data will be qualified as estimated, (J) and (UJ), when the spiked sample %R is <75%. If the %R is >125%, only positive results are impacted and qualified as estimated, (J). If a spike

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%R is < 30%, associated nondetects will be qualified as rejected, (R), and positive results will be qualified as estimated, (J).

8.6.4.4 Duplicates

Qualification of sample data based on duplicate precision is left to the professional judgment of the validator. Generally, an aqueous quality control limit of $\pm 20\%$ and a solid quality control limit of $\pm 30\%$ is used to evaluate the relative percent difference (RPD) between the sample and laboratory duplicate results. An aqueous quality control limit of $\pm 30\%$ and a solid quality control limit of $\pm 50\%$ is used to evaluate the RPD between field duplicate results; qualification based on field duplicate imprecision for general chemistry parameters is applied to the field duplicate pair only.

8.6.4.5 Sample Quantitation

All reported sample concentrations should fall within the range of the calibration curve. If samples having detected concentrations > the highest calibration standard were not diluted and reanalyzed, associated sample data will be qualified as estimated. (J).

The validator should verify that sample results were properly quantitated.

8.6.5 **Deliverables Guidance**

The content and format of the data package generated for phosphorus analysis may vary significantly depending upon the work request.

In addition to any work-request requirements (e.g., data validation memorandum), all laboratory data package quality control summary forms, laboratory summaries of sample results and laboratory method blanks, and COCs must be provided to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

8.7 Sulfate (EPA 600 Series Method 375.4)

8.7.1 **Applicability**

Method 375.4 is used to determine the concentration of sulfate in domestic and industrial effluents, and drinking and surface waters. Although all sulfate concentration ranges can be measured by this turbidimetric method, a sample aliquot should not contain more than 40 mg/L of sulfate since the suspensions lose stability at concentrations > 50 mg/L. The minimum detection limit for this method is 1 mg/L.

8.7.2 **Interferences**

Interferences are noted from silica concentrations > 500 mg/L, suspended matter, and color in samples.

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8.7.3 Holding Times

Samples should be collected in plastic or glass bottles and cooled to 4°C. No preservative is necessary.

Holding time, which is specified as 28 days for this method, is defined as the elapsed time period from sample collection to analysis. Chain of Custodies (COCs) and raw data are reviewed to determine if holding times were met for all samples. Sample data will be qualified as estimated, (J) and (UJ), if holding times were exceeded. Gross holding time violations (>2X holding time) will warrant rejection, (R), of nondetects.

8.7.4 Quality Control

8.7.4.1 Calibration

The raw data will be reviewed to ensure that the following calibration requirements have been met:

- The calibration curve used for sample quantitation should consist of standards at increments of 5 mg/L in the 0 to 40 mg/L sulfate range.
- A continuing calibration verification (CCV) standard is analyzed every 3 or 4 samples.

Associated sample data will be qualified as estimated, (J) and (UJ), if the above requirements have not been met.

The calibration curve should be checked for linearity (correlation coefficient >0.995). In general, sample results associated with nonlinear calibration curves are qualified as estimated, (J) and (UJ). Professional judgment should be used to qualify sample data in instances where sample results fall outside a linear portion of the calibration curve.

The percent recovery (%R) of the CCV should be within an 85-115% quality control range. Associated sample data will be qualified as estimated, (J) and (UJ), if the CCV %R is <85%. Only positive results in the affected samples will be qualified as estimated, (J), if the CCV %R is >115%.

8.7.4.2 Blanks

Laboratory method blanks (other than the blank used for the calibration curve) should be analyzed and evaluated for contamination. The COCs should be consulted to determine if any field quality control blanks (field, rinsate, equipment, etc.) are associated with the samples. If contamination is noted in the associated blanks, positive sample results < the maximum amount detected in the blanks will be qualified as undetected, (U). Sample digestion and moisture content factors will be taken into consideration when qualifying the associated sample data.

8.7.4.3 Spikes/Duplicates

The method does not require the analysis of spikes or duplicates. However, if these quality control (QC) analyses were performed by the laboratory the following criteria will be used to evaluate the associated sample data.

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QC Parameter	Control Limits
Spike %R	75 - 125%
Duplicate RPD	±20% for waters or ±30% for solids

If the spike %R is < 75%, the associated sample data will be qualified as estimated, (J) and (UJ). Only positive results will be qualified as estimated, (J), when the spike %R is > 125%. Associated nondetects will be qualified as rejected, (R), and positive results will be qualified as estimated, (J), in the event that the spike %R is < 30%.

Generally, associated sample results are qualified as estimated, (J) and (UJ), if the relative percent difference (RPD) between the sample and laboratory duplicate results did not meet the quality control criterion. However, in some cases, qualification of sample data based on duplicate precision is left to the professional judgment of the validator. An aqueous quality control limit of ±30% and a solid quality control limit of ±50% is used to evaluate the RPD between field duplicate results; qualification based on field duplicate imprecision for general chemistry parameters is applied to the field duplicate pair only.

8.7.4.4 Sample Quantitation

All reported sample concentrations should fall within the range of the calibration curve. If samples having detected concentrations > the highest calibration standard were not diluted and reanalyzed, the associated sample data will be qualified as estimated, (J).

The validator will verify that sample results were correctly quantitated.

8.7.5 **Deliverables Guidance**

The content and format of the data package generated for sulfate analysis may vary significantly depending upon the work request.

In addition to any work-request requirements (e.g., data validation memorandum), all laboratory data package quality control summary forms, laboratory summaries of sample results and laboratory method blanks, and COCs must be provided to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

8.8 Sulfides (EPA SW-846 Method 9030)

8.8.1 **Applicability**

Method 9030 is iodometric method used to determine the concentration of total and dissolved sulfides in excess of 1 mg/L in drinking, surface and saline waters. Acid-insoluble sulfides, such as copper sulfide, can not be measured by this titrimetric method.

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8.8.2 Interferences

A main source of interference for this method is the reduction of iodine by various chemicals (thiosulfate, sulfite, and organic compounds). Samples are treated at collection with zinc acetate and sodium hydroxide to minimize interferences.

In addition, sulfides are susceptible to volatilization and reaction with oxygen which can form unmeasurable states of sulfides. Aeration should be minimized during sample collection.

8.8.3 Holding Times

Samples are preserved with zinc acetate, treated with sodium hydroxide to a pH >9, and cooled to 4°C.

Holding time is defined as the elapsed time period from sample collection to analysis. The following holding times apply to sulfide analyses:

- Unpreserved samples: Immediate analysis
- Preserved samples: 7 days

Chain of Custodies (COCs) and raw data are reviewed to determine if holding times were met for all samples. In the event that holding times are exceeded, positive results and nondetects will be qualified as estimated, (J) and (UJ), respectively. Gross holding time violations (>2X holding time) will warrant rejection, (R), of nondetects.

8.8.4 Quality Control

8.8.4.1 Calibration

The raw data will be reviewed to ensure that the following calibration requirements have been met:

- The calibration curve should consist of a blank and three standards (at a minimum).
- A new calibration curve should be performed for every hour of continuous sample analysis.
- A continuing calibration verification (CCV) standard should be analyzed every 15 samples.

Associated sample data will be qualified as estimated, (J) and (UJ), if the above requirements have not been met.

The calibration curve should be checked for linearity. Generally, associated sample data is qualified as estimated, (J) and (UJ), if the calibration curve correlation coefficient is <0.995. Professional judgment should be used to qualify sample data in cases when sample results fall outside a linear portion of the calibration curve.

An 85-115% quality control range will be used to evaluate the percent recovery (%R) of a CCV. Associated sample data will be qualified as estimated, (J) and (UJ), if the CCV %R is <85%. Only positive results in the affected samples will be qualified as estimated, (J), if the CCV %R is >115%.

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8.8.4.2 Blanks

At a minimum, one laboratory method blank (other than the blank used for the calibration curve) should be analyzed per sample batch (maximum of 20 samples). The COCs should be consulted to determine if any field quality control blanks (field, rinsate, equipment, etc.) are associated with the samples. If contamination is noted in the associated blanks, positive sample results < the maximum amount detected in the blanks will be qualified as undetected, (U). Sample dilution and moisture content factors will be taken into consideration when qualifying the associated sample data.

8.8.4.3 Spikes/Duplicates

A spiked sample and spiked duplicate sample should be analyzed for every 10 samples. If a spike or duplicate spike %R is <75%, associated sample data will be qualified as estimated, (J) and (UJ). If the %R is > 125%, only positive results are impacted and qualified as estimated, (J). If a spike %R is <30%, associated nondetects will be qualified as rejected, (R), and positive results will be qualified as estimated, (J).

Qualification of sample data based on duplicate precision is left to the professional judgment of the validator. Generally, a $\pm 20\%$ aqueous quality control limit and a $\pm 30\%$ solid quality control limit are used to evaluate the relative percent difference (RPD) between the spiked sample and spiked duplicate sample results. An aqueous quality control limit of $\pm 30\%$ and a solid quality control limit of $\pm 50\%$ is used to evaluate the RPD between field duplicate results; qualification based on field duplicate imprecision for general chemistry parameters is applied to the field duplicate pair only.

8.8.4.4 Sample Quantitation

All reported sample concentrations should fall within the range of the calibration curve. If samples having detected concentrations > the highest calibration standard were not diluted and reanalyzed, the associated sample data will be qualified as estimated, (J).

The validator will verify that sample results were properly quantitated.

8.8.5 Deliverables Guidance

The content and format of the data package generated for sulfide analysis may vary significantly depending upon the work request.

In addition to any work-request requirements (e.g., data validation memorandum), all laboratory data package quality control summary forms, laboratory summaries of sample results and laboratory method blanks, and COCs must be provided to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

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8.9 Total Suspended Solids (EPA 600 Series Method 160.2)

8.9.1 Applicability

Method 160.2 is a gravimetric method used to determine nonfilterable residue (total suspended solids) in domestic and industrial wastes, and drinking, surface and saline waters. The optimum range of total suspended solids (TSS) determined by this method is 4 to 20,000 mg/L.

8.9.2 Interferences

Requirements for apparatus and analytical techniques are specified in the method to eliminate or reduce procedural interferences. Saline waters, brines, and samples high in dissolved solids must be analyzed carefully to minimize elevated sample results.

8.9.3 Holding Times

Samples should be collected in plastic or glass containers and cooled to 4°C to reduce microbiological decomposition of solids. No preservative is needed.

Holding time is defined as the elapsed time period from sample collection to analysis. Chain of Custodies (COCs) and sample data are reviewed to determine if the 7-day holding time required by this method was met for all samples. Positive results and nondetects will be qualified as estimated, (J) and (UJ), respectively, if holding times were exceeded. Gross holding time violations (>2X holding time) will warrant rejection, (R), of nondetects.

8.9.4 Quality Control

Method 160.2 does not require specific quality control analyses (i.e., blanks, duplicates, etc.). However, if these analyses were performed by the laboratory, the following criteria will be used to evaluate the associated sample data.

8.9.4.1 Verification

If a verification standard is analyzed, the percent recovery (%R) of the standard should be within a quality control range of 90-110%. Associated sample data will be qualified as estimated, (J) and (UJ), if the verification %R is <90%. Positive sample results will be qualified as estimated, (J), if the verification %R is >110%; nondetects are not impacted.

8.9.4.2 Blanks

Laboratory method and field quality control blanks, if analyzed, should be evaluated for contamination. Field quality control blanks (field, rinsate, equipment, etc.) can be identified by consulting the COCs. Positive sample results for TSS < the maximum amount detected in the blanks will be qualified as undetected, (U).

8.9.4.3 Duplicates

Qualification of sample data based on duplicate precision is left to the professional judgment of the validator. Generally, a quality control limit of ±20% is used to evaluate the relative percent difference (RPD) between the sample and duplicate results. An aqueous quality control limit of ±30% and a solid quality control limit of ±50% is used to evaluate the RPD between field duplicate results; qualification

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based on field duplicate imprecision for general chemistry parameters is applied to the field duplicate pair only.

8.9.4.4 Sample Quantitation

The validator should verify that sample results were calculated accurately. The following equation is used to calculate TSS:

$$TSS (mg/L) = \frac{wt_{crucible+residue} - wt_{crucible}}{VOL_{sample\ aliquot\ used}} \times \frac{1,000\ mL}{1\ L}$$

where: wt = weight (mg)
vol = volume (mL)

8.9.5 Deliverables Guidance

In addition to any work-request requirements (e.g., data validation memorandum), all laboratory data package quality control summary forms, laboratory summaries of sample results and laboratory method blanks, and COCs must be provided to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.

8.10 Total Dissolved Solids (EPA 600 Series Method 160.1)

8.10.1 Applicability

Method 160.1 is a gravimetric method used to determine filterable residue (total dissolved solids) in domestic and industrial wastes, and drinking, surface and saline waters. The optimum range of total dissolved solids (TDS) determined by this method is 10 to 20,000 mg/L.

8.10.2 Interferences

Interferences during the drying stages of the analytical procedure are observed. Samples containing high concentrations of calcium, magnesium, chloride, sulfate and bicarbonate may require longer desiccation and drying times to minimize interferences. Total residue should be limited to 200 mg to prevent entrapment of water in the evaporating dish.

8.10.3 Holding Times

Samples should be collected in plastic or glass containers and cooled to 4°C to reduce microbiological decomposition of solid matter. No preservative is needed.

Holding time is defined as the elapsed time period from sample collection to analysis. A 7-day holding time is specified by the method. Chain of Custodies (COCs) and raw data are reviewed to determine if holding times were met for all samples. Positive results and nondetects will be qualified as estimated,

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(J) and (UJ), respectively, if holding times were exceeded. Gross holding time violations (>2X holding time) will warrant rejection. (R), of nondetects.

8.10.4 Quality Control

Method 160.1 does not require specific quality control analyses (i.e., blanks, duplicates, etc.). However, if these analyses were performed by the laboratory, the following criteria will be used to evaluate the associated sample data.

8.10.4.1 Verification

If a verification standard is analyzed, the percent recovery (%R) of the standard should be within a quality control range of 90-110%. Associated sample data will be qualified as estimated, (J) and (UJ), if the verification %R is <90%. Positive sample results will be qualified as estimated, (J), if the verification %R is >110%; nondetects are not impacted.

8.10.4.2 Blanks

Laboratory method and field quality control blanks, if analyzed, should be evaluated for contamination. Field quality control blanks (field, rinsate, equipment, etc.) can be identified by reviewing the COCs. Positive sample results for TDS < the maximum amount detected in the blanks will be qualified as undetected, (U).

8.10.4.3 Duplicates

Qualification of sample data based on duplicate precision is left to the professional judgment of the validator. Generally, a quality control limit of ±20% is used to evaluate the relative percent difference (RPD) between the sample and duplicate results. An aqueous quality control limit of ±30% and a solid quality control limit of ±50% is used to evaluate the RPD between field duplicate results; qualification based on field duplicate imprecision for general chemistry parameters is applied to the field duplicate pair only.

8.10.4.4 Sample Quantitation

The validator should verify that sample results were calculated accurately. The following equation is used to calculate TDS:

$$TDS \text{ (mg/L)} \times \frac{wt_{\text{dish+residue}} - wt_{\text{dish}}}{vol_{\text{sample aliquot used}}} \times \frac{1,000 \text{ mL}}{1 \text{ L}}$$

where: wt = weight (mg)
vol = volume (ml)

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8.10.5 Deliverables Guidance

In addition to any work-request requirements (e.g., data validation memorandum), all laboratory data package quality control summary forms, laboratory summaries of sample results and laboratory method blanks, and COCs must be provided to the Data Validation Quality Assurance Officer (DV/QAO) for quality assurance review.

The validator should ensure that the format of the data validation deliverable is complete and correct and that the validation narrative is free of transcription and typographical errors before submitting all requested items for DV/QAO review.



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Applicability B&R Environmental, NE	
Prepared Risk Assessment Department	
Approved D. Senovich <i>DS</i>	

Subject
DATABASE RECORDS AND QUALITY ASSURANCE

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1.0 PURPOSE

The purpose of this document is to specify a consistent procedure for the quality assurance review of electronic and hard copy data bases.

2.0 SCOPE

The methods described in this Standard Operating Procedure (SOP) shall be used consistently for all projects managed by personnel located in the Northeast Region of Brown & Root Environmental (Pittsburgh, PA; Wayne, PA; Wilmington, MA; and Holt, MI), for any large contracts managed by the Northeast Region (e.g., NORTHDIV CLEAN, SOUTHDIV CLEAN, ARCS I, ARCS III, etc.), and by other offices of Brown & Root Environmental at the discretion of the Project Manager. Smaller projects (as determined by Project Manager) are outside the scope of this SOP.

3.0 GLOSSARY

Chain-of-Custody Form - A Chain-of-Custody Form is a printed form that accompanies a sample or a group of samples from the time of sample collection to the laboratory. The Chain-of-Custody Form is retained with the samples during transfer of samples from one custodian to another. The Chain-of-Custody Form is a controlled document that becomes part of the permanent project file. Chain-of-Custody and field documentation requirements are addressed in SOP SA-6.1.

Electronic Data Base - A database provided on a 5.25" or 3.5" diskette or a laser disk. Such electronic data bases will generally be prepared using public domain software such as DBase, RBase, Oracle, Visual FoxPro, Microsoft Access, Paradox, etc.

Hardcopy Database - A printed copy of a data base prepared using the software discussed under the definition of an electronic data base.

Sample Tracking Summary - A printed record of sample information including the date the samples were collected, the number of samples collected, the sample matrix, the laboratory to which the samples were shipped, the associated analytical requirements for the samples, the date the analytical data were received from the laboratory, and the date that validation of the sample data was completed. The sample tracking summary is a document maintained and prepared in accordance with the requirements outlined in Standard Operating Procedure CT-02

4.0 RESPONSIBILITIES

Database Records Custodian - It shall be the responsibility of the Database Records Custodian to update and file the Sample Tracking Summaries for all active projects on a weekly basis. It shall be the responsibility of the Database Records Custodian to ensure that the most recent copies of the Sample Tracking Summaries are placed in the Database Records file. It shall be the responsibility of the Database Records Custodian to ensure that a copy of all validation deliverables is provided to the Project Manager (for placement in the project file). It shall be the responsibility of the Database Records Custodian to ensure that photocopies of all validation deliverables and historical data and reports (as applicable) are placed in the Database Records file.

Data Validation Coordinator - It shall be the responsibility of the Data Validation Coordinator (or designee) to ensure that the Sample Tracking Summaries are maintained by the Database Records Custodian. It shall be the responsibility of the Data Validation Coordinator (or designee) to ensure that

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photocopies of all data validation deliverables are placed in the applicable Database Records file by the Database Records Custodian.

Earth Sciences Department Manager - It shall be the responsibility of the Earth Sciences Department Manager (or equivalent) to ensure that all field personnel are familiar with the requirements of this Standard Operating Procedure (specifically Section 5.3).

Field Operations Leader - It shall be the responsibility of the Field Operations Leader of each project to ensure that all field technicians or sampling personnel are thoroughly familiar with this SOP, specifically regarding provision of the Chain-of-Custody Forms to the Database Records Custodian. Other responsibilities of the Field Operations Leader are described in Sections 5.4 and 5.5.

Information Management Systems Manager - It shall be the responsibility of the Information Management Systems Manager to ensure that copies of original electronic deliverables (diskettes) are placed in both the project files and the Database Records File. It shall be the responsibility of the Information Management Systems Manager (or designee) to verify the completeness of the database (presence of all samples) in both electronic and hardcopy form in the Database Records File. It shall be the responsibility of the Information Management Systems Manager to ensure that Quality Assurance Reviews are completed and are attested to by Quality Assurance Reviewers. It shall be the responsibility of the Information Management Systems Manager to ensure that records of the Quality Assurance review process are placed in the Database Records File. It shall be the responsibility of the Information Management Systems Manager to ensure that both electronic and hardcopy forms of the final data base are placed in both the project and the Database Record File. It shall be the responsibility of the Information Management Systems Manager to ensure that data validation qualifiers are entered in the data base in a timely fashion.

Program/Department Managers - It shall be the responsibility of the Department and/or Program Managers (or designees) to inform their respective department's Project Managers of the existence and requirements of this SOP.

Project Manager - It shall be the responsibility of each Project Manager to determine the applicability of this SOP based on: (1) program-specific requirements, and (2) project size and objectives. It shall be the responsibility of the Project Manager (or designee) to ensure that the Field Operations Leader is familiar with the requirements regarding Chain-of-Custody Form provision to the Data Base Records Custodian. It shall be the responsibility of the Project Manager (or designee) to determine which, if any, historical data are relevant and to ensure that such data (including all relevant information such as originating entity, sample locations, sampling dates, etc.) are provided to the Database Records Custodian for inclusion in the Database Records File.

Risk Assessment Department Manager - It shall be the responsibility of the Risk Assessment Department Manager to monitor compliance with this Standard Operating Procedure, to modify this SOP as necessary, and to take corrective action if necessary. Monitoring of the process shall be completed on a quarterly basis.

Quality Assurance Reviewers - It shall be the responsibility of the Quality Assurance Reviewers to verify the completeness of the sample results via review of the Chain-of-Custody Forms and Sample Tracking Summaries. It shall be the responsibility of the Quality Assurance Reviewers to ensure the correctness of the data base via direct comparison of the hardcopy printout of the data base and the hardcopy summaries of the original analytical data (e.g., Form 1s provided in data validation deliverables). Correctness includes the presence of all relevant sample information (all sample information fields), accuracy of the analytical results, and the presence and appropriateness of data validation qualifiers.

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5.0 PROCEDURES

5.1 Introduction

Verification of the accuracy and completeness of an electronic data base can only be accomplished via comparison of a hardcopy of the database with hardcopy of all relevant sample information. The primary purpose of this SOP is to ensure that all necessary hardcopy information is readily available to Quality Assurance Reviewers. Therefore, the emphasis of this SOP is the establishment and maintenance of the Database Record File. The Database Record File is an additional file to the project file. The project file shall also contain all of the information contained in the Database Record file.

5.2 File Establishment

A Database Record file shall be established for a specific project at the discretion of the Project Manager. Initiation of the filing procedure will commence upon receipt of the first set of Chain-of-Custody documents from a Field Operations Leader or sampling technician. The Database Record Custodian shall establish a project-specific file for placement in the Database Record File and will ensure that no information is removed from the file without the use of an "outcard." Each file in the Database Record File shall consist of standard components placed in the file as the project progresses. Each file shall be clearly labeled with the project number, which shall be placed on the front of the file drawer and on each and every hanging file folder relevant to the project. The following constitute the minimum components of a completed file:

- File Index
- Electronic Deliverables
- Sample Tracking Forms
- Chain-of-Custody Forms
- Data Validation Letters
- Historical Data (if applicable)
- Final Electronic Data Base
- Final Hardcopy Data Base
- Quality Assurance Records

Each file in the Database Record File must have an index summarizing the contents of the file. It shall be the responsibility of the Database Record Custodian to maintain the file index such that it is always current. The file index should specifically list the content of each of the subsections of the file and must also summarize the Sample Delivery Group numbers and samples and associated analyses associated with each Sample Delivery Group. Additional file requirements as well as database quality assurance procedures are summarized in the remainder of this section.

5.3 Electronic Deliverables

The integrity of all original electronic data deliverables shall be maintained. This shall be accomplished via the generation of copies of each electronic deliverable provided by the laboratory. The original electronic deliverable shall be provided to the project manager for inclusion in the project file. A copy of the original electronic deliverable shall be placed in the Database Record File. The second copy shall be maintained by the Information Management Systems Manager (or designee) to be used as a working copy. The original and Database Record File copy of the electronic deliverable shall be converted to read only files by the Information Management Systems Manager or designee.

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5.4 Sample Tracking Forms

Updated versions of the sample tracking form for each relevant project shall be maintained by the Database Record Custodian. The Sample Tracking Forms shall be updated any time additional Chain-of-Custody Forms are received from a Field Operations Leader or sampling technician, or at any time that data are received from a laboratory, or at any time that validation of a given data package (sample delivery group) is completed. The Data Validation Coordinator shall inform the Database Record Custodian of the receipt of any data packages from the laboratory and of completion of validation of a given data package to facilitate updating of the Sample Tracking Form. The Database Record Custodian shall place a revised copy of the Sample Tracking Form in the Database Record File anytime it has been updated. Copies of the updated Sample Tracking Form shall also be provided to the project manager to apprise the project manager of sample package receipt, completion of validation, etc. Sample tracking is addressed in SOP CT-02.

5.5 Chain-of-Custody Forms

The Chain-of-Custody Forms for all sampling efforts will be used as the basis for (1) updating the Sample Tracking Form, and (2) confirming that all required samples and associated analyses have been completed. It shall be the responsibility of the Field Operations Leader (or sample technician) to provide a photocopy of all Chain-of-Custody Forms to the Database Record Custodian immediately upon completion of a sampling effort. The Database Record Custodian shall then place the copies of the Chain-of-Custody Form(s) in the Database Record File. Upon receipt of a sample data package from an analytical laboratory, the Data Validation Coordinator shall provide a copy of the laboratory Chain-of-Custody Form to the Database Record Custodian. The Database Record Custodian shall use this copy to update the Sample Tracking Summary and shall place the copy of the laboratory-provided Chain-of-Custody Form in the Database Record File. The photocopy of the laboratory-provided Chain-of-Custody Form shall be stapled to the previously filed field copy. Upon receipt of all analytical data, two copies of the Chain-of-Custody will therefore be in the file. Review of the Chain-of-Custody Forms will therefore be a simple mechanism to determine if all data have been received. Chain-of-Custody is addressed in SOP SA-6.1.

5.6 Data Validation Letters

All data validation deliverables (or raw data summaries if validation is not conducted) shall be provided for inclusion in both the Database Record File and the project file. If USEPA regional- or client-specific requirements are such that Form Is (or similar analytical results) need not be provided with the validation deliverable, copies of such results must be appended to the deliverable. It is preferable, although not essential that the validation qualifiers be hand-written directly on the data summary forms. The data validation deliverables (and attendant analytical summaries) will provide the basis for direct comparison of the database printout and the raw data and qualifiers.

5.7 Historical Data

At the direction of the Project Manager, historical data may also be included in a project-specific analytical data base. In the event that historical data are germane to the project, hardcopy of the historical data must be included in the Database Record File. Historical data may be maintained in the form of final reports or as raw data. The information contained in the historical data file must be sufficient to identify its origin, its collection date, the sample location, the matrix, and any and all other pertinent information. All available analytical data, Chain-of-Custody Forms, boring logs, well construction logs, sample location maps, etc. shall be photocopied by the Project Manager (or designee) and placed into a 3-ring binder. All information shall be organized chronologically by matrix. It shall be the responsibility

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of the Project Manager (or designee) to ensure that all inconsistencies between analytical data, Chain-of-Custody Forms, boring logs, etc. are accounted for and corrective actions are taken. For example, the Chain-of-Custody may list a particular sample as S42GW1 while the analytical data summary lists the sample as S42-01 and the well construction form may list S42-MW01. The Project Manager (or designee) shall decide which nomenclature is appropriate and edit, initial and date all relevant forms. Data entry may only be performed on information that has gone through the aforementioned editing process, thereby having a direct correlation between hardcopy information and what will become the electronic database.

Sample spreadsheets shall be generated for all samples previously collected at the site (see Attachment A). The sample spreadsheets shall have specific references to all source documents. If many historical reports exist, the Project Manager shall maintain an organized library with outcards for tracking purposes.

5.8 Final Electronic Data Base

The final electronic database shall be filed in both the project and Database Record Files on diskettes, tapes, laser disks, etc. The final files shall be toggled as read only files. It shall be the responsibility of the Information Management Systems Manager to ensure that the final electronic files are provided to both the project and Database Record Files.

5.9 Final Hardcopy Data Base

The final hardcopy data base shall be filed in both the project and Database Record Files as legible, reproducible printouts. The final database printouts shall be clearly identified as such on the cover page(s). It shall be the responsibility of the Information Management Systems Manager to ensure that the final hardcopy of the database are provided to both the project and Database Record Files.

The final hardcopy database must also clearly display an attestation that Quality Assurance review has been completed. Specifically, the signature of the Information Management Systems Manager (or designee must appear on the final hardcopy. The date of the final review and an attestation that the final review was completed must be provided. The attestation shall take the following form:

"Final Database Quality Assurance Review Completed By: _____ on __/__/__."

5.10 Quality Assurance Procedures

The Information Management System Manager (or designee) shall assign one or more individuals (Quality Assurance Reviewers) to complete Quality Assurance Review of the data base, either in its entirety or on an Sample Delivery Group-specific basis. Such review shall focus on the accuracy of the analytical results (do the numerical values agree with the results as provided by the laboratory), have the data validation qualifiers (if applicable) been entered and are they correct, are all requested analytical results present in the Sample Delivery Group(s) or the database, are all required data base fields provided (e.g., northing, easting, sample depth, sampling date, matrix, site name, etc.), are units provided and are they the correct units, are any fractions that were not analyzed in specific samples identified as such, does the data base indicate that validation has been completed, etc. Upon completion of such Quality Assurance review, the Quality Assurance Reviewer shall attest that the review has been completed via the following statements:

"Intermediate Database QA Review Completed By: _____ on __/__/__."

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"Data correct as provided in the attached summary." or

"Data incorrect as provided in the attached summary. Submitted for correction."

Copies of such intermediate database reviews shall be placed in the Database Record File.

5.11 Quality Assurance Records

Quality Assurance records for the Database Record File include the intermediate and final attestations discussed in the preceding two sections.

6.0 RECORDS

Records regarding database preparation and quality assurance review include all those identified in the previous section. Upon closeout of a given project, records from the file will be placed in bankers boxes (or equivalent) for storage. The final records for storage shall include the following minimum information on placards placed on both the top and end of the storage box:

Database Record File
PROJECT NUMBER: _____
SITE NAME: _____
DATE FILED: __/__/____
SUMMARY OF CONTENTS ENCLOSED
BOX _ OF _

**ATTACHMENT A
HISTORICAL DATA FOR _____
GROUNDWATER**

Investigations	Investigative Well Identification	Installation Company & Date	Laboratory Parameters				
			09/82	11/82	01/83	02/83	04/83
Groundwater Monitoring Program (USACEWES, 1981).	WES-05-01-81	WES 09/14/81	C, D, E	B	F	A	
	WES-05-02-81	WES 09/15/81	C, D, E	B	F	A	
Hydrogeological Investigation of Waste Disposal Sites at the NWSC, Crane, Indiana (Dunbar 1982).	WE-05-03-81	WES 09/16/81	C, D, E	B	F	A	
	WES-05-04-81(*)	WES 10/01/81	C, D, E	B	F	A	
	05-04A (**)	WES 1986					
Definition of Contaminated Groundwater Plumes at Selected Waste Disposal Sites; Draft (Dunbar 1984).	WES-05-05-81	WES 10/02/81	C, D, E	B	F	A	
	WES-05-06-81	WES 10/10/81	C, D, E	B	F	A	
	WES-05-07-81	WES 10/20/81	C, D, E		F	A	
	WES-05-08-81	WES 11/04/81	C, D, E	B	F	A	
U.S. Dept. of the Navy IRP RFI Phase III Groundwater Investigations for NWSC, Crane, Indiana Old Burn Pit; U.S. Army Corps of Engineers; WES (June 1991).	WES-05-09-82	WES 10/27/82		B			
	WES-05-10-82	WES 10/27/82		B			
	WES-05-11-82	WES 10/29/82		B			
	WES-05-12-82	WES 10/30/82		B			
	WES-05-13-82	WES 11/01/82		B			
	WES-05-14-83	WES 01/10/83			B		
	WES-05-15-83	WES 01/11/83			B		G
	WES-05-16-83	WES 01/11/83			B		
	WES-05-17-83	WES 02/02/82			B		G
	WES-05-18-83	WES 02/03/83			B		G
	WES-05-19-83	WES 02/03/83			B		G

- (*) Original contaminated well yielding highest concentrations of contaminants.
- (**) Replacement well.
- A Metals, chloride, specific conductance, TOC, phenols, sulfate, TOX, pH.
- B VOCs.
- C Metals, fluoride, nitrate-nitrate, pest., chlorinated herbicides, GRA/GRB, chloride, phenols, sulfate, pH specific conductance, TOC, TOX.
- D GRA.
- E GRB.
- F Metals.

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BROWN & ROOT ENVIRONMENTAL

STANDARD OPERATING PROCEDURES

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Applicability B&R Environmental, NE	
Prepared Earth Sciences Department	
Approved D. Senovich	

Subject
ANALYSIS FOR VOLATILE COMPOUNDS USING
PURGE-AND-TRAP GAS CHROMATOGRAPHY

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1.0 PURPOSE

The purpose of this document is to describe the procedure for the analysis of volatile organic compounds by purge-and-trap (P-T) gas chromatography using a portable gas chromatograph. This procedure may be used on site during a field investigation to provide analytical results on quick turnaround basis.

2.0 SCOPE, APPLICATION, AND LIMITATIONS

2.1 Scope of Method

This field method covers the determination of volatile organic compounds in aqueous and solid samples by P-T gas chromatography. Table 1 lists the volatile organic compounds (VOCs) that may be determined by this method and their practical quantitation limits (PQLs). The PQLs for a specific sample may differ from those listed, depending on the nature of interferences in the sample matrix. In particular, the analyst must be aware that instrument sensitivities for methylene chloride, 1,1-dichloroethane, 1,2-dichloroethane, and 1,2-dichloropropane are approximately one-fiftieth of the sensitivities for most other compounds. Therefore, reported detection limits for these compounds will have to be adjusted (elevated) whenever other sample components elute near their expected retention times (RTs), even when such interferences are on scale and less than internal standard (IS) heights.

2.2 Target Compound List (TCL)

To utilize this field method to provide analytical data in the most timely and efficient manner for guidance of ongoing work, the project planning phase must identify the target compounds that are likely to be present and their general expected concentration ranges. The site work plan (WP) and quality assurance project plan (QAPP) should specify the selected subset of the target compound list (TCL) that is required to be determined and reported. This will expedite the analysis and reporting of samples by tailoring the quality control (QC) criteria for this method to the site-specific compounds instead of all compounds. Inclusion of the four gases (chloromethane, chloroethane, bromomethane, and vinyl chloride) can decrease sample throughput by half or more.

2.2.1 Calibration/Reporting Options

In general, two options are suggested for calibration and reporting purposes: first, only the site-specific compounds would be present in all calibration and QC standards; only these compounds would be quantitated and reported. Or all compounds listed in Table 1, including all site-specific compounds, would be present for the initial calibration analyses and continuing calibration analyses but only the site-specific compounds would present in all other QC analyses and would be subject to the stated QC criteria; other compounds would be quantitated and reported as estimated. The WP and/or the QAPP should state which option will be used.

2.3 Analysis of Solid Samples

The analysis of solid samples by the P-T method does not determine the true concentration of contaminants in soil. The analysis determines only the concentration of contaminants that will dissolve into water under the conditions of the analysis (mild heating).

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TABLE 1
TARGET COMPOUND LIST AND PRACTICAL QUANTITATION LIMITS (PQLS)

Volatile Organic Compound	CAS Number	PQLs	
		Water (µg/l)	Soils (µg/kg)
chloromethane	74-87-3	5	5
vinyl chloride	75-01-4	5	5
bromomethane	74-83-9	5	5
chloroethane	75-00-3	5	5
acetone	67-64-1	5	5
1,1-dichloroethene	75-35-4	1	1
methylene chloride	75-09-2	1	1
carbon disulfide	75-15-0	1	1
trans-1,2-dichloroethene	156-60-5	1	1
1,1-dichloroethane	75-34-3	1	1
2-butanone	78-93-3	5	5
cis-1,2-dichloroethene	156-59-4	1	1
chloroform	67-66-3	1	1
1,1,1-trichloroethane	71-55-6	1	1
carbon tetrachloride	56-23-5	1	1
benzene	71-43-2	1	1
1,2-dichloroethane	107-06-2	1	1
trichloroethene	79-01-6	1	1
4-methyl-2-pentanone	108-10-1	5	5
toluene	108-88-3	1	1
1,1,2-trichloroethane	79-00-5	1	1
2-hexanone	591-78-6	5	5
tetrachloroethene	127-18-4	1	1
chlorobenzene	108-90-7	1	1
ethylbenzene	100-41-4	1	1
m,p-xylenes	1330-20-7	1	1
o-xylene	95-47-6	1	1
styrene	100-42-5	1	1
bromoform	75-25-2	1	1
1,1,2,2-tetrachloroethane	79-34-5	1	1

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2.3.1 Analysis of Aqueous Samples

In the analysis of aqueous samples, quantitation is based upon the assumption that the concentrations of compounds found in the vapor phase over the sample are directly proportional to the actual concentrations of compounds in the sample. This assumption is valid mainly for clean matrices. Interferences such as high levels of dissolved salts, suspended solids, oil, or other solvents can alter the assumed partitioning between the liquid and vapor phases and substantially bias quantitative results.

2.3.2 Method Limitation

A limitation of the P-T method is the dissolution of the volatile compounds in water prior to analysis. For hydrophobic volatile compounds such as the ketones, the air/water partition is very low; these compounds tend to remain in the water phase and do not readily volatilize under the moderate heating of the purge-and-trap method.

2.4 High-Level Contamination

The efficiency of the field analysis will be adversely affected by unexpected high levels of contaminants that require dilutions and system bakeout. Therefore, samplers must provide information as to suspected contaminated samples and useful field observations such as total organic vapor readings.

2.5 Target Analyte Identification

When this method is used to analyze unfamiliar samples for any or all of the compounds in Table 1, compound identifications should be supported by at least one additional qualitative technique. Compound identities are most often corroborated by confirmatory analyses of a representative subset of samples collected, taking into account the proximities and matrix similarities within groups of samples, the sample-specific complexity of chromatographic interferences, and the different target compounds identified in the various field samples. Gas chromatography/mass spectrometry (GC/MS) techniques generally provide reliable confirmation data, particularly when replicates or duplicates of field samples are collected and analyzed using the protocols of the EPA Contract Laboratory Program (CLP).

2.6 Confirmation Samples

The required type and frequency of confirmation will depend on the objectives of the sampling investigation and the intended use of the data. For example, the client may require that a rigorous type of confirmation (e.g., GC/MS) be utilized whenever results are meant to be used in certain critical data categories for risk assessment or other decision making.

2.7 Client Review of WP/QAPP

The client will approve the site-specific WP and QAPP before on-site analysis and will approve the confirmation requirements for each site. No general confirmation scheme that applies to all circumstances is provided in this SOP because the combination of site-related and sample-specific data quality needs may be unique to each sampling investigation. Confirmation requirements that are proposed in the above documents will specify the objectives, mechanisms, and guidelines for confirmational analysis. Consideration should be given to the need for any pre-determined sampling locations for GC/MS or other confirmation and also for an overall frequency

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for GC/MS or other confirmation of field results. To achieve maximum confidence in particular field sample results used to support important findings or site-related decisions, the confirmation scheme may also require in-field evaluation of GC results in order to identify the most significant results and/or unusual results that will be scheduled for GC/MS or other confirmation.

2.8 Analyst Training

This method is to be used only by trained analysts under the supervision of a chemist experienced in the operation of a GC using P-T methodology and in the interpretation of gas chromatograms. Analysts must be aware that, in order to achieve acceptable accuracy and precision using manual injections, particular attention must be paid to the techniques of sample handling and injection.

3.0 GLOSSARY

- TCL - Target Compound List. A complete listing of chemicals that can be detected and reported using this SOP.
- MDL - Method Detection Limit. The anticipated detection limit using the equipment and method specified under this SOP.
- PQL - Practical Detection Limit. The actual detection limit established prior to the start of sample analysis using the site-specific equipment and chemical standards.
- RT - Retention Time. The time it takes a compound from injection to elution at the detector, usually measured in minutes.
- ECD - Electron Capture Detector. Responsive to halogenated compounds (F, Cl, Br, and I ions in decreasing sensitivity)
- PID - Photoionization Detector. Responsive to aromatic and unsaturated aliphatic compounds.
- IS - Internal Standard. A solution of non-target compounds that is injected into the sample container just prior to sample analysis. Necessary for the internal standard method of sample quantitation. See Section 12.
- RRF - Relative Response Factor. Calculation of the response (measured as area counts/concentration) of the compound standard as compared with the response of the internal standard. See Section 12.
- PD - Percent Difference. Calculation of the change in response between the average RRF for a compound in the initial calibration standard curve compared with the response for the same compound in the continuing calibration standard. See Section 12.
- RPD - Relative Percent Difference. Used to calculate the difference in concentration between the initial sample analysis and the duplicate sample analysis.
- RTW - Retention Time Window. Calculation of the expected "window" or range of retention times expected to allow for a 95 percent confidence level that the compound eluting in that retention time window is the expected compound. This is very important for gas chromatographic systems.

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RSD - Relative Standard Deviation. Calculation that measures the linear fit of the target compounds in the initial calibration curve. See Section 12.

4.0 RESPONSIBILITIES

GC Analyst/Chemist - Responsible for all aspects of sample preparation and analysis including equipment maintenance. Also responsible for maintaining chain-of-custody and refrigeration of samples once they are received from sampling personnel.

5.0 PROCEDURES

5.1 Summary of Method

5.1.1 Soils

A measured amount of soil (approximately 5 grams) is placed into a 3/4-inch test tube containing 5 ml of reagent water and sealed. The ratio of the soil to the liquid volume is kept constant for all samples and standards. The sample is subjected to a heated purge with an inert gas to produce the VOCs in the sample, which is injected into the GC. The GC is temperature programmed to separate the VOCs. The VOCs are then detected with a PID and an ECD, which are arranged in series to accept the effluent gas from the GC.

5.1.2 Aqueous

A 5-ml aliquot of a water sample is placed into a 3/4-inch test tube or standard purge vessel. The ratio of the sample volume to the liquid volume is kept constant for all samples and standards. The sample is subjected to a heated purge with an inert gas to produce the VOCs in the sample, which is injected into the GC. The GC is temperature programmed to a separate the VOCs. The VOCs are then detected with a PID and an ECD, which are arranged in series to accept the effluent gas from the GC.

5.1.3 Quality Control

The Quality Control requirements for this method are summarized in chart form in Figure 3 of this SOP.

5.2 Interferences

5.2.1 Contamination Sources

Impurities in the carrier gas, syringe contamination, organic compounds outgassing from the plumbing ahead of the column or temperature-programmed sections of transfer lines, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks, as described in Section 5.9.3. The use of non-Teflon tubing, non-Teflon thread sealants, or flow controllers with rubber components should be avoided.

5.2.2 VOCs (Trip Blanks)

Samples can be contaminated by diffusion of VOCs (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during storage and handling. A trip blank prepared from reagent water and carried through the field activity and the analysis protocol serves

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as a check on such contamination. The trip blank must be prepared by the field analyst according to the frequency specified in the WP or QAPP.

5.2.3 Contaminant Carry-Over

Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sampling syringe should be rinsed with VOC-grade methanol and dried for at least 15 minutes at 60°C to 70°C with the plunger removed from the syringe between sample analyses. Whenever analysis of an unusually concentrated sample (or series of samples, each having similar concentrated contaminant levels) indicates that any target analyte is present at a level of more than 60 times the method reporting limit, then this contaminated sample (or series of samples) should be followed by an analysis of reagent water to check for cross contamination. In addition to preventative measures, if carry-over is suspected after the fact [as defined by a sample containing a positive (reportable) target contaminant level that is less than 1.7 percent of the level detected in the preceding analysis of a higher concentration sample], then the sample in question shall be rerun after the system has been decontaminated and a reagent blank has been acceptably analyzed. For samples containing high VOC levels, it may be necessary to rinse the syringe with methanol several times and then dry it in an oven between analyses as described above.

5.2.4 Solvents

The laboratory where volatile analysis is performed should be completely free of solvents.

5.3 Safety

5.3.1 Reagent Toxicity

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each compound should be treated as a potential health hazard, and exposure to these chemicals should be minimized. The laboratory is responsible for maintaining an awareness of applicable Occupational Safety and Health Administration (OSHA) regulations.

5.3.2 Material Safety Data Sheets

Material safety data sheets (MSDS) must be available at each location of use or storage (mobile laboratory or fixed laboratory) for each chemical used and stored in the laboratory.

5.3.3 Protective Equipment

Analysts must wear appropriate protective equipment when handling samples, standards, or chemical reagents. At a minimum, this will include eye protection. Disposable plastic gloves must be worn whenever sample aliquots are being transferred from one vessel to another and whenever pure or high-concentration chemical standards are being opened or transferred. Pure analytical standards must be opened only under a hood or outdoors, in a restricted-access situation, while wearing respiratory protection to prevent inhalation of organic vapors.

5.3.4 Eyewash Facilities

Eyewash facilities must be available.

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5.3.5 Fire Extinguisher

Fire extinguisher must be present and in good working order.

5.3.6 Spill Control

Spill-control pillows or equivalent spill-control systems must be present and in good working order.

5.4 Apparatus and Materials

5.4.1 Gas Chromatograph

An analytical system, complete with a temperature-programmable GC and purge-and-trap unit is required, and all necessary accessories including injector and detector systems must be designed or modified to accept the appropriate analytical column (packed or megabore). The system shall have a data-handling system attached to the detectors that is capable of labeling, relative retention time (RRT) comparisons, and providing relative and absolute peak height and/or peak area measurements.

5.4.1.1 Capillary Column

Capillary Column: 30 m x 0.53 mm I.D. DB-624 or RT_x 624 fused silica megabore column or equivalent.

5.4.1.2 Detectors

A Tracor PID or its equivalent with a 10.2 eV lamp is connected in series to an ECD.

5.4.1.3 Gas Supply

The carrier gas (helium) and the make-up gas (nitrogen) must be of ultra-high purity grade or better. All gases should pass through oxygen traps before reaching the analytical system to prevent degradation of the column analytical coating. A hydrocarbon trap is recommended ahead of each oxygen trap to extend the life of the oxygen trap and to further reduce interferences causing elevated baseline.

5.4.1.4 Purge-and-Trap Device

The purge and trap device consists of three separate pieces of equipment: The sample purger, the trap, and the desorber. The Tekmar LSC 2000 or its equivalent can be used for this method, with or without the Tekmar ALS 2016 autosampler accessory.

The sample purge vessel must be designed to accept 5-ml samples with a water column at least 3 cm deep. (For the low detection limit option, a 25-ml purge vessel is required.) The gaseous headspace between the water column and the trap must have a total volume of less than 15 ml. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column.

The specifications for the trap are equivalent to those of the Supelco VOCARB 3000 trap. The trap must be 30.5 centimeters long and have an inside diameter (ID) of 0.105 inch. It must be

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packed to contain the following four adsorbent beds, which are specified in the order of desorption flow:

- 50 mg Carboxen-1001, 60/80 mesh carbon molecular sieve
- 150 mg Carboxen-1000, 60/80 mesh carbon molecular sieve
- 200 mg Carbopack B, 60/80 mesh graphitized carbon
- Remainder (fill to void), Carbopack C, 60/80 mesh graphitized carbon

The desorber should be capable of rapidly heating the trap to 250°C. The trap should not be heated higher than 280°C during the bakeout mode.

The purge and trap chassis may be attached to the chassis of the GC or may be configured as a separate unit (connected with a heated transfer line). The use of a directly coupled fused silica transfer line/capillary column interface is recommended to minimize dead volume and achieve optimum separation capability with the GC column.

5.4.2 Sample Injection Syringes

Sample injection syringes must be gas tight, with Teflon-tipped plungers and leur-lock tips. A 5-ml size is most frequently used for samples, smaller sizes (250 uL, 500 uL, 100 uL, 50 uL, and 25 uL) are required for sample dilutions and standards.

5.4.3 Standard Solution Syringes

For transfer of standard solutions, microliter syringes are required in sizes of 10 uL, 25 uL, 50 uL, 100 uL, 250 uL, 500 uL, and 1,000 uL.

5.4.4 Volumetric Flasks

Class A volumetric flasks with ground glass stoppers: 10 ml, 25 ml, 50 ml, 100 ml, and 250 ml, as needed.

5.4.5 Screw-Cap Vials

Forty-ml screw-cap vials with Teflon septa are required for working aqueous standards. One-ml screw-cap vials with Teflon septa are required for methanolic standards.

5.4.6 Drying Oven

5.4.7 Bubble Flow Meters

One 25-ml capacity volumetric burette or electronic device is required.

5.4.8 Leak Detector-Solutions for Detecting Gas Leaks

"Snoop"TM or an equivalent liquid forms bubbles at the source of the leak and should be used on hot surfaces except at or near column head fittings and injector ports. Iso- or 2-propanol should be used on cool surfaces or, if an electronic leak detector is not available, at or near column fitting and injector ports.

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5.4.9 Electronic Leak Detector

The GOW MAC model 21-150 or its equivalent is recommended for use near injectors, columns, or detectors.

5.4.10 Balance

Capable of accurately weighing 0.01 gram, with calibration weight.

5.5 Reagents and Consumable Materials

5.5.1 Reagent Water

Reagent Water - Reagent water is defined as water in which levels of site-specific target compounds are below the PQLs. Reagent water may be generated using a carbon filter bed or a water-purification system or may be purchased (HPLC grade suggested).

5.5.2 Purge-and-Trap Grade Methanol, or Equivalent

5.5.3 Stock Standard Solutions

These solutions should be purchased as manufacturer-certified solutions in methanol, if available; otherwise, stock solutions will be prepared from pure standard materials. Manufacturer-certified stock solutions are available for several internal standards and for all target compounds (although target compound stock mixtures must be custom ordered, as described in Section 5.5.3.2). Several internal standards may not be available as manufacturer-certified stock solutions; if so, these must be prepared from pure liquids. The recommended concentrations of all stock standards, together with their current availability status, are listed in Table 2.

Stock standards and pure reference materials will be documented in a standards preparation logbook (see Figure 1). All standards will be assigned an index/identification number that is listed in this logbook and on the label of the container in which the standard is stored. Purchased material certificates supplied by the manufacturer will be maintained and filed in order of date of receipt for all standards. All stock standards must be stored in a freezer at approximately -10 to -20°C and protected from light. Stock standards will be assigned an expiration date of no more than six months following date of preparation and must be replaced if degradation (color change or evaporation) is indicated. Before the first use of a new target compound stock standard, it must be diluted according to Table Nos. 2 and 3 and analyzed in sequence along with current standards (if they are still considered valid) to verify correct concentrations. If the response for any compound is more than 35 percent different from the old standard, then check the dilution procedures and integration data to verify calculations. If there is still greater than 35 percent difference, then re-analyzed the new and old standards several times in sequence until a minimum of 6 total analyses have been completed and perform a t-test for means (see Section 6.0, Reference No. 9) for each of the non-compliant compounds. If the means of the values obtained for the 2 stock solutions are considered different at the 96 percent level of confidence, then obtain and analyze standards from another source to determine whether the new or the old stock is inaccurate.

5.5.3.1 Primary Dilutions of Neat Standards

Pure compound should be opened in a hood (or using appropriate respiratory protection in a ventilated area). Dilutions of neat standards may be performed using one of two acceptable

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**TABLE 2
SUGGESTED INTERNAL STANDARDS**

Type of Stock Standard Preparation	Compound(s) in Stock Standard Solution	Concentration of Stock Solution	Concentration of Secondary Dilution Mixture	Type of Working Standard
P	3-chloro-2-methylpropene	2,000 µg/ml	250 µg/ml	Capillary column internal
P	4-bromobutene	2,000 µg/ml	250 µg/ml	
P	1,3-dibromo-1propene (cis/trans)	25,000 µg/ml	2,500 µg/ml	
MC	bromochloromethane	2,000 µg/ml	250 µg/ml	standard mixture
MC	2-bromo-1-chloropropane	2,000 µg/ml	2,000 µg/ml	

P: Prepared from pure standard materials.

MC: Manufactured-certified stock solutions.

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**TABLE 3
Suggested Stock Standard Mixtures**

Standard Mixture #1

Compound	CAS Number	Concentration
Tetrachloroethylene	127-18-4	100 ug/mL each in purge-and-trap grade methanol
Trichloroethylene	79-01-6	
Chlorobenzene	108-90-7	
Chloroform	67-66-3	
1,1,1-Trichloroethane	71-55-6	
Bromoform	75-25-2	
1,1,2-Trichloroethane	79-00-5	
1,1,2,2-tetrachloroethane	79-34-5	
Carbon tetrachloride	56-23-5	10 ug/mL in purge-and-trap grade methanol

Standard Mixture #2

Compound	CAS Number	Concentration
1,1-Dichloroethylene	75-35-4	500 ug/mL each in purge-and-trap grade methanol
cis-1,2-Dichloroethylene	156-59-4	
trans-1,2-Dichloroethylene	156-60-5	

Standard Mixture #3

Compound	CAS Number	Concentration
1,2-dichloroethane	107-06-2	500 ug/mL each in purge-and-trap grade methanol
1,1-dichloroethane	75-34-3	
Methylene chloride	75-09-2	

Standard Mixture #4

Compound	CAS Number	Concentration
Acetone	67-61-1	10,000 ug/mL each in purge-and-trap grade methanol
2-Butanone	78-93-3	
2-Hexanone	591-78-6	
4-Methyl-2-Pentanone	108-10-1	
Carbon Disulfide	75-15-0	

Standard Mixture #5

Compound	CAS Number	Concentration
Benzene	71-43-2	1,000 ug/mL each in purge-and-trap grade methanol
Toluene	108-88-3	
Ethyl benzene	100-41-4	
o-Xylene	95-47-6	
p-Xylene	106-42-3	
m-Xylene	108-38-3	
Styrene	100-42-5	

Standard Mixture #6

Compound	CAS Number	Concentration
Bromomethane	74-83-9	1,000 ug/mL each in purge-and-trap grade methanol
Chloromethane	74-87-3	
Chloroethane	75-00-3	
Vinyl Chloride	75-01-4	

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procedures. If a 0.1-mg-accuracy analytical balance is available, then the required procedure is to add several drops of the pure material after tarring a volumetric flask nearly filled with methanol. Alternatively, if a 0.1-mg-accuracy analytical balance is not available, the following procedure shall be followed to achieve dilution of pure components in a quantitative manner. Place approximately 90 ml of methanol into a 100-ml volumetric flask and tare using a top-loading balance that is accurate to ± 0.01 gram. Using a 1,000 μ L syringe, add a measured quantity (700 μ L, for example) of each desired pure compound, recording the exact weight and re-tarring after each addition. If the measured density of each compound is not within \pm five percent of the literature value, then the standard must be re-prepared. Adjust the final volume to 100 ml with methanol, insert the stopper, and mix by inverting the flask several times. Transfer the stock solution carefully (minimizing agitation) into several Teflon-lined screw cap vials with minimal headspace. Primary dilution standards will be prepared in this manner for internal standards that are not available as manufacturer-certified solutions (see Table 2 for concentrations).

5.5.3.2 Manufacturer-Certified Solutions

Upon opening ampoules, these solutions shall be used immediately or else transferred carefully (minimizing agitation) into Teflon-lined screw cap vials with minimal headspace.

5.5.4 Secondary Dilution Standards

Using stock standard solutions, prepare in methanol secondary dilution standards, in mixtures indicated by the groupings in Table 3. These secondary dilution standards shall be prepared by volumetric dilution to yield the concentrations indicated in Table 3. This will enable the aqueous calibration standards prepared in Section 5.5.5 to bracket the working range of the analytical system. Secondary dilution standards prepared in methanol shall be stored, handled, and documented in the standards logbook as described above for stock standards. Secondary dilution standards should be checked frequently for signs of degradation (color change or evaporation), especially just before preparing calibration standards from them. If degradation is suspected, discard the solution, unless standard integrity is verified by means of analysis of a fresh dilution compared to the suspect standard. If the response of the fresh dilution is not within 35 percent of the suspect standard, then the old solution must be discarded. Secondary dilution standards are valid for six months from the date of preparation or two months from the date of first use, whichever occurs first.

5.5.5 Calibration Standards

Initial calibration standards for each analyte of interest will be prepared and analyzed at a minimum of three concentration levels by dilution using a microliter syringe to aliquot secondary dilution standards into a flask or vial containing reagent water. The lowest concentration should not be greater than 2.5 times the PQLs listed in 1. Concentration intervals between adjacent levels of standards should not exceed 50 μ g/L or a factor of five, whichever is greater. To minimize dilutions of samples, the working range should be defined using at least one standard at or above 25 times the PQLs in Table 1. The continuing calibration standard must be at a fixed concentration within the working range. Aqueous standards can be stored up to 24 hours only if held at 4°C in Teflon-sealed vials with zero headspace. If not so stored, they must be discarded after one hour. Relatively lower sensitivity on the ECD shall be calibrated using a separate low-concentration standard, followed by middle- and high-level standards in which these low-sensitivity compounds are present at concentrations appropriately higher than other analytes in order to prevent masking by other compounds. The recommended initial calibration series is given in Table 4.

TABLE 4
Recommended Calibration Series Composition

Mixture No.	Compound	ECD Level 1			ECD Level 2			ECD Level 3 PID Level 1			ECD Level 4 PID Level 2			PID Level 3		
		E/P	µL inj. *	Final Conc.	E/P	µL inj. *	Final Conc.	E/P	µL inj. *	Final Conc.	E/P	µL inj. *	Final Conc.	E/P	µL inj. *	Final Conc.
1	Tetrachloroethylene	E	1.2	0.6	E	4.0	2.0	EP	8.0	4.0	EP	16.0	8.0	EP	32.0	16
	Trichloroethylene	E		0.6	E		2.0	EP		4.0	EP		8.0	EP		16
	Chlorobenzene	E		0.6	E		2.0	E		4.0	E		8.0			
	Chloroform	E		0.6	E		2.0	E		4.0	E		8.0			
	1,1,1-trichloroethane	E		0.6	E		2.0	E		4.0	E		8.0			
	Bromoform	E		0.6	E		2.0	E		4.0	E		8.0			
	1,1,2-Trichloroethane	E		0.6	E		2.0	E		4.0	E		8.0			
	1,1,2,2-tetrachloroethane	E		0.6	E		2.0	E		4.0	E		8.0			
	Carbon tetrachloride	E		0.06	E		0.2	E		0.4	E		0.8			
2	1,1-Dichloroethylene				E	1.2	3.6	EP	4.0	12.0	EP	8.0	20	EP	40	100
	cis-1,2-Dichloroethylene							P		12.0	P		20	P		100
	trans-1,2-Dichloroethylene							P		12.0	P		20	P		100
3	1,2-dichloroethane				E	10	20	E	25	50	E	50	100	E	75	150
	1,1-dichloroethane				E		20	E		50	E		100	E		150
	Methylene chloride				E		20	EP		50	EP		100	EP		150
4	Acetone							P	2.0	100	P	4.0	200	P	15	750
	2-Butanone							P		100	P		200	P		750
	2-Hexanone							P		100	P		200	P		750
	4-Methyl-2-Pentanone							P		100	P		200	P		750
	Carbon Disulfide							P		100	P		200	P		750
5	Benzene							P	1.2	6.0	P	3.6	18.0	P	18	90
	Toluene							P		6.0	P		18.0	P		90
	Ethyl benzene							P		6.0	P		18.0	P		90
	o-Xylene							P		6.0	P		18.0	P		90
	p-Xylene							P		6.0	P		18.0	P		90
	m-Xylene							P		6.0	P		18.0	P		90
	Styrene							P		6.0	P		18.0	P		90
6	Bromomethane				E	10	20	E	25	50	E	50	100	E	75	150
	Chloromethane				E		20	E		50	E		100	E		150
	Chloroethane				E		20	E		50	E		100	E		150
	Vinyl Chloride				E		20	EP		50	EP		100	EP		150

All standards are prepared in purge-and-trap grade methanol for a total volume of 10 mL.
E = Electron Capture Detector (ECD)
P = Photoionization Detector (PID)

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5.5.6 Quality Control (QC) Check Standard

A QC check standard solution should be prepared in methanol using standards prepared independently from those used for calibration. The concentration of this solution must be such that addition of no more than 300 μL to 5 ml water is required to achieve a concentration within the calibrated range.

5.5.7 Internal Standards (IS)

The recommended ISs for this method are shown in Table 2. The same amount (micrograms) of ISs must be added to all samples, blanks, and calibration standards. The IS solution should be a single mixture that is prepared using secondary dilutions of either commercially obtained standards or primary dilutions of pure reference materials. The recommended IS solution should be nominally 25.0 $\mu\text{g}/\text{ml}$ so that addition of 10 μL of this solution to 5 grams of solid sample or 5 ml of aqueous sample will result in an instrument level of 50 $\mu\text{g}/\text{L}$, assuming a 5-ml solution).

5.5.7.1 Alternative ISs

If the ISs listed in Table 2 are not available, other ISs may be substituted only if the following criteria are met: there must be at least 2 ISs for each detector that have similar sensitivity to most analytes; ISs should elute at similarly spaced intervals; ISs must be chromatographically resolved to 25 percent valley from all target compounds and to 5 percent valley from target compounds that are expected to occur or that commonly are found at hazardous waste sites; and ISs must be chemically stable.

5.5.7.2 Handling and Use of IS Solutions

IS solutions shall be prepared, labeled, handled, stored, and documented exactly as described for other standard solutions. Stock IS solutions must be stored at -10 to -20°C . Working IS solutions may be stored at 4°C while in use in the field; otherwise, they must be stored at -10 to -20°C , as with stock solutions. A six-month expiration date is applicable to IS solutions that are not in daily use (stock standards). A one-week expiration date is applicable to working IS solutions (measured from whenever usage begins for spiking of samples and standards). Working IS solutions should be monitored closely for signs of degradation. Deterioration is indicated if evaporation is noted or suggested if internal standard area criteria for a blank are exceeded. If blank IS area criteria are exceeded, check the syringe and rerun the blank. If out-of-control areas recur, run a continuing calibration standard to determine whether the IS solution (as opposed to instrument instability) is responsible for the area shift. Deterioration of the IS solution is confirmed if nearly all (more than 70 percent) of the compounds associated with the suspect IS have out-of-control percent differences (PDs) in response factors in the test continuing calibration, with the direction of bias for PDs of associated compounds opposite that of the IS area shift and with the extent of bias in percent differences similar (within ± 30 percent) for all or nearly all associated compounds.

5.5.8 Matrix Spike Solutions

Matrix spike solutions must be prepared in methanol, labeled, and stored according to the requirements specified for other standard solutions. Matrix spike solutions are valid for six months from the date of preparation or, in the case of working solutions, two months from the date of first use, whichever occurs first. Solutions must also be replaced if consistently low/high recoveries indicate that deterioration is occurring (as per Section 5.9.4). Matrix spike solutions shall be prepared by volumetric dilution of stock standards into methanol so that addition of no more than

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300 uL to a sample is required to achieve a spiking level within the calibrated range. Matrix spike solutions will contain all the project-specific target compounds.

5.6 Sample Collection, Preservation, and Handling

A complete discussion can be found in the standard operating procedures for sample collection. The analyst is responsible for maintaining chain-of-custody and for refrigeration of all samples until all analyses have been successfully completed. All analyses shall be completed within seven days of sample collection or as specified by project schedules, whichever is sooner.

5.7 Configuration, Setup, and Preventive Maintenance of the GC System

5.7.1 Configuration

Chromatographic columns will be installed according to the manufacturer's instructions. The PID shall be connected in series to the ECD. Recommended guidelines for gas flow rates, GC temperature programs, GC columns, and temperatures of heated zones are shown in Table 5. Other settings may be utilized if equivalent performance can be demonstrated and all QC criteria can be met. Other GC columns or temperature programs may be utilized if equivalent or superior resolution between target compounds and equivalent or superior peak width and symmetry can be achieved.

5.7.2 Instrument Set-Up

5.7.2.1 Installation of GC Columns

Installation of the GC column should follow the GC manufacturer's instructions. If the suggested megabore column is to be installed, request from the GC manufacturer or GC owner the prior installation of the megabore connections in the GC oven. Do not have the GC manufacturer or owner install the column prior to shipping to the site. The shock of shipping can cause a break in the column or worse, a hairline fracture that can seriously affect instrument performance and can lead to an outright break later during usage. Be sure to use the recommended ferrules for installation. Do not over-tighten the fittings because this will cause the fused silica tubing of the column to break or fracture either right away or in the future, when it will be hard to diagnose.

Be sure to cut new ends on the column before connection. The new cuts should be at right angles to the column and be burr-free. It is usually a good idea to practice cuts on a scrape piece of fused silica. If, under examination, the cut is not clean and at right angles to the column, cut again until it is. The chromatographic response is very sensitive to proper and leak-free connections of the column in the GC.

Newly installed GC columns must be conditioned for at least 8 hours at typical carrier gas flow rates at a temperature between 10 degrees below the upper operating temperature of this method and the maximum operating temperature for the column. Thereafter, a brief column conditioning equivalent to one method temperature program cycle must be employed if a column is removed from the instrument or exposed to ambient air. If this occurs, carrier gas must be flushed through a column for at least 20 minutes before heating to prevent oxidative decomposition of the stationary phase.

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**TABLE 5
SUGGESTED GC & P-T SYSTEMS SETTINGS**

GC OPERATING PARAMETERS	
UNIT/PARAMETER	SPECIFICATION/SETTING
Column	RTx 624 or DB-624 or equivalent. 30 m X 0.53 mm ID
Carrier Gas	ultra high purity helium
Carrier EPC	27.9 psi
Carrier Flow	7.0 mL/min (if not using EPC)
Anode Purge	23.0 mL/min
Inlet Pressure	45.0 psi
Operation Mode	constant pressure
ECD Aux.	30 mL/min
PID Sweep	20 mL/min
PID Aux.	20 mL/min
Inlet Temperature	200 °C
PID Temperature	220 °C
ECD Temperature	210 °C
Oven Equilibration Time	0.0 min
Oven Max. Temperature	240 °C
Initial Oven Temperature	40 °C (45 °C if not analyzing gases)
Initial Time	7.0 min
First Ramp Rate	4.0 °C
First Temperature	75 °C
First Hold Time	0.0 min
Second Ramp Rate	10 °C
Second Temperature	138 °C
Second Hold Time	0.0 min
PURGE AND TRAP OPERATING PARAMETERS	
UNIT/PARAMETER	SPECIFICATION/SETTING
Purge Flow	40.0 mL/min
Purge Time	9.0 min to 11 min
Purge Temperature (Soils)	40.0°C
Dry Purge Time	4.0 min
Desorb Preheat	220 °C
Desorb Time	2.0 min
Desorb Temperature	220 °C
Bake Bypass	3.0 min. minimum
Make Up Gas	ultra high purity nitrogen

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5.7.2.2 Purge-and-Trap (P-T)

The P-T should be connected to the GC in accordance to the manufacturer's instructions. Recommended guidelines for GC and P-T operations are found in Table 5. All P-T connections should be link-tested prior to initial use. The P-T trap should be conditioned prior to initial use and periodically (once per day) during instrument operation. If the trap was pre-conditioned by the manufacturer, then condition for approximately 10 minutes at 180°C prior to initial use and for 10 minutes at 220°C to 225°C periodically. This is performed by setting the LCS 2000 controller to the bakeout mode and setting time and temperature.

5.7.2.3 Fittings and Ferrules

Brass fittings should generally be used on copper tubing and copper or brass components, and stainless steel fittings should be used on fused silica and stainless steel components unless otherwise recommended by the manufacturers. Ferrules should match the fittings except where special temperature considerations and/or special connections (such as the column connections to the fused silica column) apply. Special ferrules such as graphite, vespel, vespel-graphite, kevlar, kelvex, etc. may be required for use with either brass or stainless nuts. Most ferrules, especially metal ferrules, should never be reused unless suggested by the manufacturer. Tying to reuse ferrules is often the cause of serious leaks.

Remember to turn swagelok fittings 1-1/2 turns past finger tight for 1/2 inch and 1/4 inch fittings and 1-1/4 turns past finger tight for 1/8 inch and 1/16 inch fittings. Tighten beyond this only if the fitting is found to be leaking, and then only slightly, checking frequently to see if the leaking has stopped. Over-tightening fittings can lead to leaking connections that are impossible to fix, fittings that are impossible to loosen, and damaged connections that are difficult or impossible to replace. Never force a nut and ferrule onto a connection; this leads to stripping the threads of the nut and often the connection as well, making it impossible to obtain a non-leaking seal without complete replacement of all components.

5.7.2.4 Transfer Line from the PID to the ECD

Most GCs are constructed to accept up to two columns and as many as three detectors. To connect the PID to the ECD in series, a special transfer line must be installed from the exhaust of the PID to the inlet of the ECD. This transfer line must be contained within the GC oven compartment if at all possible; or run immediately into the oven compartment if the PID design doesn't permit this. This is vital for proper GC separation on the ECD.

The transfer line should be composed of aluminized fused silica, or fused silica, or if necessary, deactivated nickel. There is a gradual build up of certain compounds on the nickel line that makes it the least favorite choice. Aluminized fused silica has a greater tendency to snap than plain fused silica if the location of the PID exhaust is too close to the ECD inlet. Use of a section of the megabore capillary column (fused silica) can be used for the transfer line. If a section of the column is to be used for the transfer line, it is best that it be cut prior to the column installation.

A 16-inch section is the average length used in the transfer line. Follow the GC manufacturer's, or PID manufacturer's, or the owner's recommendations for recommended lengths and materials.

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5.7.2.5 Purge and Trap Transfer Line

A heated transfer line runs from the P-T controller unit (LCS 2000) into the GC. This transfer line consists of a fused silica or aluminized fused silica line contained in a stainless steel tube which is covered by the heating gauze jacket. Under ordinary use, this transfer line remains leak-free after initial installation. However, if the individual units are moved after installation or if all other trouble shooting fails to identify a detected problem, this line should be checked.

The heating sleeve is programmed from the LCS 2000 and should also be trouble free. The control panel will give an error message if trouble develops in this line.

5.7.2.6 Leak Testing

Before initial instrument start-up, thoroughly leak test the system beginning at the gas cylinders and follow the gas flow, finishing at the ECD vent, with the system under pressure but with the heated zones still unheated. Repair any leaks and then repeat the operations with the instrument, PID, and ECD turned on and all heated zones heated at the recommended operating temperatures. Again, repair any leaks. The use of an electronic leak detector and helium as the carrier gas are preferred for all leak testing operations. If an electronic gas leak detector is not available, Snoop™ or soap bubbles can be used for exterior plumbing but must NOT be used for interior components. Instead, a solution of 50-70 percent alcohol (methyl or isopropyl) in water or the manufacturer's suggestions are to be used.

Each time the gas cylinder is changed or another connection is broken then reconnected (such as cleaning the PID lamp), leak testing of the affected connections is required before commencing analysis.

Monitor the contents of the gas cylinders on a daily basis and replace the cylinder when the remaining pressure reaches approximately 250 psig. Even UHP gases build up impurities in the bottom of the cylinder and should be replaced before the contaminants get into the GC system.

5.7.2.7 Flow Measurements

After the leak testing procedure outlined above, conduct flow measurements following the GC manufacturer's instruction. Proper gas flow is essential to proper resolution of target compounds. Be sure to record the flow measurements in the daily log or in the injection logbook and to record any subsequent adjustment or changes. If the flow measurements vary from the manufacturer's suggestions or those listed in Table 5 by a significant amount, recheck all system components, especially the transfer line, for leaks. Fix, remeasure flows, and record them in the daily log.

5.7.3 **Electron Capture Detector (ECD)**

The ECD contains a radioactive source, Ni₆₃. DO NOT ATTEMPT TO OPEN THE ECD CASING UNDER ANY CIRCUMSTANCES! If the ECD is not operating properly and all troubleshooting efforts fail, remove the entire unit and return to the owner or instrument manufacturer for replacement and/or repair.

The results of a recent radiation "wipe test," which checks for radiation leaks, should be available for any newly purchased or leased instrument. This test must be performed at a minimum once every 3 years and may be required as frequently as once every six months, depending in which "state" (US states, territories, military bases, Indian reservations) the instrument manufacturer or

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owner resides. The leak test information should be posted near the instrument at all times. The Nuclear Regulatory Commission (NRC) will provide information on leak test frequency if consulted.

If the instrument is to be used on a military base or on an Indian reservation, or in certain states called "agreement states," written notification and permission to transport and operate the instrument must be obtained prior to shipping. Many agreement states require 30 days written notice and the payment of fee if operated in the state more than 30 days under a specific license. Again, the NRC will provide the necessary information and contacts for agreement states. Exempt radiological instruments such as the ECD may be under either a general or specific license. A general license is held by the ECD manufacturer and allows the owner or leasee agrees to perform wipe tests at required intervals, return the unit for all repairs, source replacement, or disposal. A specific license is held by the owner (not the leasee) and requires the owner to provide a fee, maintain a safety program, have an assigned radiation safety officer, provide training to all maintenance personnel, and perform wipe tests at required intervals, with the results being sent on to the state in which the owner resides. The specific license holder must return the ECD to the instrument manufacturer for source replacement and disposal and may only perform repairs if authorized by the instrument manufacturer.

5.7.4 ECD Maintenance

The ECD's response can be negatively impacted through oxygenation of the source at operating temperatures. The use of ultra high purity (UHP) gases and/or an oxygen trap installed on the gas line between the gas cylinder and the GC can help minimize this problem. If moisture and hydrocarbon traps are also to be installed, install the oxygen trap after the moisture and hydrocarbon traps in the gas supply line. Monitor the contents of the gas cylinder on a daily basis and replace the cylinder when the remaining pressure reaches approximately 250 psig. Even UHP gases build up impurities in the bottom of the cylinder and should be replaced before the contaminants get into the GC system.

Before initial instrument start-up, thoroughly leak test (use of an electronic leak detector and helium as the carrier gas are preferred) the system from the gas cylinder to the ECD vent under pressure but with the heated zones still unheated (see Section 5.7.2.4). Repair any leaks and then repeat the operations with the heated zones heated at operating temperatures. If an electronic gas leak detector is not available, Snoop™ or soap bubbles can be used for exterior plumbing but must NOT be used for interior components. Instead, a solution of 50-70 percent alcohol (methyl or isopropyl) in water or the manufacturer's suggestions are to be used.

If the ECD is totally non-responsive, check the following:

- That the power is on for the GC. Check that the instrument is turned on, both at the instrument itself and in the computer program if one is being used. Also check that the plug is plugged in, and the circuit breaker is not tripped. Remember these can happen to even the most experienced chromatographer; it is better to look for yourself than to have someone else discover it for you.
- That the power is on for the ECD. Check the detector section of the GC to be sure the ECD is turned on there and on the ECD power source if it is separate from the GC. If the ECD is being operated from a computer program such as STAR™ or HP's Chem Station™, check the appropriate screen to be sure the program calls for the detector to be on and at the proper operating temperature.

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- That the correct operating temperature has been set for the ECD and all other heated zones.
- That the gas cylinder regulator is set to the correct pressure and the cylinder valve has been fully opened.
- That the transfer line between the PID and ECD is intact and doesn't have a major crack or hairline fracture. A complete break will be readily visible; use the electronic leak detector or alcohol solution to check for cracks or hairline fractures. This is the most common cause of ECD failure once the GC is operating on a daily basis. If it is leaking, replace the entire transfer line.
- Check the solution preparation to be sure that ECD compounds were included in the preparation of the standard solutions. Check for the presence of chlorobenzene, TCE, and PCE on the PID if contained in the same mixture; check the standard preparation log and standard ampoules if it is not. If no obvious problem is found, re-prepare and reanalyze the standard compound solution. Preparing and analyzing only the mixture containing the missing ECD compounds can also be performed if this is the first time the lot has been analyzed. Occasionally the standard manufacturer mis-prepares the stock solutions, in which all compounds may or may not be present. It is also useful to analyze a standard solution prepared by a separate manufacturer to ensure correct operation of the GC, PID, ECD, and data acquisition systems.

If the ECD has less response (as evidenced by lower area counts in chromatogram):

- Check to see if the transfer line between the PID and ECD is slightly cracked or has a hairline fracture by leak testing with the electronic leak detector or alcohol solution. If it is leaking, replace the entire transfer line.
- See if the PID compounds are similarly affected. This may indicate a leak prior to the PID, or, most likely, degradation of standard solutions. If the preparation and analysis of fresh solutions do not improve the response, search for leaks in the PID seal (especially if the lamp has recently been cleaned and/or replaced), the column, the injection port septum seal if recently replaced, and then begin at the ECD vent and work your way through the plumbing back to the gas cylinder. Occasionally, this may occur if the gas cylinder regulator is not fully open. The solution is to fully open the gas cylinder regulator.

If only some ECD compounds have low or no response:

- Check the preparation of the standard solution if freshly remade, or for solution degradation if the solution has been successfully analyzed previously. Re-prepare the solution in accordance with Section 5.8.

5.7.5 Photoionization Detector (PID)

5.7.5.1 PID Lamps

If an 11.7 electron-volt (eV) lamp is used for the PID, the lamp window material is extremely sensitive to any moisture in the system. A moisture trap must be installed in the gas supply line between the gas cylinder and the GC prior to the installation of the lamp. The lamp window will become opaque and useless once exposed to ambient atmosphere for any length of time (if installed, its expected life is 1 to 3 months). It is important to note that the lamp window must not

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be exposed to water and should be cleaned, when necessary, with a cesium oxide compound. Even the purest of alcohols and other solvents contain significant amounts of water and should not be used.

if a 10.0 or 10.2 eV lamp is used, moisture sensitivity is not a problem but it does have a lesser sensitivity to certain compounds such as methylene chloride.

5.7.5.2 Hydrocarbon Trap

Use of a hydrocarbon trap on the gas supply line between the gas cylinder and the GC is recommended where UHP gases are not used or are not available. If UHP gases are used, the hydrocarbon trap is not necessary but can be installed if desired. If the oxygen trap is also installed, place the hydrocarbon and moisture traps before it in the gas supply line to remove most impurities to increase the effective life of the oxygen trap. See the trap manufacturer's instructions before installation.

5.7.5.3 PID Maintenance

If the PID is totally non-responsive, check the following:

- That the power is on for the GC. Check that the instrument is turned on, both at the instrument itself and in the computer program if one is being used. Also check that the plug is plugged in, and the circuit breaker is not tripped. Remember these can happen to even the most experienced chromatographer; it is better to look for yourself than to have someone else discover it for you.
- That the power is on for the PID. Check the detector section of the GC to be sure the PID is turned on there and on the PID power source if it is separate from the GC. If the PID is being operated from a computer program such as STAR™ or HP's Chem Station™, check the appropriate screen to be sure the program calls for the detector to be on and at the proper operating temperature.
- That the correct operating temperature has been set for the PID and all other heated zones.
- That the gas cylinder regulator is set to the correct pressure and the cylinder valve has been fully opened.
- Check the solution preparation to be sure that PID compounds were included in the preparation of the standard solutions. Often most of the PID compounds (benzene, toluene, chlorobenzene, ethyl benzene, and xylenes) are contained in one solution. Check for the presence of chlorobenzene on the ECD if contain in the same mixture, check the standard preparation log and count ampoules if it is not. If no obvious problem is found, re-prepare and reanalyze the standard compound solution. Preparing and analyzing only the mixture containing the missing PID compounds can also be performed if this is the first time the lot has been analyzed. Occasionally the standard manufacturer mis-prepares the stock solutions, in which all compounds may or may not be present. It is also useful to analyze a standard solution prepared by a separate manufacturer to ensure correct operation of the GC, PID, ECD, and data acquisition systems.

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If the PID has less response (as evidenced by lower area counts in chromatogram);

- The PID lamp window may require cleaning. This would be especially likely if all of the ECD compounds show normal responses. To remove and clean the lamp, follow the manufacturer's instructions. Be sure to cool down the detector before starting to clean the lamp. It is recommended that the lamp window be cleaned either last thing at night or early in the morning, and that the entire instrument be cooled to prevent excessive contamination of the system during the cleaning process. However, turning off the PID and cooling down its heated zone is acceptable if suggested by the instrument manufacturer. It is often safest to turn it off and on at the instrument or power supply rather than using the software if possible. Pulling out the plug on the power supply is also good practice.
- See if the ECD compounds are similarly affected. This may indicate a leak prior to the PID (such as the column or injection port) or, most likely, degradation of standard solutions. If the preparation and analysis of fresh solutions do not improve the response, search for leaks in the PID seal (especially if the lamp has recently been cleaned and/or replaced), the column, the injection port septum seal if recently replaced, and then begin at the ECD vent and work your way through the plumbing back to the gas cylinder. Occasionally, this may occur if the gas cylinder regulator is not fully open. The solution is to fully open the gas cylinder regulator.

If only some PID compounds have low or no response:

- Check the preparation of the standard solution if freshly remade, or for solution degradation if the solution has been successfully analyzed previously. Re-prepare the solution in accordance with Section 5.8.

5.7.6 Preventative Maintenance

5.7.6.1 Once Per Project

- Leak test entire GC system

5.7.6.2 On a Daily Basis

- Check the contents of the gas cylinders. Replace when approximately 250 psig remains.
- Check the pressure of the gas regulators.
- Check and record the temperatures of the heating oven, refrigerator, freezer or cooler, and ambient room temperature.
- Back up all chromatographic and other computer data on floppy disks (or CD if available).

5.7.7 Critical Spare Parts

The following are suggested critical spare parts:

- 2 Swagelok fittings connecting gas regulator with 1/8 inch copper tubing
- 1/8 copper tubing, pre-cleaned, approximately 10 to 50 feet
- 2 or more capillary column repair connectors (Alltech or equivalent)
- one spare cylinder of UHP helium
- one spare cylinder of UHP nitrogen
- 50-100 Thermogreen™ or equivalent low-bleed septa for the injection port
- 1 spare PID lamp

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- 1 spare set PID seals
- 2 sets of the ferrules required for capillary column installation
- 2 sets of the ferrules required for PID to ECD transfer line
- Fused silica for transfer lines (10 to 30 feet)
- 4 each 1/8 swagelok caps and nuts
- 4 each 1/16 swagelok caps and nuts
- 2 each 1/8 to 1/16 swagelok reducing unions
- 2 each 1/8 swagelok unions
- 2 each 1/16 swagelok unions
- 1 full set of fuses for all electrical equipment
- Back up copy of all computer programs, especially the data acquisition program
- Copies of the manuals for all equipment

5.8 Calibration

The calibration program required for this method consists of an initial multi-level calibration to establish linearity within the working range, followed by continuing calibration standards before and after each sample analysis period of up to 12 hours. Calibration QC criteria for this method are summarized in Figure 3.

5.8.1 Initial Calibration

5.8.1.1 Calibration Requirements

A multi-level calibration sequence that meets the requirements of Section 5.5.5 must be analyzed before the analysis of any samples. This initial calibration must be performed each time a new GC column is installed, whenever column flow rates are changed by more than 10 percent, after any maintenance that might conceivably alter the linear dynamic range, or every 30 days, whichever is more frequent. In addition, a new initial calibration must be performed when the continuing calibration criteria described in Section 5.8.2 cannot be met.

5.8.1.2 Initial Calibration Run

Prepare a low-concentration aqueous calibration standard in a Class A volumetric vial according to the procedure in Section 5.5.5. Inject 10 μ L of the internal standard solution described in Section 5.5.7 into the syringe, holding the tip of the syringe needle just beneath the surface of the water. Pour into 5 ml syringe and inject into clean test tube. Proceed with sample injection and analysis following the procedure in Section 5.10.

5.8.1.3 Evaluation of Chromatogram

Evaluate the chromatogram from the first initial calibration standard to make sure that peak tailing, symmetry, width, and retention times indicate typical system performance. All peaks contained in the standard chromatogram must be sharp and symmetrical. Peak widths should be less than 0.40 minute in the early part of the megabore capillary chromatogram or poor injection focusing may be indicated. (The sharpness and width of peaks may need to be optimized by adjustment of injection technique, flow rates, and GC temperature program following instrument operations procedures.) Significant peak tailing must be corrected. All analytes must be visible in the low-concentration standard at least 10 times the baseline noise level. (This will be established for all compounds if the peak height of the smallest peak in the standard chromatogram is greater than five times the height that envelopes peak-to-valley noise fluctuations.) If any significant adjustments are made, repeat the prior initial calibration standard(s).

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5.8.1.4 Response Factors

Analyze the remaining initial calibration standards in the order of ascending concentration levels. After all standards have been analyzed, calculate the relative response factor (RRF) for each of the site-specific target analytes. The RRF, the average of the initial calibration RRFs, and the relative standard deviation (RSD) of the RRFs for each analyte must be calculated using the formulas in Section 5.11.1. The closest eluting internal standard shall be utilized to compute response factors for each target compound, unless it can be shown over three or more initial calibration data sets that smaller percent differences in response factors are achievable by using the other adjacent internal standard.

5.8.1.5 RSD/RRF Criteria

The RSD of the RRF for each of the site-specific target compounds should not exceed 30 percent. The percent RSD of non-target compounds that are to be quantified should not exceed 35 percent.

5.8.1.6 Corrective Actions

If any target compound percent RSD exceeds the acceptance criteria, first verify the associated chromatographic data and calculations for the errant analyte, then prepare fresh standards and reanalyze. If the errant compound performs similarly, then analysis of the QC check solution can serve as verification of the presence or absence of a target compound in the standards. If the compound performs similarly in both solutions, then check the entire chromatographic system and make any necessary repairs. After adjustments are complete, repeat the initial calibration sequence until the calibration criteria in Section 5.8.1.5 are met for the target analytes.

5.8.1.7 Detector Selection

For compounds with similar sensitivity on both detectors (specifically, methylene chloride, trichloroethene, and tetrachloroethene), quantitation should be pre-selected for routine reporting of results from one detector or the other at the time of initial calibration. RSD criteria must be met for the detector used for quantitation. Note that the data system should calculate RRFs and levels on both detectors as a form of corroboration and to allow alternate quantitation for samples with interfering peaks on one detector.

5.8.2 **Continuing Calibration**

5.8.2.1 Calibration Requirements

A calibration standard (containing all target analytes) that meets the requirements of Section 5.5.5 must be analyzed at the beginning and end of each period of up to 12 hours of sample analysis. In addition, this continuing calibration standard must be analyzed after every 20 analytical runs or after any system adjustments or maintenance that might alter quantitative response or retention times, whichever is more frequent.

5.8.2.2 Response Factors

After the continuing calibration standard has been analyzed following the procedures in Section 5.10, calculate the RRF for each target analyte and compute the percent difference (%D) for each

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RRF relative to the initial calibration RRF, according to the formula presented in Section 5.11.2. Note that, if samples are to be analyzed in the 12-hour period following an initial calibration, there is no requirement to compute the %D from any standard run before the samples, as long as quantitation for this group of samples is performed using the average RRF. Alternatively, if the data system is not capable of quantitation using the average RRF, quantitation may be performed using one of the mid-range initial calibration standards. However, in this case, the %D of RRFs in this standard, relative to the average RRFs from all standards, must be computed and evaluated.

5.8.2.3 Percent Difference (%D)

The absolute percent difference (%D) between the initial and the continuing calibration standard for each of the site-specific target compound should not exceed 25 percent. The %D of non-target compounds that are to be quantified should not exceed 30 percent.

5.8.2.4 Corrective Actions

If any site-specific target compound %D exceeds the acceptance criteria, first verify the associated chromatographic data and calculations for the errant analyte. If out-of-control system response is confirmed, check the system and make any necessary repairs. If only minor adjustments are required (i.e., cleaning the PID window) that do not mandate a new initial calibration as per Section 5.8.1.1, then a new continuing calibration standard may be analyzed. All sample analyses since the last acceptable calibration standard must be repeated after appropriate correctable action and acceptable calibration analyses have been performed. Sample reanalysis may not begin until an acceptable calibration standard that meets the requirements established above has been performed.

5.8.3 Calibration Using External Standards

When sample-specific interferences exist with an internal standard, the analyst may choose to quantify using the external standard method. If the external standard method is selected, initial calibration data and the continuing calibration standards run before and after the sample must be reprocessed to generate and compare calibration factors (CFs) instead of RRFs, using the formulas presented in Sections 5.11.4 and 5.11.5. Quantitation may not be performed using the external standard method unless the RSDs of the CF (from the initial calibration) for the target analyte(s) being quantitated are all less than or equal to 30 percent and unless the CFs for these analytes in the standards run before and after the sample in question all exhibit a %D less than 25% relative to the initial calibration average CF.

5.9 Quality Control

The QC program required for this method includes analysis of QC check standards, trip blanks, equipment rinsate blanks (where appropriate), laboratory reagent blanks, spiked samples, laboratory duplicate samples, field duplicate samples, retention time window monitoring, internal standard monitoring, and maintenance of a QC records database. For all the above areas, any identified problems and corrective action must be documented in the instrument run log, analysis narrative report, and instrument maintenance log or standards log (as applicable). Temperatures of the oven and/or waterbath, freezer, refrigerator, and room used for analysis will also be recorded in the log book on a daily basis. An example page format for the instrument run log is shown in Figure 4 and a standards log is in Figure 1. A summary of the QC requirements for this method is provided in Figure 3.

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5.9.1 QC Check Standard

A QC check standard solution, prepared as in Section 5.5.6, must be analyzed at least once each field analysis project or once each initial calibration, whichever is more frequent. The results of the QC check standard must fall within 50 percent to 150 percent of the true value. If these criteria are not met, check the entire analytical procedure to locate and correct the problem source. Corrective action may include preparation and/or analysis of a new QC check standard or new calibration standards followed by re-analysis of the QC standard.

5.9.2 Field Quality Assurance Blanks

Trip blanks and equipment rinse blanks must be prepared according to the frequency specified in the WP or QAPP. If any of these blanks are contaminated with target analytes at levels greater than five times the method reporting limits, the problem must be investigated, corrected, and reported to the project leader for the sampling investigation. These blank data should be evaluated immediately after analysis in sufficient time to allow re-analysis or other corrective action. If any of these blanks are found to be contaminated with target analytes above ten times the PQLs, then a laboratory reagent blank shall be prepared and analyzed immediately following the field QC blank to test whether the problem can be traced to the laboratory procedure. If the associated laboratory reagent blank is also contaminated, the trip blank and any affected samples associated with the contaminated laboratory blank must be re-analyzed according to the requirements of Section 5.9.3. Affected samples are defined as those with instrument levels less than five times the instrument level in the associated laboratory blank.

5.9.3 Laboratory Reagent Blanks

A laboratory reagent blank must be analyzed after each initial calibration sequence, after each continuing calibration standard that precedes associated sample analyses, after any sample run that might be high enough to produce instrument carryover at reportable levels in a subsequent sample (see Section 5.2.3 for criteria), and whenever a new batch of reagents (e.g., methanol or reagent water) is introduced. The results of the laboratory reagent blank must be evaluated before analysis of any subsequent samples. If any target analytes are present at levels greater than five times the method reporting limits, then sample analysis may not proceed until the problem has been corrected and an acceptable reagent blank has been analyzed.

5.9.4 Matrix Spike Samples

Spiked sample analysis shall be performed at the frequency specified in the WP or QAPP. Samplers will identify samples to be used for spiking on the chain-of-custody form and will supply additional containers for such samples. If samplers do not designate samples to be matrix spiked, then the analyst shall select one sample to be spiked per each group of 1 to 20 solid or aqueous samples of a similar matrix. The corresponding unspiked sample should be analyzed first in order to allow calculation of an appropriate level of spike to be added (within the calibrated range but greater than three times the indigenous concentration of the same analytes). Inject an appropriate quantity of the spiking solution described in Section 5.5.8, containing all site-specific target compounds (at the minimum) through the septum of the sample bottle, with the tip of the syringe needle beneath the surface of the water. Add 10 uL of the internal standard solution in the same manner and proceed with aliquot injection and analysis of the spiked sample following the procedures specified in Section 5.10. After completion of both the spiked and unspiked analysis, calculate the percent recovery for each analyte added according to the formula presented in Section 5.11.7. If the recovery of any analyte is outside the control limits of 50 to 150 percent, then investigate and correct the problem following the decision scheme given below:

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- Repeat the spike analysis on a fresh aliquot. If results are still outside the limits then:
- Double check the chromatographic identification and integration data and recalculate the spike results.
- If the out-of-control analyte was positive in the unspiked sample and if all spike analytes that are not found in the unspiked sample are in control, then repeat the spike analysis using a five times higher relative spiking level by reducing the sample volume and/or increasing the amount of spike added. Note that the volume of spike solution added should not exceed 300 uL and spike results should be within the calibrated range.
- If only the more volatile spike compounds have low recoveries (those with boiling points under 75°C) and internal standard areas are acceptable, then deterioration of the spiking solution shall be investigated. A new spiking solution should be prepared and the spiked sample should be re-analyzed. Alternatively, a reagent water spike may be performed to verify the integrity of the spiking solution. If the reagent water spike exhibits similar performance, then a fresh spiking solution must be prepared and a new spiked sample analysis performed.
- If spike results from the current sample and the most recent previous sample spiked with the same solution all exhibit out-of-control recoveries for the same analytes, with a comparable direction and extent of bias (within ± 30 percent), then the integrity of the spiking solution shall be investigated as described in bullet No. 4.
- If spike recoveries are all high or all low with a similar extent of bias (within ± 30 percent), but internal standards are within control limits, then a spiking error is suggested and the spiked analysis shall be repeated.
- If the recovery for any analyte is outside the limits 50 percent to 150 percent and if the preceding steps do not resolve the problem, then a repeat of the matrix spike shall be performed to verify a matrix effect (if not already conducted per the preceding bullets).

5.9.5 Laboratory Duplicate Samples

Laboratory duplicate sample analysis shall be performed at the frequency specified in the WP or QAPP. Samplers will identify samples to be used for laboratory duplicate analysis on the chain-of-custody form and will supply extra volume for such samples. Analyze the same aliquot size that was used for the initial sample analysis. Calculate the relative percent difference (RPD) using the formula presented in Section 5.11.8. If the RPD for any analyte is not within warning limits of ± 50 percent or if any analyte is present at a level greater than five times the PQL in one analysis but not detected in the other analysis, then data shall be further scrutinized according to the following scheme and appropriately discussed in the narrative report:

- Verify that sample labeling, chromatographic identification and integration data, and calculation of duplicate results are correct.
- If any of the three largest component peaks in the sample are above the PQL in both analyses but exhibit an RPD of greater than 150 percent (a factor of 4 disagreement), then the project leader shall be informed and a third aliquot or a fresh sample obtained from the same location shall be analyzed.

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- If any target compound is detected in one analysis at a level above five times the PQL but not found in a duplicate analysis, then the project leader shall be informed in sufficient time to allow re-analysis or other corrective action. (These options depend on site-specific objectives, which are beyond the scope of this analysis SOP.)

5.9.6 Field Duplicate Samples

Field duplicate samples will be collected at the frequency specified in the WP or QAPP. Evaluation and corrective action shall be handled as for laboratory duplicates, as discussed in Section 5.9.5.

5.9.7 Retention Time (RT) Monitoring and Control

Since analyte identification is based solely upon RT matching, established procedures must be followed to determine the width of RT windows. If the widths of RT windows used for identification are unrealistically narrow, false negatives may occur. Conversely, windows that are too wide will increase the likelihood that interfering compounds will elute within analyte identification windows.

5.9.7.1 Calibration Standard Runs

To establish the width of the RT window for each analyte on a given GC column and under a particular set of operating conditions, before any samples are analyzed, at least five calibration standards must be analyzed over the course of a 7- to 12-hour period. These standards must be representative of RT behavior over a typical analysis period (analogous to samples run at various intervals). Therefore, between 20 and 60 percent of the total number of standards used to develop each RT window must consist of standards analyzed within the middle one-third of the time interval between the first and the last standard for the 7- to 12-hour period.

5.9.7.2 Compound Identification

After the above standards have been run, carefully evaluate all standards to make sure that no compounds have been misidentified. Whenever any doubt exists about the identity of a component peak, an individual standard containing the component in question must be analyzed to confirm elution times. Elution orders of previous standard chromatograms obtained on the same column should be compared as a check against misidentification each time new RT windows are established.

5.9.7.3 Calculation of RT Window Width

Using retention time data from the above-referenced standards, the width of RT windows shall be calculated as described in Sections 5.11.9 and 5.11.10, based upon an IS method for RT prediction. The formula in Section 5.11.9, which uses the Relative Retention Time (RRT) method, shall be used for all analytes. Section 5.11.10 also contains an alternate calculation technique for computing the width of the RT windows based upon an external standard method for RT prediction, which shall be used for target compounds only in situations where sample components obscure ISs.

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5.9.7.4 RT Window Widths for Target Analytes

Using the formula in Section 5.11.9.2, compute the width of the RT window for each target analyte as plus or minus the square root of the variance of the observed minus the predicted RTs within the standard set, multiplied by the student's t-value using an 0.995 confidence level and given the number of degrees of freedom in the set of standards used to calculate the variance.

5.9.7.5 RT Window Width - Modification

The RT windows calculated above must be modified if they are unrealistically narrow, given the limitations of the data system and chromatographic resolution. The most important application of this principle is when two compounds co-elute in the standard chromatogram. If two separate peak maxima do not exist, then the overall width of the combined peak shall be compared to that of a normal (fully resolved) nearby component to determine the approximate retention time error. The RT difference between the width of a "normal" peak and that of the co-elution peak shall be added to the RT window width determined above in order to obtain a realistic retention time window for both components of the co-eluting pair.

5.9.7.6 RT Window Width - Optimization

Uncertainty in RTs must also be considered for fully resolved components in the sense that locations of peak apexes are not precisely known. Therefore, the working RT window for each analyte must be greater than or equal to the maximum of the quantities: ± 1.5 times the step size of the integrator or \pm three times the uncertainty in the measurement of the retention time of a typical peak apex or centroid (which is a function of peak widths). When the megabore capillary column is optimized to achieve peak widths less than or equal to 0.33 minute (measured to include 95 percent of total area) and when the packed column is optimized for peak widths of 0.70 minute or less, then the calculated RT windows must be greater than or equal to ± 0.02 minute on the megabore column and on the packed column. (Note that the sharpness of chromatographic peaks can be optimized by adjustment of injection technique, flow rates, etc.) If the RT windows calculated in 10.7.4 are less than the above values for any analyte, then substitute the largest of the alternate limiting values defined above.

5.9.7.7 RT Window Widths - Utilization Time Frame

Once RT window widths have been established, they may be utilized for a maximum of 90 days. (Although the widths of the RT windows remain constant over this 90-day period, the center of each compound's prediction window varies with each 12-hour calibration and with internal standard shifts in each sample.) Irrespective of this maximum, revised RT windows must be developed if the continuing calibration retention time criteria in Section 5.9.7.9 recurrently cannot be achieved, if absolute retention times shift more than 10 percent for any compound, if a new GC column is installed, if a new GC temperature program is adopted, or if carrier gas flow rates used for analysis are altered by more than 15 percent from the values used in window development, whichever occurs first.

5.9.7.8 RT Window Widths - 12 Hour Cycles

A calibration standard containing all target analytes must be analyzed at the beginning and end of each period (of up to 12 hours) of sample analysis. The standard run immediately before each group of samples will be used in conjunction with internal standard elution times in these samples, to predict the RTs for each analyte. Using the formulas in Section 5.11.9.3, the RT window for

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each analyte will be calculated as the predicted RT plus or minus the RT window width computed in Sections 5.9.7.1 through 5.9.7.5.

In the event of sample-specific interferences with internal standards, the center of each analyte's RT window will be defined as equal to the absolute RT from the most recent calibration standard, and the plus or minus RT window width will be calculated according to the alternate external standard formula in Section 5.11.10.2.

5.9.7.9 RT Window Widths - Corrective Actions

The calibration standard analyzed at the end of each period of up to 12 hours of sample analysis must exhibit RTs for all target analytes that fall within the windows predicted from the calibration standard run immediately before the group of samples. If any analyte in this standard elutes outside established RT windows, appropriate corrective action must be taken, after which affected samples must be re-analyzed. If criteria are exceeded, first verify associated chromatographic calculation data. If out-of-control RTs are confirmed, then check the system (flow rates, leak checks, etc.) and make any necessary adjustments or repairs. A new continuing calibration standard must be run following any minor system adjustments, whereas a new initial calibration must be performed if any of the more serious adjustments described in Section 5.8.1.1 are made. New RT window widths must be developed if any of the major system adjustments described in Section 5.9.7.7 are made or if repetitive problems with out-of-control RTs are experienced.

5.9.7.10 RT Window Widths - Revisions

Revision of RT window widths may be performed by the analysis of five or more standards in one 12-hour period (as described in Section 5.9.7.1).

5.9.8 **Internal Standard (IS) Monitoring and Control**

IS retention times and area response shall be monitored and controlled in all analytical runs. IS retention times in all sample runs must fall within established RT windows to ensure that overall retention time performance for the GC system is stable and in control and to ensure that nearby co-eluting compounds are not mistaken for an internal standard (thereby causing erroneous analyte RT prediction or quantitation). Similarly, all IS area responses must fall within established QC limits to ensure stable and accurate quantitative performance of the injection, GC, and detectors and to ensure that unknown compounds co-eluting with an IS cannot cause seriously biased quantitation.

5.9.8.1 Calculation of IS Retention Time Window Width

IS retention time window widths shall be established concurrently, using the same calibration standard run data and whenever RT windows are established for target analytes. Therefore, all procedures specified in Sections 5.9.7.1 through 5.9.7.10 for target analyte RT windows are also applicable to the establishment and control of RT windows for ISs with one exception: the calculation techniques and formulas referred to as the "external standard technique" in Section 5.9.7.3 shall be used to establish the width of RT windows for internal standards and in Section 5.9.7.8 to establish the center of the RT windows for ISs. This is necessary because IS elution times in sample analyses are predicted using data from only the calibration standard runs (as opposed to using one IS in a sample to predict the RT for another IS in the same sample).

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5.9.8.2 IS Performance

IS performance in each analytical run must be evaluated and compared to the most recent calibration standard (run at the beginning of the 12-hour period). If any IS elutes outside its established RT window, first check the associated chromatographic data to determine whether IS retention times (or IS areas) are obscured by an unknown co-eluting sample component.

5.9.8.3 IS Performance - Retention Times

If IS areas are within the control limits specified in Section 5.9.8.5 and if peak width and symmetry for the IS with out-of-control retention times appear normal, then the sample must be rerun under the assumption that the actual elution times for the IS have shifted and are out of control. If this occurs, first check the system for malfunctions. If any adjustments are made, then the appropriate recalibration must occur before sample re-analysis.

5.9.8.4 IS Performance - Alternate Quantitation

Conversely, if peak shape is atypical (unusually wide or asymmetric) for the IS with out-of-control RTs or if IS areas are high (above limits) for the IS with noncompliant RTs, then a co-eluting interference is suggested. In this case, the alternate quantitation (external standard) option shall be performed to evaluate data associated with the noncompliant IS.

5.9.8.5 IS Performance - Area Response

Concurrent with the evaluation of RTs, the area response of each IS in each analysis must be evaluated to ensure that the percent difference in areas are between -50 percent and +200 percent of the IS areas in the most recent calibration standard. If criteria are exceeded, check the associated chromatographic data to determine if co-elutions or peak overlaps have biased the IS area response. Re-integrate the IS peak only if incorrect integration endpoints or baseline were selected by the data system. (Re-integration solely to achieve area criteria that skew or distort accurate IS area measurement is strictly forbidden.)

5.9.8.6 IS Performance - Overlapping Area Response

If out-of-control IS areas are associated with overlapping peaks having greater than 33 percent valley relative to the IS height or if a high IS area (above limits) is associated with either out-of-control retention times or wide or asymmetric peak shape, then a co-eluting chromatographic interference is suggested. In this case, the alternate quantitation (external standard) option shall be performed to evaluate data associated with the noncompliant IS.

5.9.8.7 IS Performance - Out-of-Control IS Areas

Conversely, if out-of-control IS areas exist but are not associated with the conditions specified in 10.8.6, then the sample must be rerun under the assumption that the quantitative response of the IS is biased due to matrix effects, poor injection performance, or inaccurate system performance. If this occurs, first check the system for malfunctions. If any adjustments are made, then appropriate recalibration must occur before sample reanalysis. In the special case of blank analysis, if both initial and re-analysis exhibit out-of-control IS areas, then the required corrective action will be to run a continuing calibration standard to check whether system response or IS solution integrity are at fault, following the procedure in Section 5.5.7.2.

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5.9.8.8 IS Performance - Corrective Action

If chromatographic interferences are suggested for one IS and inaccurate system performance is indicated for another IS, then both types of corrective action shall be taken. System performance shall be checked first to allow adjustments to be made before reanalysis.

5.9.8.9 Analytical Results

Whenever a re-analysis is performed, the analyst shall follow the procedures for data reduction, validation, and reporting in order to determine which of the analyses (or whether both analyses) is to be reported.

5.9.9 **QC Records Database**

All the QC data in this section and the quantitative calibration QC data must be maintained in a QC records database for the project. Any adverse trends in QC parameters shall be investigated, corrected, and documented in the QC database for the project. QC database items shall include RT window data, initial and continuing calibration response summaries, blank results, duplicate results, matrix spike and QC check standard recoveries. In addition, any quantitative comparison data from the evaluation of standard solution integrity shall be retained. Instrument logbooks and standard preparation logbooks that are no longer in use must also be retained in the project files.

5.10 Procedure for Sample Analysis

5.10.1 **GC Operating Conditions**

Table 5 summarizes the recommended GC operating conditions for this method. The sample analysis sequence and analytical decision scheme shown in Figure 2 may begin after all required QC criteria have been met, procedures have been completed as specified for GC system setup and configuration (Section 5.7), calibration standards preparation (Section 5.5) and analysis (Section 5.8), and RT windows have been established as per Section 5.9.7.

5.10.2 **Syringe Preparation and Handling**

5.10.2.1 Syringe Preparation

The 5 ml sample injection syringe for aqueous samples must be rinsed with methanol and dried in an oven for at least 15 minutes at 65°C to 70°C (but never hotter) before each injection. The plunger must be removed from the syringe bore before baking and should be re-inserted upon removal from the oven. For soil samples, the syringe should be cleaned once before the start of use and at frequent intervals thereafter.

5.10.2.2 Syringe Inspection/Maintenance

The syringe should be examined frequently for signs of leakage or blockage. During the methanol rinse step, as methanol is withdrawn into the syringe, there should be no air bubbles forming or entering the syringe near the plunger tip or the point of needle attachment. Leakage from the plunger tip can be remedied by replacing the Teflon tip on some syringe models. Leakage from the needle can be remedied by tightening or replacing the removable needle assembly. Blockage of the syringe needle is suggested when excessive resistance is encountered as the plunger is withdrawn or depressed or when the methanol rinse solution is expelled from the needle as an uneven spray as opposed to a steady flow. If blockage of the needle is suspected, clean the

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needle using the fine-gauge wire supplied with the syringe. If this is not successful, replace the needle and again clean the syringe assembly with methanol.

5.10.2.3 Sample Injection Volume

A 5.0 mL syringe should be used for all standards, water, and soil injection. If a dilution is indicated, a smaller sample size will be utilized.

5.10.3 **Sample Introduction**

5.10.3.1 Aqueous Samples

Remove the plunger from a 5-ml Luerlok syringe and close the two-way valve at the tip. Carefully pour (without agitation) the aqueous sample into the syringe, filling to just above the 5-ml mark. Immediately replace the plunger, invert the syringe, open the two-way valve, carefully vent any entrapped air bubbles, and adjust the volume to 5 ml.

If a dilution of the sample was indicated based upon prior analysis or based upon field measurements (e.g., total organic vapor readings), an aliquot of sample (5 ml or less) is transferred to a 10 ml Class A volumetric flask and diluted up to the mark. This solution is thus used to fill the syringe, as described in the previous paragraph.

Add 10 ul of the IS solution described in 5.5.7 through the syringe valve bore, then close the syringe valve.

Attach the syringe to the syringe valve on the purging device. Open the valve and inject the sample into the purging chamber. Close the valve.

5.10.3.2 Soil Samples

Remove the plunger from a 5-ml Luerlok syringe and close the two-way valve at the tip. Pour reagent water into the syringe, filling to just above the 5-ml mark. Replace the plunger, invert the syringe, open the two-way valve, carefully vent any entrapped air bubbles, and adjust the volume to 5 ml.

Add 10 ul of the IS solution described in 5.5.7 through the syringe valve bore, then close the syringe valve.

The sample (for volatile organics) consists of the entire contents of the sampling container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh five grams of sample into a tared purging device. Use a top loading balance. Note and record the actual weight to the nearest 0.1 gram. Note: If a dilution of the sample was indicated based upon prior analysis or based upon field measurements (e.g., total organic vapor readings), then a smaller weight of sample shall be utilized, down to a minimum of 1.0 gram.

Add the spiked reagent water to the purge device and connect the device to the purge and trap system.

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5.10.4 Qualitative Data Evaluation

5.10.4.1 Sample Chromatogram Review

Carefully compare the sample chromatograms with those of the most recent calibration standard. Determine if any peaks interfere with or possibly prevent detection of target compounds that might be present at a level equal to the PQL.

5.10.4.2 Peak Interference

If one or more interfering peaks (as defined above) are present, notify the project leader in sufficient time to consider possible re-analysis options (CLP or dilution). (Decision criteria for these options are based upon site-specific objectives, which are beyond the scope of this analysis SOP).

5.10.4.3 Sample Dilution/Reanalysis

To prevent damage to the instrumentation and/or excessive carry-over, the analyst shall ensure that appropriate dilution levels are utilized for any required re-analyses. Any re-analysis must be performed using a dilution whenever target compounds are above the upper limit of the calibrated range or whenever non-target compounds cause gross saturation. For any dilution, no more than 25 percent of the chromatogram should consist of a peak envelope that continuously exceeds the height of the nearest IS above the baseline observed in the blank nor should more than 4 interfering peaks be present in the chromatogram of the dilution run at a peak height greater than 5 times IS heights or overrange.

5.10.4.4 Contaminant Carry-Over

High-level sample(s) (defined as containing any target compound at a level more than 300 times the PQLs) should be followed by an analysis of reagent water (and possibly additional decontamination measures) as described in Section 5.2.3. If carry-over is suspected after the fact, as defined by a sample containing a positive (reportable) target contaminant level that is less than 1.7 percent of the level detected in the preceding analysis of a higher concentration sample, then the sample that exhibits possible carry-over shall be rerun after the system has been decontaminated and a reagent blank has been acceptably analyzed.

5.10.5 Internal Standards Evaluation

5.10.5.1 RT Windows

Determine whether ISs elute within their established RT windows according to the procedures specified in Sections 5.9.8.1 through 5.9.8.4. Concurrently, evaluate whether IS areas are within control limits or are biased by peak overlaps, co-elutions, poor injection, or poor system performance, as per Sections 5.9.8.5 through 5.9.8.7.

5.10.5.2 Corrective Action

IF IS retention time or area criteria are exceeded, follow the decision scheme and specified corrective action procedures in Section 5.9.8 to determine whether to reprocess the data using the external standard method, re-analyze the sample on a second GC column, or correct system malfunctions, recalibrate, and then perform re-analysis. If IS area criteria are exceeded for a

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blank, follow the decision scheme and specified corrective action procedures in Sections 5.5.7.2 and 5.9.8.7.

5.10.6 Compound Identification

5.10.6.1 Target Compound Identification

Determine whether target compounds are present in the sample by comparing each analyte's predicted RT window with the observed peak RTs in the sample, following the procedure in Section 5.9.8.7 and using the formula in Section 5.11.9.3. The IS prediction technique(s) shall be used except when the interferences defined in Section 5.9.8 mandate the use of the external standard methods.

5.10.6.2 Peak Interference

If more than one peak elutes within the RT window for an analyte, then the analyst shall report the higher concentration peak and explain the possibility that a lower level may be present in the text (one of the two peaks must be an interference).

5.10.6.3 Co-elution

When two compounds co-elute in the standard chromatogram, compound identifications shall be reported for both analytes, with an explanation of the inability of the chromatography to distinguish between the two compounds. Note that this does not apply if only one of the coeluting compounds responds on two detectors, such that the second detector can determine which compound is present.

5.10.6.4 Dual Detector Response

When both detectors respond to an analyte in the standard chromatogram (specifically, for methylene chloride, trichloroethene, and tetrachloroethene), then the analyst shall check whether peaks elute within RT windows on both detectors. For any of these particular analytes to be considered present, peaks must elute within RT windows on both detectors and the computed amounts must agree within a factor of 3 or, alternatively, the lack of agreement with the second detector must be explainable by visible chromatographic interferences from compounds at nearby RTs. If the only evidence of interference consists of an abnormal concentration ratio between the two detectors, then the lower concentration shall be reported as the sample detection limit.

5.10.7 Compound Quantitation

5.10.7.1 Target Analyte Quantification

Compute the concentration of the detected target analytes using the most recent calibration standard data according to Section 5.8.2.2 and using the formula in Section 5.11.3. The IS quantitation technique shall be used except when the interferences defined in Section 5.9.8 mandate the use of external standard quantitation (Section 5.11.6).

5.10.7.2 Integration Endpoints and Baseline

Evaluate the chromatogram and integration report of the sample to ensure that correct integration endpoints and baseline were applied for each target analyte identified in Section 5.10.7.1. Re-integrate analyte peaks if errors are discovered.

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5.10.7.3 Co-elution

If any interfering chromatographic peak is not resolved to less than 33 percent valley relative to the height of an adjacent peak for an identified target analyte or if any target compound exhibits an unusually wide or asymmetric peak that, in the opinion of the analyst, represents the effects of co-elution, then the project leader shall be informed in sufficient time to consider possible re-analysis options (CLP or re-analysis). (These options depend on site-specific objectives that are beyond the scope of this analysis SOP.) Any reported sample results associated with such co-elutions shall be qualified with an explanation of the influence of the co-elution on the quantitative accuracy for the analyte concentration.

5.10.7.4 Sample Dilution

If any target compound is present at a level that exceeds the calibrated range of the system, a dilution shall be required. Note that a fresh (unused) aliquot of sample must be utilized for all re-analyses or dilutions as the integrity of the sample becomes suspect with repeated heating and septum punctures.

5.11 Calculations

5.11.1 Initial Calibration Relative Response Factors (Internal Standard Method)

5.11.1.1 Relative Response Factor of Standard i (RRF_i)

$$RRF_i = \frac{A_c}{A_i} \times \frac{Q_i}{Q_c}$$

Where: A_c = area of target compound in standard
A_i = area of internal standard in standard
Q_c = amount of target compound in standard (nanograms)
Q_i = amount of internal standard in standard (nanograms)

5.11.1.2 Average Relative Response Factor (RRF_{ave}) of N Standards

$$RRF_{ave} = (1/N) \times \sum_{i=1}^N RRF_i$$

5.11.1.3 Relative Standard Deviation (RSD) of RRF

$$\text{percent RSD} = \frac{100}{RRF_{ave}} \times \sqrt{\sum_{i=1}^N (RRF_i - RRF_{ave})^2 / (N - 1)}$$

5.11.2 Continuing Calibration Percent Difference (PD) (Internal Standard Method)

$$PD = \frac{RRF_{cont} - RRF_{ave}}{RRF_{ave}} \times 100$$

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Where: RRF_{cont} = RRF of continuing calibration standard

5.11.3 Concentration of Target Compound in Sample (Internal Standard Method)

$$\text{conc. (ug / kg)} = \frac{A_{C(SPL)}}{A_{I(SPL)}} \times \frac{Q_I}{RRF_{cont}} \times \frac{DF}{\text{sample wt. (g)}}$$

Where: $A_{C(SPL)}$ = area of target compound in sample
 $A_{I(SPL)}$ = area of internal standard in sample
 Q_I = amount of internal standard in sample (nanograms)
 DF = dilution factor, if applicable (equal to standard over sample injection volume)

5.11.4 Initial Calibration - Calibration Factors (External Standard Method)

5.11.4.1 Calibration Factor of Standard i (CF_i)

$$CF_i = \frac{A_C}{Q_C}$$

Where: A_C = area of target compound in standard
 Q_C = amount of target compound in standard (nanograms)

5.11.4.2 Average Calibration Factor (CF_{ave}) of N Standards

$$CF_{ave} = (1/N) \times \sum_{i=1}^N CF_i$$

5.11.4.3 Relative Standard Deviation (RSD) of CF

$$\text{percent RSD} = \frac{100}{CF_{ave}} \times \sqrt{\sum_{i=1}^N (CF_i - CF_{ave})^2 / (N - 1)}$$

5.11.5 Continuing Calibration Percent Difference (PD) (External Standard Method)

$$PD = \frac{CF_{cont} - CF_{ave}}{CF_{ave}} \times 100$$

Where: CF_{cont} = calibration factor in continuing calibration standard

5.11.6 Concentration of Target Compound in Sample (External Standard Method)

$$\text{conc. (ug / kg)} = \frac{A_{C(SPL)}}{CF_{cont}} \times \frac{DF}{\text{sample wt. (g)}}$$

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Where: A_C , DF defined as in 12.3

5.11.7 Matrix Spike Recovery

$$\text{percent recovery} = \frac{(\text{conc. in spike}) - (\text{conc. in sample})}{(\text{conc. spike added})} \times 100$$

5.11.8 Relative Percent Difference (Rpd) of Duplicate Samples

$$\text{RPD} = \frac{(\text{conc. in sample}) - (\text{conc. in duplicate})}{(\text{conc. in sample}) + (\text{conc. in duplicate})} \times 200$$

5.11.9 RT Windows Using Relative Retention Times (RRTS) (An Internal Standard Method)

5.11.9.1 Variance of Observed Minus Predicted Retention Time (RRT Method)

The following acceptable approximation is valid when used to predict retention times using one continuing calibration standard run before a group of samples.

$$\text{Var} [RT_{\text{obs}} - RT_{\text{pred}}] = \{2 / (N - 1)\} \times \left\{ \sum_{i=1}^N (RT_{C(i)} - RT_{I(i)} \times M)^2 \right\}$$

Where:

$$M = \frac{\sum_{i=1}^N (RT_{I(i)} \times RT_{C(i)})}{\sum_{i=1}^N (RT_{I(i)})^2}$$

N = number of standards in set used to determine RT window width
 $RT_{C(i)}$ = retention time of target compound C in standard i
 $RT_{I(i)}$ = retention time of internal standard associated with compound C in standard i

The error in the above expression is nearly identical to the percent difference of the retention time of the internal standard in the sample versus that in the prior standard. The actual equation, without approximation, is found by substituting for the numeral "2" just to the right of the equals sign with the following expression:

$$\left\{ 1 + \frac{(RT_{I(\text{SPL})})^2}{(RT_{I(\text{STD})})^2} \right\}$$

Where: $RT_{I(\text{SPL})}$ = retention time of internal standard in sample
 $RT_{I(\text{STD})}$ = retention time of internal standard in continuing calibration standard run prior to sample

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5.11.9.2 Retention Time Window Width (RRT Method)

$$RT \text{ window width} = \pm t_{0.995, N-1} \times \sqrt{\text{Var} [RT_{\text{obs}} - RT_{\text{pred}}]}$$

Where: t = value from table of student's t distribution
0.995 = confidence level for prediction interval (one-tailed)
N = number of standards used to determine RT window width

5.11.9.3 Retention Time Window for a Sample (RRT Method)

$$RT \text{ window} = RT_{C(\text{STD})} \times \frac{RT_{I(\text{SPL})}}{RT_{I(\text{STD})}} \pm t_{0.995, N-1} \times \sqrt{\text{Var} [RT_{\text{obs}} - RT_{\text{pred}}]}$$

Where: $RT_{C(\text{STD})}$ = RT of the target compound in the standard run before sample
 $RT_{I(\text{SPL})}$ = RT of the internal standard in the sample
 $RT_{I(\text{STD})}$ = RT of the internal standard in the standard run before sample

5.11.10 Rt Windows Using the External Standard Method

5.11.10.1 Variance of Observed Minus Predicted Retention Time (External Standard Method)

The following expression is valid when used to predict retention times using one continuing calibration standard run before a group of samples.

$$\text{Var} [RT_{\text{obs}} - RT_{\text{pred}}] = \left\{ 2 / (N-1) \right\} \times \sum_{i=1}^N [RT_{C(i)} - (1/N) \times \sum_{j=1}^N RT_{C(j)}]^2$$

Where: N = number of standards in set used to determine RT window width
 $RT_{C(i)}$ = retention time of target compound C in standard i

5.11.10.2 Retention Time Window Width (External Standard Method)

$$RT \text{ window width} = \pm t_{0.995, N-1} \times \sqrt{\text{Var} [RT_{\text{obs}} - RT_{\text{pred}}]}$$

Where: t = value from table of student's t distribution
0.995 = confidence level for prediction interval (one-tailed)
N = number of standards used to determine RT window width

5.11.10.3 Retention Time Window for a Sample (External Standard Method)

$$RT \text{ window} = RT_{C(\text{STD})} \pm t_{0.995, N-1} \times \sqrt{\text{Var} [RT_{\text{obs}} - RT_{\text{pred}}]}$$

Where: $RT_{C(\text{STD})}$ = retention time of compound C in standard run before sample

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Figure 3

Summary of Quality Control (QC) Requirements

Note: This is a condensed summary. For a complete description of contingencies, etc., see the appropriate section referenced below.

Description of QC Audit Item	Required Frequency of Performance	QC Criteria Limits	Required Action if Limits are Exceeded	Reference Section Number
Stock Standard Solutions Expiration Dates	Stock standards are valid for six months from the date of preparation, unless degradation is indicated. New and old standards must be run back-to-back and compared before the first use of the new standard	Warning Limit: Response within ± 35 percent of old standard Action Limit: t-Test fails at 0.95 confidence level	If warning limit is exceeded, check dilution procedures and re-analyze new and old standards to achieve a minimum 4 degrees of freedom for t-test comparison of means with 95 percent confidence level. If suspect compounds also fail t-test, obtain and run standards from another source.	5.5.3
Secondary Dilution Standards and Matrix Spike Solutions Expiration Dates	Secondary dilution standards and matrix spike solutions are valid for six months from the date of preparation or two months from the date of first use, whichever occurs first. If degradation is suspected (color change, evaporation, percent R matrix spike low), discard the solution unless integrity is verified by the analysis of the fresh dilution versus the suspect standard.	Response of suspect standard dilution within ± 35 percent of fresh dilution	Discard the standard dilution if the comparison against the fresh dilution disagrees by more than 35 percent.	5.5.4, 5.5.5, 5.5.8, and 5.9.4
Working Internal Standard (IS) Solutions Expiration Dates	Working internal standard solutions are valid for six months from the date of preparation or one week from the date of first use, whichever occurs first. If degradation is suspected (IS area criteria is exceeded for a blank), run a continuing calibration standard and evaluate the RRF percent difference for all compounds associated with IS.	RRF percent difference for associated compounds opposite bias to IS area shift and outside criteria	Discard IS solution and prepare fresh dilution if QC criteria at left indicate deterioration of IS solution.	5.5.7 and 5.9.8

Figure 3

Summary of Quality Control (QC) Requirements

Note: This is a condensed summary. For a complete description of contingencies, etc., see the appropriate section referenced below.

Description of QC Audit Item	Required Frequency of Performance	QC Criteria Limits	Required Action if Limits are Exceeded	Reference Section Number
Aqueous Calibration Standard Solutions Expiration Dates	Aqueous calibration standards are valid for only 1 hour, unless kept at 4°C with no headspace, in which case they are valid for 24 hours.	1 hour or 24 hours (cannot be heated more than once)	Discard standard solution and prepare fresh dilution.	5.5.5
Sample Holding Times	Laboratory holding times are set at 7 days or as specified by project schedules, whichever is shorter.	7 days or less	If analyses cannot be performed within holding times, notify the project manager and project leader immediately upon discovery of the problem (to plan resampling strategies, etc).	5.6
Initial Calibration Compound Sensitivities	All compounds that are on the site-specific target compound list (TCL) must have S/N at least 10:1 in the low-concentration standard.	Peak height of compound divided by height of peak-to-valley noise fluctuations ≥ 5	Perform adjustments/check standard integrity, correct problem, and restart initial calibration sequence.	5.8.1
Initial Calibration Chromatographic Resolution	The resolution of all compounds must be equivalent to or better than the stated method.	Resolution \geq method chromatogram	Perform adjustments and restart initial calibration sequence.	5.7.1
Initial Calibration Peak Width	Early eluting target compounds on megabore capillary column must have peak width (95 percent area) of less than 0.4 minute.	Peak width ≤ 0.4 minute	Adjust injection technique or GC parameters and restart calibration sequence.	5.8.1.3
Initial Calibration Relative Standard Deviation (RSD) of Response Factors (RRFs)	Perform after instrument alterations (see SOP), or every 30 days, whichever is more frequent. RSD criteria must be achieved for all compounds that are on the site-specific selected TCL (subset of TCL).	RSD ≥ 30 percent for site-specific targets	Check data, calculations, and system performance. Make any necessary adjustments, then repeat the initial calibration sequence.	5.8.1
Continuing Calibration (run before samples) Percent Difference (PD) of RRFs for Internal Standard Quantitation	Perform before each 12-hour period of up to 20 analytical runs. %D criteria applicable to all compounds that are on the site-specific selected TCL.	%D $\leq 25 $ for site-specific targets	Check data, calculations, and system performance. Rerun standard if minor adjustments may correct problem. Perform new initial calibration if problem is uncorrected.	5.8.2

Figure 3

Summary of Quality Control (QC) Requirements

Note: This is a condensed summary. For a complete description of contingencies, etc., see the appropriate section referenced below.

Description of QC Audit Item	Required Frequency of Performance	QC Criteria Limits	Required Action if Limits are Exceeded	Reference Section Number
Final Continuing Calibration (run after samples) PD of RRFs	Perform after each 12-hour period of analysis, after every 20 analytical runs, or after all runs done for current 12-hour period, whichever is more frequent.	$%D \leq 30\% $ for site-specific targets	Check data, calculations, and system performance. Correct problem, recalibrate, and re-analyze samples from last 12-hour period.	5.8.2
Initial and Continuing Calibration Criteria for External Standard Quantitation Using Calibration Factors (CFs)	External standard quantitation only allowed for samples with internal standard interferences. Calibration factor RSD and %D criteria applicable to all site-specific selected target compounds associated with obscured internal standard.	$RSD \leq 30\%$, $%D \leq 25 $	Check data, calculations, and system performance. If problem persists, perform new initial calibration or run samples on optional second GC column to avoid internal standard co-elution.	5.8.3
QC Check Standard Solution Percent Accuracy (percent A)	Analyze once each initial calibration or once each project, whichever is more frequent. Percent A criteria must be achieved for all compounds that are on the site-specific selected TCL.	Percent accuracy ≥ 50 percent and ≤ 150 percent	Locate the source of the problem, correct and achieve successful analysis of QC check solution.	5.9.1
Trip Blanks and Equipment Rinsate Blanks	Analyze at frequency specified in WP or QAPP. QC criteria must be achieved for all compounds that are on the site-specific selected TCL.	Concentration ≤ 5 times MDLs	Evaluate immediately after analysis. If outside criteria, run laboratory reagent blank immediately and locate problem source. Report to project leader to allow resampling or other corrective action.	5.9.2
Laboratory Reagent Blanks	After each initial calibration sequence, after each continuing calibration standard that precedes sample analysis, after high-level samples, and whenever starting a new batch of reagent water or methanol. QC criteria applicable to all site-specific target compounds.	Concentration ≤ 5 times MDLs	Evaluate immediately after analysis. If outside criteria, correct problem and run a new blank. Criteria must be achieved before sample analysis can proceed.	5.9.3, 5.2.3

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Figure 3
Summary of Quality Control (QC) Requirements

Note: This is a condensed summary. For a complete description of contingencies, etc., see the appropriate section referenced below.

Description of QC Audit Item	Required Frequency of Performance	QC Criteria Limits	Required Action if Limits are Exceeded	Reference Section Number
Matrix Spike Analysis Percent Recovery (percent R)	Analyze at frequency specified in WP or QAPP. If samplers do not designate samples to be spiked, then analyst shall select one sample per each group of up to 20 samples of a similar matrix. Percent R criteria apply to all compounds on the site-specific TCL.	Percent R \geq 50 percent and \leq 150 percent	Investigate problem as per SOP. Check spike solution and repeat spike analysis.	5.9.4
Laboratory and Field Duplicate Sample Analysis Relative Percent Difference (RPD)	Analyze at frequency specified in WP or QAPP. QC criteria apply to all target compounds in sample.	50 RPD warning limit; 150 RPD action limit	If warning limit is exceeded, first check sample ID, integration data, and calculations. If action limit is exceeded for any of the three largest peaks that are above the MDL in both analyses, inform the project leader and analyze a third aliquot or fresh sample from the same location. Also inform the project leader if any target compound > MDL versus not detected in duplicate.	5.9.5 and 5.9.6

Figure 3

Summary of Quality Control (QC) Requirements

Note: This is a condensed summary. For a complete description of contingencies, etc., see the appropriate section referenced below.

Description of QC Audit Item	Required Frequency of Performance	QC Criteria Limits	Required Action if Limits are Exceeded	Reference Section Number
Establish Width of Retention Time Windows for Target Compounds	Initially done when new system configuration is first established. The plus or minus window widths must be revised after 90 days (although the center of the prediction window varies with each 12-hour calibration and with each sample's internal standard shifts). Revision of windows required if recurrent problems in final calibration standards, if absolute RTs shift more than 10 percent for any compound, if new GC column or temperature program adopted, or flow rates changed > 15 percent.	RT shifts (observed minus predicted RTs) in final continuing calibration runs $\leq \pm$ RT window for each target compound	If any site-specific target compound elutes outside its established window in the final calibration standard, then corrective action must be taken, after which affected samples must be re-analyzed.	5.9.7
Establish Width of Retention Time Windows for Internal Standards (IS)	IS RT windows are established concurrently and whenever target compound RT window widths are established. The plus or minus window widths are valid for the duration when target compound RT windows are valid (although the center of the prediction window varies with each 12-hour calibration).	In each sample, RT shifts (observed minus predicted RTs) must be $\leq \pm$ RT window for each IS	Evaluate in conjunction with IS areas as per SOP. If co-elution caused appearance of RT shift, quantitate sample using external standard method. If actual elution times of IS shifted, then check/correct system performance (recalibrate if adjustments) and re-analyze sample once.	5.9.8

Figure 3

Summary of Quality Control (QC) Requirements

Note: This is a condensed summary. For a complete description of contingencies, etc., see the appropriate section referenced below.

Description of QC Audit Item	Required Frequency of Performance	QC Criteria Limits	Required Action if Limits are Exceeded	Reference Section Number
IS Area Control Limits	Each analytical run must be evaluated to determine if IS areas are within control limits relative to IS areas in continuing calibration standard run before samples.	Percent difference in IS areas in sample versus continuing calibration $\geq - 50$ percent and $\leq + 100$ percent	Check integration data as per SOP. If co-elution caused appearance of abnormal IS area, quantitate sample using external standard method (if external standard QC criteria can be met) or re-analyze sample on second GC column. If co-elution is not indicated, then check/correct system performance (recalibrate if adjustments) and re-analyze sample. If criteria exceeded for initial and reanalysis of a blank, then a continuing calibration standard is mandatory before further analysis can occur.	5.9.8
Quantitation of Compounds Within Linear Range	For each sample run, concentrations of any site-specific selected target compounds must be less than or equal to the highest initial calibration standard.	Concentration \leq highest standard	Dilute sample to achieve level above method reporting limit and within calibrated range.	5.10.5.3
Carry-Over Check: Comparison of Sample Instrument Level to Level in Preceding Run	Applicable to any sample or field QC sample found to contain a positive (reportable) quantity of any site-specific selected target compound that is also present in the preceding analysis at a higher level.	Instrument level in sample < 1.7 percent of level in preceding run	If carry-over criteria are exceeded, then the sample must be rerun after the system has been decontaminated and a reagent blank has been acceptably analyzed.	5.2.3 and 5.10.5.4

APPENDIX D

**BROWN & ROOT ENVIRONMENTAL
AUDIT CHECKLIST**



Brown & Root Environmental

FIELD AUDIT CHECKLIST - February 1997

QA/QC Procedures

1. Were any field observations, deficiencies, nonconformances, or complaints recorded by the site QA/QC Officer or other personnel?
If so, summarize below.

2. Based on personnel interview, did any variances from the project planning documents occur? If so, what were they?

3. Were field modification records pertinent to the above initiated in an appropriate manner?

4. If applicable, were corrective action plans implemented (according to proper procedure)?

5. Were field QC samples obtained with the frequency specified in the QAPP, WP, or FSP?

6. For all sites, were field duplicates submitted "blind" laboratory?

7. For all sites, are sufficient replicate aliquots of samples designated to the laboratory for the matrix spike/duplicate analyses specified in the QAPP, WP, or FSP?

FIELD AUDIT CHECKLIST - February 1997

Boring Samples

8. Is the drilling method specified in the WP or FSP being used?

9. Are the sampling devices designated in the WP, FSP, or applicable B&RE SOP being used?

10. In accordance with B&RE policies and field SOPs, the FOL has the authority to change drilling methods if site conditions so dictate. Did any change in drilling methods from that cited in the project planning documents occur? If so, discuss.

11. If a change in drilling methods was required, did the FOL properly document the change and the rationale for the change?

12. Were any field changes initiated by the drilling subcontractor? If so, was the FOL notified and were the changes documented?

13. Per B&RE SOP GH-1.3, Sect. 5.2.1 (hollow stem auger drilling methods), was the auger plugged until the desired sampling depth was reached? (If the sample is to be taken at a relatively deep point, the auger may be advanced without a plug to within five feet of the sample depth. Beyond that point, the procedure outlined in the SOP must be observed.)

FIELD AUDIT CHECKLIST - February 1997

14. If water was used to prevent blowback or plugging of the hollow stem auger, has the following been recorded:

corollary field blank sample identification _____
amount of water introduced _____
amount of water recovered _____
amount of water extracted during well development _____

15. Have all abandoned borings been backfilled as specified in the WP, FSP, or applicable SOP?

16. When applicable, was the casing cleaned before sampling? (In most cases, an inch or two of cuttings may be left in the borehole with little or no problem. However, if more than a few inches for cuttings are encountered, the borehole must be recleaned prior to attempting sampling.)

water wash (disturbed samples above and below water table) _____
clean-out auger (undisturbed samples below water table) _____
dry method (undisturbed samples above water table) _____

17. Were any drilling lubricants used? If so, were the procedures cited in B&RE SOP GH-1.4, Sect. 5.5 observed?

18. Were detailed boring logs maintained by the site geologist for each borehole? (Logging is not required if explicitly stated so in the associated FSAP.)

19. Was the following information complete on the borehole logs:

description of materials _____
description of samples _____
sampling method _____
blow counts _____
final location for drilling _____

20. Was the following information recorded in the boring logs or the field notebook?

For soil classification from core samples:

FIELD AUDIT CHECKLIST - February 1997

Was the USCS classification indicated per Exhibit 4-2 (attached)? _____

Were the following characteristics indicated per the relevant B&RE SOP GH-1.5 sections (attached)?

color _____
soil type _____
relative density and consistency _____
weight percentage _____
moisture _____
stratification _____
texture/fabric/bedding _____

21. If classification was performed based on soil and rock drill cuttings, were the following requirements satisfied:

were cuttings obtained from 5-foot intervals? _____
were cuttings preserved in a glass sample jar or ziploc prior to classification? _____
were any changes in color or lithology recorded? _____
were any potential fracture zones noted? _____

22. Were sample aliquots from split-spoon samplers obtained representatively?

23. For samples acquired by thin-walled Shelby tubes, was at least an inch of soil removed from the upper and lower ends of the tube, an impervious disk inserted at both ends, a half-inch (minimum) wax seal applied, the voids at either ends filled with inert material, plastic encaps affixed and sealed with wax in accordance with B&RE SOP requirements?

24. Were Shelby tube samples handled in accordance with the following?

up direction marked with indelible ink _____
complete sample information _____
stored vertically with same orientation as in ground _____
stored out of the sun _____

FIELD AUDIT CHECKLIST - February 1997

Soil Sampling

25. For surface soil samples obtained by hand auger or scoop or trowel, were the following practices followed?

area cleared of loose debris prior to sampling _____
location marked with numbered stake or pinflag _____
sketch approximate locations of sample points in site notebook _____

26. If test pitting is being performed, are plan and profile sketches included in the site notebook?

27. When test pitting, did the backhoe operator immediately cease digging if any of the following conditions occurred:

encounter of any fluid or seepage; encounter of any drums, potential waste containers, obstructions, or utility lines; encounter of distinct changes of material.

28. Describe how samples were obtained (e.g., from pit via entry, from backhoe bucket, composted in buckets) and indicate if quality standards of B&RE SOP SA-1.3, 5.1.3 were met.

29. Do the site notebook entries for test pitting operations include the following information?

name, work assignment, location of job _____
date of digging or trenching _____
surface elevation _____
depth, surface area, orientation of pit _____
associated sample numbers _____
method of sample acquisition _____
type and size of samples _____
approximate water levels after stabilization (if below water table) _____
location and depth of any seeps encountered _____
description of soil _____
other pertinent info. (OVA readings, weather conditions) _____
list of photographs _____
contractor name, backhoe operator, sampler _____
date and type of backfill _____

FIELD AUDIT CHECKLIST - February 1997

Groundwater Sampling

30. Were all monitoring wells properly developed, purged and recovered prior to sampling?
- _____
- _____
31. Were the requirement of SOP SA-1.1 met for well preparation prior to sampling wells that cannot be evacuated to dryness?
- _____
32. When applicable, were well volumes calculated as described in SOP SA-1.1, 5.3?
- _____
33. If a peristaltic pump was used to obtain Volatile Organic Compound (VOC) samples, was it verified that no degassing "bubbles" developed?
- _____
34. If samples were acquired by a pump, was the pump lowered to midscreen (middle of open section of uncased wells) for sample acquisition?
- _____
35. If samples were collected using bailers, were only bailers equipped with check balls used?
- _____
36. For samples acquired by packer assembly, was the packer positioned just above the screen (or open section for uncased wells), prior to inflating?
- _____

Surface Water and Sediment Sampling

37. In accordance with SOP SA 1-2, surface water samples taken from different depths or cross-sectional locations may be composited. However, samples collected along the length of the water course or a different times shall not be composited. If composited surface water samples were obtained, was the above rule observed?
- _____
- _____
38. Per SOP SA 1-2; it is preferable to sample larger streams (and rivers) by compositing a sample from (1) just below the surface, (2) at mid-depth, (3) just above the bottom. If applicable, was this practice observed?
- _____
- _____

FIELD AUDIT CHECKLIST - February 1997

39. SOP SA 1-2, states that it is preferable to obtain surface water samples from a stream area that is well mixed. If applicable, was this observed?

40. For larger streams and river surface water samples, were DO, pH, temperature, and conductivity recorded for each aliquot as well as the whole composite per SOP SA-1.2?

41. If applicable, were lakes, ponds, impoundments, and reservoirs sampled using the vertical composite approach listed in audit question No. 38 above?

42. Were DO, pH, temperature, and conductivity recorded for each aliquot as well as the whole composite?

43. If applicable, did estuary sampling endeavors include the following:

samples obtained during slack tide _____
vertical salinity measurements (1-5' increments) _____
vertical dissolved oxygen profile _____
vertical temperature profile _____

44. Were specific conductance and temperature measured for each surface water obtained?

FIELD AUDIT CHECKLIST - February 1997

45. SOP SA-1.2, 5.3.5 states that "Even though the containers used to obtain the samples are previously laboratory cleaned, it is suggested that the sample container be rinsed at least once with the water to be sampled before the sample is taken." This is not applicable when containers are provided pre-preserved. If applicable, was this practice observed?

46. SOP SA-1.2, 5.3.5 states that "For sampling running water, it is suggested that the farthest downstream sample be obtained first and that subsequent samples be taken as one works upstream." Furthermore, the SOP states that work should be directed from "zones suspected of low contamination to zones of high contamination". If applicable, where these practices observed?

47. In accordance with SOP SA-1.2, 5.4.5, sampling at the surface should never be performed unless specifically sampling for a known constituent which is immersible and on top of the water. Sample containers should be inverted, lowered to the approximate sample depth, then positioned at an approximate 45-degree angle with the mouth of the bottle facing upstream in order to acquire the sample. If applicable, was this technique observed?

Calibration and Use of Field Monitoring Equipment

48. Were the following calibration criteria observed:

calibration according to manufacturer's instructions _____
calibration only by qualified individuals _____
calibrated and operationally checked prior to project assignment _____
use of certified/traceable standards _____
calibration documented _____
if applicable, maintenance documented _____

49. For Photoionization Detectors (PIDs), is the proper ev lamp (e.g., 9.5, 10.2, 11.7) installed?

FIELD AUDIT CHECKLIST - February 1997

50. Because PIDs will not respond to methane or hydrogen cyanide, confirm that the instrument is not being used for this purpose, or for the detection of combustible gases or oxygen deficiency.

51. Confirm that proper PID Start-up and Shut-down procedures are performed as required.

52. Has PID UV light source window cleaning been conducted as required?

53. Has the PID ionization chamber been cleaned as required?

54. Has the PID unit been recharged after every use?

Equipment Decontamination Procedures

55. Has an adequate pre-determined area for steam-cleaning of equipment been established?

56. Is the decontamination (decon) area lined and/or bermed?

57. Is equipment decontaminated by steam-cleaning as required (e.g., transport vehicles, drill rigs, backhoes, downhole tools, augers, well casings, screens)?

58. Was steam-cleaning conducted:

prior to commencement of field activities? _____

between boring/pit locations? _____

at the end of field activities? _____

FIELD AUDIT CHECKLIST - February 1997

59. The sequence of solvents used is contingent upon the target analytes of concern (and Health & Safety considerations). Is the decon sequence outlined in the project planning documents being strictly observed?

60. Verify that all sampling equipment not subject to steamcleaning (e.g., trowels, mixing bowls, bailers, etc.) are subjected to decontamination per the sequence outlined in the project planning documents.

61. Have all water level indicators been contaminated via (1) potable water rinse, (2) deionized water rinse, (3) acetone/methanol (or by substitution, isopropanol for both), (4) deionized water rinse per SOP SF-2.3, 5.2.1?

Waste Handling Procedures

62. Were cuttings or fluids disposed of in accordance with project planning document (i.e., discharged to ground, drummed, or tanked)?

63. Do the project planning documents provide for the disposal of Personal Protective Equipment (PPE) by double-bagging and discard?

64. By what method are PPE disposed of?

65. If applicable, were used spill-containment materials containerized or otherwise acceptably disposed of?

FIELD AUDIT CHECKLIST - February 1997

Sample Handling

66. Are the appropriate containers provided by the laboratory being used for each fractional type of sample?

67. Has a Trip Blank been submitted with each cooler of VOC samples?

68. Has the Ambient Temperature blank been handled properly and one submitted with each cooler of samples?

69. Have equipment rinsate blanks of the proper type and frequency been obtained?

70. Have Field Blanks been obtained from water sources applicable to the field effort?

71. Have the rinsate and field blanks been designated for the same analyses as the associated samples?

72. Have all samples been properly preserved in accordance with the project planning documents?

73. Is field filtration conducted in accordance with the requirements of SOP SA-6.1?

FIELD AUDIT CHECKLIST - February 1997

74. If applicable, have the hazardous sample packaging and shipping procedures outlined in SOP SA-6.1 been followed?

75. Has sample custody been maintained with regard to the following criteria:

A sample is under an individual's custody if:

- it is in the individual's actual possession
- it is in the individual's view after
- it was locked up to prevent tampering
- it was placed in a designated and identified secure area

(The sample remains in the individual's custody until it is entrusted to a laboratory courier or commercial express carrier.)

Documentation

76. Are all sample logs complete (i.e., containing all information stipulated in SOP SA-6.3)?

77. Have chain-of-custody (COC) forms been filled out for all samples, including field quality control samples and samples designated for **on-site** analysis?

78. Have the COC forms been signed by the appropriate individual at each step that the samples are relinquished?

79. Have the COC forms been filled-out using black waterproof ink?

FIELD AUDIT CHECKLIST - February 1997

80. If the COC form was corrected, was a line drawn through the information and was the change dated and initialed? (Use of white-out or erasure is not permitted.)

81. Have the appropriate analyses (per the project planning documents) been properly designated for each sample on the chain-of-custody form?

82. Have all sample labels been filled out appropriately and completely?

83. Have all sample labels been filled out using indelible ink?

84. Have the samples been identified according to the scheme depicted in the project planning documents?

85. Do the sample identifications agree between the sample log, field notebook, sample label and chain-of-custody form?

86. When applicable, have the name of the photographer, date, time, site location, and site description been entered sequentially into the site logbook as documentative photographs of the sampling been taken?

87. Where samples have been split with a private party or government agency, have Receipt of Samples forms been filled-out and signed?

FIELD AUDIT CHECKLIST - February 1997

88. Has the following information (at minimum) been recorded in the site logbook:

- arrival/departure of site visitors
- arrival/departure of equipment
- sample pickup, COC form nos., carrier company, time
- sampling activities/sample logsheet nos.
- start/completion of boreholes, trenches, monitoring wells
- health and safety issues

89. Is the site logbook a bound notebook with consecutively numbered pages that cannot be easily removed?

90. As required by SOP SA-6.3, does the cover of the site logbook contain the following information?

project name _____
project number _____
contractor (or Teaming firm) name _____
sequential book number _____
start date _____
end date _____

91. As required by SOP SA-6.3, has the following information been recorded at the beginning of each day?

date _____
start time _____
weather conditions _____
all field personnel present _____
any visitors present _____

92. Do the site logbook entries summarize the daily activities and refer to other site notebooks or logsheets where applicable?

93. Have all site logbook entries been made in black indelible ink?

FIELD AUDIT CHECKLIST - February 1997

94. If a logbook entry was corrected, was a line drawn through the information and was the change dated and initialed? (Use of white-out or erasure is not permitted.)

95. Did the individual making the logbook entry signed it?

96. Did the Field Operations Leader sign all logbook pages utilized that day at the end of each day?
