N00164.AR.000308
NSWC CRANE
5090.3a

DEPARTMENT OF THE NAVY
CRANE DIVISION
NAVAL SURFACE WARFARE CENTER
300 HIGHWAY 361
CRANE, INDIANA 47522-5000

IN REPLY REFER TO

5090
Ser 095/7222

12 DEC 1997

11-20-1997

U.S. Environmental Protection Agency, Region V
Waste, Pesticides, & Toxics Division
Waste Management Branch
Illinois, Indiana, and Michigan Section
ATTN: Ms. Carol Witt-Smith (DRP-8J)
77 West Jackson Blvd.
Chicago, IL 60604

Dear Ms. Witt-Smith:

The Morrison Knudsen Corporation forwarded to your office an advanced copy of the Crane Division, Naval Surface Warfare Center (NAVSURFWARCENDIV Crane) Quality Assurance Project Plan for Release Characterization at the Dye Burial Grounds (dated November 20, 1997). This letter is to acknowledge that advanced submittal. Enclosure (1) is the required certification statement.

NAVSURFWARCENDIV Crane point of contact is Mr. Thomas J. Brent, Code 09510, telephone 812-854-6160.

Sincerely,

JAMES M. HUNSICKER
Director, Environmental Protection Department
By direction of
the Commander

Encl:
(1) Certification Statement

Copy to:
ADMINISTRATIVE RECORD (w/2 copies)
COMNAVSEASYSCOM (SEA OOT) (w/o encls)
SOUTHNAVFACENGCOM (Code 1864) (w/o encls)

I certify under penalty of law that this document and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gather and evaluate the information submitted. Based on my inquiry of the person or persons who manage the system, or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations.

James M. Hirsch

SIGNATURE

Environmental Prot. Dept. Mg.

TITLE

12/12/97

DATE

Enclosure (1)

QUALITY ASSURANCE PROJECT PLAN

FOR RELEASE CHARACTERIZATION AT THE DYE BURIAL GROUNDS SOLID WASTE MANAGEMENT UNIT - 02/11

NSWC CRANE
CRANE, INDIANA

CONTRACT #N62467-93-D-1106
DELIVERY ORDER #0009
STATEMENT OF WORK #0007

November 20, 1997

Prepared for:

SOUTHERN DIVISION
NAVAL FACILITIES ENGINEERING COMMAND
2155 EAGLE DRIVE
P.O. BOX 190010
NORTH CHARLESTON, SOUTH CAROLINA 29419-9010

Prepared by:

MORRISON KNUDSEN CORPORATION
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NORTH CHARLESTON, SOUTH CAROLINA 29411

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MK Program Manager	12/8/97 Date
MK Program Quality Control Manager	12/8/97 Date
US Navy Responsible Authority	Date
USEPA RCRA Project Coordinator	11/21/97 Date
USEPA Region V QAPP Coordinator	11/21/97 Date
Laboratory Representative	12/2/97 Date

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ACRONYMS AND ABBREVIATIONS

C	Celsius
CAAA	Crane Army Ammunition Activity
CAS	Chemical Abstract Service
CFR	Code of Federal Regulations
CLP	Contract Laboratory Program
cpm	Counts per minute
DBG	Dye Burial Grounds
DOE	United States Department of Energy
DPM	Disintegrations per minute
DQO	Data quality objective
ECR	Environmental Construction Representative (NSWC)
EPD	Environmental Protection Department (NSWC)
ESB	Explosive Services Branch
FT/IR	Fourier transform infrared spectroscopy
GC/MS	Gas chromatography/mass spectrometry
HCl	Hydrochloric acid
HDPE	High-density polyethylene
HPLC	High-performance liquid chromatography
H_2SO_4	Sulfuric acid
HSWA	Hazardous and Solid Waste Amendments (of RCRA)
HV	High voltage
IAS	Initial Assessment Study
IEC	Ion exchange chromatography
IRP	Installation Restoration Program
KBr	Potassium Bromide
lb	Pound
L	Liter
LDPE	Low-density polyethylene
MK	Morrison Knudsen Corporation
ml	Milliliter
NAD	Naval Ammunition Depot
NaI	Sodium Iodide
NAVFAC	Naval Facilities Engineering Command
NEESA	Naval Energy and Environmental Support Activity
NH_4	Ammonia
NSWC	Naval Surface Warfare Center
PM	Project Manager
PMO	Program Management Office
ppb	Parts per billion
ppm	Parts per million
QAPP	Quality Assurance Project Plan
Ra	Radium

ACRONYMS AND ABBREVIATIONS, Continued

RCRA	Resource Conservation and Recovery Act
ROICC	Resident Officer in Charge of Construction (ROICC)
RPC	Region Project Coordinator (EPA Region V)
RPM	Remedial Project Manager
SEM	Scanning electron microscopy
SOP	Standard operating procedure
SQCS	Site Quality Control Supervisor
SSHO	Site Safety and Health Officer
SSHP	Site Safety and Health Plan
SWMU	Solid waste management unit
TLC	Thin-layer chromatography
TOC	Total organic carbon
TSS	Total suspended solids
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
µml	microliter

SECTION 1
PROJECT DESCRIPTION

1.1 INTRODUCTION

Naval Surface Warfare Center (NSWC), Crane Division, is located in southwestern Indiana and provides support for equipment, shipboard weapons systems, and ordnance. NSWC Crane also supports the Crane Army Ammunition Activity (CAAA), including production and renovation, storage, shipment, demilitarization, and disposal of conventional ammunition.

The Dye Burial Grounds (DBG), Solid Waste Management Unit (SWMU) 02/11, is located in the eastern section of NSWC Crane, northeast of the Ammunition Burning Ground. From the 1940s until 1964, the DBG was the site for disposal of scrap, dyes, and dye-contaminated materials. The scope of work described in this *Quality Assurance Project Plan* (QAPP) is part of a phased investigation of the DBG to determine the nature, extent, and rate of migration of dye-related constituents and to establish appropriate cleanup levels.

This QAPP describes the sampling and analytical procedures used to collect and analyze dye-contaminated water, including potentially dye-contaminated water likely to be encountered and containerized during cap construction; establishes the quality parameters that will be used for future sampling and analyses; and, should the data need to be reassessed, provides the necessary information to allow future re-creation of the sampling and analytical processes in order to understand the basis for and interpretation of the program results.

This QAPP differs from the "typical" QAPP in that it reports on sampling and analytical events that previously occurred as well as presenting the quality aspects related to sampling and analytical activities yet to be performed. The discussion associated with the past sampling and analytical events is to document the methods that were used and their associated results and how this earlier data can aid in guiding the future program. Importantly, this QAPP expands upon the quality related aspects to be employed for the future sampling and analytical program, for example, in fully presenting detailed analytical procedures to be used, allowing replication of these analytical techniques by an independent laboratory, for example, one functioning in an auditing capacity. This QAPP also discusses the additional sampling that will be performed to more fully quantify the quality of the to-be-collected data. A basis for use of various analytical procedures is presented along with revised analytical programs to more completely calibrate equipment and methods to ensure that all sample analyses are bracketed by analysis of standards. Lastly, this QAPP discusses collection and transport of samples

to an Environmental Protection Agency lab for essentially simultaneous analysis of some or all of the samples. (The number and type of samples to be analyzed by a U.S. EPA laboratory, whose role is to largely function in an auditing capacity is indicated in Table 1-1.)

1.2 SITE DESCRIPTION

The main portion of the DBG consists of at least four trenches, each approximately 50 feet long, 10 feet wide, and 6 feet deep. The trenches were backfilled with soil in 1972. The DBG is located atop a northeast trending ridge. The ridge is relatively flat and can pond precipitation for a period of time. The burial trenches can receive infiltrating water from snow or rainfall and may retain water during periods of high precipitation. The bottoms of the trenches are expected to be in either soil or weathered rock. Site clearing activities conducted in the fall of 1996 revealed additional dye burial locations outside the main trench area. Cap construction was started during the summer of 1997.

Reconnaissance surveys conducted in 1994 and 1995 indicated that soils surrounding the trenches are generally medium stiff to hard, moist to almost dry silt and silty clay. The depth to weathered rock is 6.5 to 8 feet. The soils overlying the apparent trench locations are generally brown to gray, very soft to soft silt and silty clay.

Groundwater monitoring wells installed around the trench area in 1981 and 1988 indicate that depth to groundwater ranges from 12 to 20 feet below the ground surface, or approximately 6 to 14 feet below the base of the trenches.

1.3 SITE HISTORY

In 1940, Congress authorized construction of a Naval Ammunition Depot (NAD) in southern Indiana, and in late 1941, the Burns City Ammunition Depot was commissioned. In 1943, NAD Burns City was renamed NAD Crane, and the Town of Crane was built to house the rapidly growing number of civil service employees. NAD Crane's mission was to load, prepare, renovate, receive, store, and issue ammunition to the fleet.

During World War II, NAD Crane's mission expanded to include pyrotechnics production, mine filling, rocket assembly, field storage, torpedo storage, and ordnance spare parts and mobile equipment storage. During the 1950s, several new departments were created, the Ammunition Loading and Production Engineering Center was transferred to Crane, and the Central Ammunition Supply Control Office was established. NAD Crane supplied ammunition to the fleet during the Korean and Vietnam conflicts.

In 1976, NAD Crane was renamed NSWC Crane. Its new mission was to provide support for ships and crafts equipment, shipboard weapons systems, and assigned ordnance items, and to perform additional functions as directed.

In 1977, the Single Manager Concept was implemented. The CAAA was created, and the Army assumed ordnance production, storage, and related responsibilities as a tenant organization. Other functions remained the responsibility of the Navy, and the Navy currently retains ownership of all real estate and facilities at NSWC Crane. Responsibility for station safety, security, and environmental protection remains with the Commanding Officer, NSWC Crane.

During the late 1970s and early 1980s, a variety of liquid wastes from both ordnance and non-ordnance activities were disposed of on site without treatment. Disposal activities included discharging ordnance-impacted wastewaters into unlined ponds or into storm drains and ditches; discharging wastewaters generated from cleaning operations into an unlined pond; dumping oily waters, battery acids, paint thinner, acetone, boiler blowdown and solvents behind buildings or into ravines; and spreading waste hydraulic oil on dirt roads. Since that time, treatment plants have been built, wastewater streams have been connected to the sanitary sewer, and oils and solvents have been collected, segregated, and recycled, sold, or properly disposed of.

Because air pollution control devices were not installed until the late 1970s, ventilation systems at the bomb loading facilities and the incinerator had no scrubber systems. Waste management activities included the burning of solid wastes and subsequent disposal of ash in unlined pits or gullies. Also, dye and dye-impacted materials were disposed of in trenches on site.

Activities at NSWC Crane also included radiological operations, and some radioactive materials were disposed of on site during the early 1950s. Known burial grounds were excavated, decontaminated, and released for unrestricted use in 1974.

Promulgation of the U.S. Environmental Protection Agency's (USEPA) Resource Conservation and Recovery Act (RCRA) hazardous waste regulatory program provided the impetus to identify and control environmental contamination from past practices at NSWC Crane. Corrective action programs established as part of the RCRA Hazardous and Solid Waste Amendments (HSWA) required NSWC Crane to address past releases of hazardous waste or hazardous constituents at selected SWMUs. In October 1980, NSWC Crane filed notification and application to operate as a treatment, storage, and disposal facility. Interim status was granted, subject to operating requirements and applicable technical standards found in Title 40 Code of Federal Regulations, Part 265 (40 CFR 265).

In April 1981, the Navy implemented the Navy Assessment and Control of Installation Pollutants, subsequently known as the Installation Restoration Program (IRP). The purpose of the NSWC Crane IRP was to identify and control environmental contamination from past practices. An Initial Assessment Study (IAS) was conducted in April and May 1981 by a team from the Naval Energy and Environmental Support Activity (NEESA), the Ordnance Environmental Support Office, and the Army Corps of Engineers. Using historical records, aerial photographs, field inspections, and personnel interviews, the IAS identified 17 potentially impacted sites at NSWC Crane; 14 of the 17 sites, including the DBG, were recommended for confirmation studies, including sampling and monitoring.

The IAS team reported that an estimated 50,000 pounds (lbs) of various dyes and dye-contaminated materials were deposited into three open trenches at the DBG from 1952 until 1964. These trenches were each about 10 feet wide, 6 feet deep and 50 feet long. Deposited materials included magnesium, dye-contaminated boxes and rags, and approximately 60 drums of dyes. In 1972, the trenches were backfilled to ground surface with soil, but were not permanently capped. Subsequent investigations identified areas of contamination in addition to these three trenches. There are now at least four trenches known to be present.

In 1981, the U.S. Army Corps of Engineers Waterways Experiment Station conducted a hydrologic investigation of waste disposal sites at NSWC Crane. Eight exploratory borings and wells were placed near the DBG to depths as great as 70 feet. The eight wells provided preliminary data on water table elevations and direction of groundwater flow in the uppermost aquifer. Additional monitoring wells were installed in 1987 and 1988.

In January 1985, NSWC Crane submitted a Hazardous Waste Management Report to the USEPA. The report listed the IAS-identified hazardous waste sites as SWMUs. Following the Hazardous Waste Management Report, a RCRA Facility Assessment was conducted to characterize the potential for releases of hazardous waste or constituents from 100 SWMUs. The DBG was identified as SWMU 02/11.

On December 23, 1989, the USEPA issued the federal portion of the Final RCRA Permit for NSWC Crane to the U.S. Navy; on July 31, 1995, the USEPA renewed the permit for five years. In addition to the Federal Permit Conditions, this permit contains State Permit Conditions that were issued separately by the State of Indiana RCRA program. This permit established the HSWA Corrective Action Requirements and Compliance Schedules requiring the U.S. Navy to perform RCRA Facility Investigations at 33 SWMUs, conduct Corrective Measures Studies, and implement corrective measures if needed. A RCRA Facility Investigation Interim Measure, Source Location Geophysical Survey, was required for the DBG. This investigation was conducted in 1991 to comply with the permit's corrective action requirements.

In 1994, Morrison Knudsen Corporation (MK) was contracted by the Southern Division, Naval Facilities Engineering Command (NAVFAC) to perform remedial actions at various facilities including NSWC Crane. In December 1996, a large storm event produced a significant volume of runoff at the DBG, which was visibly contaminated with a green dye. Approximately 80,000 gallons of contaminated runoff was pumped into twelve (originally six) temporary storage tanks at the DBG. Since December, 1988 another approximately 70,000 gallons of contaminated water has been containerized bringing the total containerized water volume to 150,000 gallons.

This QAPP discusses the sampling and analysis program used to initially characterize this water. This QAPP also addresses the revised sampling and analytical program for additional water collected after December 1996 or to be collected and containerized during cap construction. Currently, there are ten tanks and two mud boxes containing approximately 150,000 gallons of water. Nine of the tanks contain fluid. The remaining tank and the mud boxes are currently empty but must be flushed prior to release. Additional tanks or 55 gallons drums may be used, if necessary, to contain potentially dye contaminated water that may be encountered during cap construction. The project objectives described in this QAPP focus on the disposition of the contaminated runoff already containerized and characterizing additional water that will likely need to be containerized in the future, including any decontamination-related wash water.

1.3.1 Dye Analysis

As discussed in Section 1.3, water sampling was performed to assess the presence of dyes in the approximately 80,000 gallons of containerized runoff water. Analysis of this water provided important insight both into dyes known to exist and those found to be undetectable. This information is significant in helping to guide the sampling and analysis to be performed for water likely to be containerized in the future. The following subsection summarizes the laboratory sampling procedure, qualitative dye identification results, and quantitative analysis of the dyes and total organic carbon that were employed for these samples. (The analytical procedures are admittedly brief and are presented to quickly summarize certain elements of the analysis. A discussion of the detailed analytical protocol used (and also to be used) is presented in Section 7)

1.3.2 Laboratory Sampling Procedure

Three composite water samples were collected from holding tanks and were submitted to the NSWC Crane Explosive Sciences Lab in Building 2707. One 100-ml water sample was evaporated to dryness using nitrogen purge of the containers at room temperature. Infrared analysis of the residues after evaporation indicated that sulfate minerals were the major components of the samples. The residues were extracted with ethanol to remove colored components from sulfate minerals. Additional extraction of the mineral residues with acetone did not remove additional colored components. The

green-colored ethanol extracts were spotted on thin-layer chromatography (TLC) plates and developed with ethanol. Separation of the color components was poor. Therefore, a mixture of ethanol plus one percent acetic acid was tried for TLC separation. The separation of components indicated that the sample contained multiple dyes, a green fluorescent dye and one or two blue dyes. The exact number of blue dyes present could not be ascertained because of tailing of the dye spots on the TLC plate.

1.3.3 Dye Identification

The Explosive Sciences Lab has a collection of dyes, dating back over 40 years, that were originally submitted for analysis during periods when dyes were used in production at NSWC Crane. The dyes were pulled from storage and screened for properties that were similar to the dyes found in the contaminated water from the dye burial ground. Only two stored dye samples had the solubility and color that matched the dyes found in the containerized water. The green fluorescent dye appears to be Disodium fluorescein (uranine). Uranine dye is used for dyeing silk and wool yellow, tracing subterranean waters, marking water for air-sea rescues, and clinical test solution. The blue dye components appear to match a blue dye mixture described in Mil-D-16627(BuOrd) for Dyes, Projectile-spotting: 30 percent Alphazurine B and 20 percent Acid Fast Violet BG. The Mil-D-16627 blue dye mixture also contained 48 percent sugar and 2 percent Naccosol A, a wetting agent . Alphazurine is a trademark for triphenylmethane acid blue dyes. Acid Fast Violet BG is also a triphenylmethane dye with a Society of Dyers and Colourists Color Index number of 699. Mixtures of the known dyes gave a similar pattern of tailing TLC spots that had been observed for the dyes extracted from the burial ground samples.

When an ethanol solution of the known dye mixture is acidified with 1 percent acetic acid, the dye color changes from green to blue. The dye extract from the burial ground behaves the same way, changing from green to blue when acidified with acetic acid.

A high-performance liquid chromatography (HPLC) procedure for separation of food dyes, found in the Hewlett Packard Catalog, was used on the known and unknown dye samples. The procedure gave a good separation for the Disodium fluorescein standard and a peak with the same retention time was observed in the unknown sample. This was confirmed by adding Disodium fluorescein to the unknown sample and obtaining a single peak without a shoulder. (The procedure uses a C18 column with a 1-ml-per-minute flow rate of 50/50 mixture of methanol and water. The solvent is buffered with A, tetrabutylammonium phosphate solution from Hewlett Packard. A 254-nanometer wavelength detector was used for data collection). This separation procedure can be used for quantitative analysis of the Disodium fluorescein (uranine) dye.

The blue dyes were not detected with the HPLC procedure even when the ratio of methanol to water was changed over the full range. Literature references indicate that a

mixture of methanol and chloroform may be a suitable carrier solvent for separating the triphenylmethane acid dyes by LC and quantitative analysis. This procedure has not been tested as yet. Attempts were made to find a HPLC procedure for the blue dye mixture. In the short time available, no method was located for the blue dyes. Since there were no pure blue dye standards, it was not certain which of the Mil-D-16627 dye components were detected.

All data, to date, indicate that the green water from the dye burial ground contains soluble sulfate minerals as the major constituents. The samples also contain small quantities of three dyes: uranine, Alphazurine B and Acid Fast Violet BG. The Alphazurine B and Acid Fast Violet BG dyes are components Mil-D-16627 blue projectile-spotting dye.

1.3.4 Quantitative Analysis of Dyes

Disodium Fluorescein Analysis

In order to obtain a representative sample from the water storage tank, samples from the top middle and bottom of the storage tank were collected. A 300-ml aliquot of each of the three samples was placed in its own 1-L beaker to increase surface area for evaporation. Dry nitrogen was used to evaporate the water to dryness in each of the beakers. The beakers were rinsed with multiple small aliquots of methanol (about 0.2 ml) until no color was obtained from the beakers. The combined methanol washings were evaporated to approximately 2 ml. The solution was filtered and quantitatively transferred to a 5-ml volumetric flask. The 5-mil volumetric flask was then filled with methanol. A 10-µml aliquot of the methanol dye solution was then injected into an HPLC.

HPLC Parameters

The following HPLC parameters were then used for Disodium fluorescein analysis.

Column Packing:	Alltech Econosil, C18, 10 micron
Column Size:	Length: 250 millimeters (mm) Inside Diameter: 4.6 mm
Mobile Phase:	50% Methanol, 50% Water and a PIC A Kit from Hewlett Packard
Flow Rate:	1.0 ml per minute
Detector:	Ultraviolet at 254 nanometers
Injection Volume:	10 microliters
Standard:	Disodium fluorescein, Eastman Catalog # 735, Lot # AGA, (85% min. by spectroscopic analysis, corrected for water)
Sample Filter:	Anotec Syringe Filter, Catalog # 2001050U, 0.2 micrometers

Disodium fluorescein standards were prepared in methanol. HPLC analysis of the sample concentrate for Disodium fluorescein found that the tank water contained 27 parts per billion (ppb) Disodium fluorescein. The limit of detection for Disodium fluorescein is about 10 ppb, but additional concentration could lower the limit of detection if this was determined to be necessary.

Blue Dye Analysis

A sample of the green dye methanol concentrate was diluted by one-half to a 90-times concentrate of the original tank water sample. One drop of concentrated acetic acid was added to the 5-ml volumetric flask to eliminate interference from Disodium fluorescein and other components. The sample was placed in a 1-centimeter cuvette in the sample beam of a Perkin-Elmer model 552 spectrophotometer. The reference cuvette contained methanol. Standards were prepared by dissolving a weighed sample of Mil-D-16627 dye in methanol and diluting in volumetric flasks.

The final dilution was in a 5-ml volumetric flask; one drop of acetic acid was added. The sample and standards were scanned from 700- to 300-nanometer wavelength. The blue dye has a maximum absorbance at 408 nanometers, with a shoulder peak at about 390 nanometers. The maximum absorbance was used to determine the dye concentration. No attempt was made to distinguish between Alphazurine B and Acid-Fast Violet BG dyes. The blue dye concentration in the tank was determined to be 14 ppb. The limit of detection for the blue dye was about 5 ppb. Further concentration of the sample would not improve the limit of detection because of the high background absorbance.

Total Organic Carbon Analysis

A Dohrman Model DC-80 total organic carbon (TOC) analyzer was used to analyze the composite sample of the tank water. Dohrman's TOC analysis procedure was used. The tank water contains 5 to 6 parts per million (ppm) organic carbon.

1.4 TARGET COMPOUND ANALYSIS FOR FUTURE SAMPLES

Based on the earlier analysis and reflecting the decision that screening for radium is warranted in the surface soils the following target compounds will be analyzed for in the surface soils and containerized water, as noted below.

1.4.1 Radium-226/228 in Surface Soil

The surface soil at the DBG will be radiologically surveyed for the presence of radium-226/228 (Ra-226/228). There is no documentation of the use of Ra-226/228 in any of the dyes disposed of at NSWC Crane; however, the survey will be performed to ensure

worker safety in case an undocumented disposal has occurred. In the event that radium is detected in the surface soils or it is determined to be appropriate, dye-contaminated water retained in the tanks will be analyzed for radium.

1.4.2 Dye Compounds and Other Possible Parameters of Concern in Containerized Water

Based on the preliminary analyses, presented in Section 1.3.1, of the contaminated runoff stored in the ten holding tanks at the DBG the presence of three dyes was indicated:

1. Disodium fluoroscein ($C_{20}H_{12}O_5$•2Na), also called uranine, Chemical Abstract Service (CAS number 518-47-8), is a yellow-green dye used as a fluorescent label.

2. Alphazurine B ($C_{37}H_{36}N_2O_9S_3$•$2H_3N$) (CAS number 2650-18-2), is a blue dye and a component of military specification Mil-D-16627 projectile-spotting dye.

3. Acid Fast Violet BG ($C_{39}H_{41}N_3O_6S_2$•Na), also called benzyl violet (CAS number 1694-09-3), is a violet dye and is also a component of Mil-D-16627.

Presently, there is documented evidence only for these three dye compounds. However, additional testing will be implemented under the scope of this QAPP to determine the presence or absence of additional dye and explosive compounds to stated toxicological levels of concern when these levels are known. In the absence of toxicological data, the analytical procedures presented herein will be employed with stated limits of detection. Specifically, analysis for the dye compounds listed in Section 7, along with selected explosive compounds will be performed. Explosive compounds for which analysis will be performed include those listed in Appendix A along with nitroglycerin and nitroguanidine. It is acknowledged that many, or in fact most, of the compounds listed in Section 7 are not expected to be detected, nonetheless this screening stage is regarded as necessary in order to confirm their absence to a given level of detectability. It is expected that only the three previously detected dyes will be identified. However, in the event that analysis reveals the presence of anomalous peaks, adsorption bands, or "shoulders" associated with other potentially identifiable peaks, then additional analysis will be focused on identifying the cause for these "unusual" signatures. This focus will be explicitly directed at determining if these unusual signatures are indicative of previously undetected dyes found in the listing in Section 7 or explosive compounds. The methods that may be employed in the event that unusual signatures are noted will be dependent on the specific type of unusual (or unexpected) signature. One could reasonably anticipate a variety of analytical methods may be employed in assessing the cause, for this "unusual"

signature, which may be, for example an analytical artifact and not necessarily indicative of the presence of a previously unidentified dye(s).

To accomplish the screening for various dyes and explosive compounds the following "levels" of analysis will be performed:

Environmental Setting Analysis

This effort will be directed at determining the presence and general concentration of "background" compounds. This effort will provide information helping to assess whether a given compound or suite of compounds may cause interferences with proposed analytical techniques and also possibly help in explaining an otherwise "anomalous" analytical signature. Knowledge that a given compound exists in sufficient background concentrations to generate such an otherwise anomalous signature will help prevent significant extraneous effort to identify such an anomalous peak or stray signature in investigation samples of containerized water. Analytical methods to be used for this level of analysis include: Scanning Electron Microscopy (SEM), Total Organic Carbon (TOC), Total Suspended Solids (TSS), and Ion Exchange Chromatography (IEC).

Screening for the Presence of "All" Dyes and Explosives

This level of analysis focuses on qualitatively screening for the presence of all possible dyes (listed in Section 7) and explosive compounds in investigation samples of containerized water. Analytical methods to be employed at this level include: TSS, Thin Layer Chromatography (TLC), Fourier Transform / Infrared Spectroscopy (FT/IR), Gas Chromatography - Mass Spectroscopy (GC-MS), High Performance Liquid Chromatography (HPLC), and IEC.

Quantitation of Water-Soluble Dyes

Given that water-soluble dyes are identified during the above screening stage analytical techniques will be performed to quantify their concentrations. These methods include: HPLC and Ultraviolet-Visible Spectrophotometry.

Discharge Criteria for Containerized Water

Ultimately the containerized water will need to be appropriately disposed. After, for example, activated carbon adsorption the analytical methods for determination of explosives and ammonia will include: HPLC (explosives) and ammonia-nitrogen analysis. It is acknowledged that additional analysis to quantify dye concentrations in the treated water may be performed using the techniques discussed above. These methods may need to be appropriately modified in order to provide a possibly to-be-determined level of detectability.

1.5 PROJECT OBJECTIVES

The specific objectives of the DBG investigation for future samples are as follows:

1. Determine if Ra-226/228 is present in the surface soils.

2. Identify, refine, and implement the methods for characterizing samples collected from the dye-contaminated runoff water contained in ten holding tanks at the DBG or water to be collected that may be encountered during cap construction. The USEPA will use the analytical method information to perform comparative analyses on duplicate samples. Characterization data will be used to identify treatment and disposal options for the dye-contaminated water. Identifying methods and developing analytical strategies will assist future phases of the investigation, including developing a basis for disposal criteria.

3. Determine toxicological health standards for identified compounds. (This specific objective needs to be more fully discussed in that it should be recognized that many of the dyes listed in Section 7 were manufactured in the 1940s and 1950s, when less (or virtually no) emphasis was placed quantifying toxicity. Also as reported in Section 7 are the amounts of these various dyes that remain. Very limited quantities (literally only a few grams) of certain dyes still exist. The likelihood that limited or indeed the absence of any toxicity data for some or many of the dyes, combined with the limited amount of dye still available, argues that even if one was so motivated to enter into a research program to assess the toxicity of these dyes, this program would be constrained in its effectiveness. Consequently, for certain dyes, the "industry standard" analytical techniques previously employed and those to be employed cannot be guaranteed to have a detection limit that is less than a given toxicological threshold due to the absence of this toxicological data and the inability to determine this toxicological for the reasons stated above. A Microtox test, described in Appendix B, may provide some general information on the possible toxicity of a disodium fluorescein standard with results that may correlate in general with human health effects. Specifically, the Microtox test will be used as an indicator of the effectiveness of final treatment of the dye contaminated materials. Comparisons of the Microtox results from the untreated material to the treated effluent will provide an additional measure of the efficiency of the treatment method. To provide the most complete database of information possible the Microtox test will be performed on every sample. Literature-based research will continue to be performed to determine the degree of existing toxicological information pertaining to the dyes. Since the toxicological levels most significantly impact release criteria, this issue does not prevent the planned additional sampling

and analysis program. Treatment goals of the containerized water will need to emphasize risk-based discharge criteria.)

1.6 SAMPLE NETWORK AND RATIONALE

Sampling will address both potential radiological and chemical contamination, which are addressed separately below.

1.6.1 Radiological Survey for Surface Soil

A radiological survey of the DBG area for Ra-226/228 will be performed by establishing 6-foot-wide survey lanes across the entire cap area to ensure complete coverage. The area survey will be performed by a technician walking the length of each survey lane and swinging the probe back and forth across the lane approximately 12 inches from the surface. Areas that show levels of radiation above background will be marked for a more concentrated fixed-point survey. The area survey, combined with the fixed-point survey, will delineate any potential Ra-226/228 contamination within the cap construction area. The detailed SOP is found in Appendix C.

1.6.2 Chemical Survey for Containerized Water

It was determined from the earlier round of sampling that samples of the dye-contaminated runoff from all ten holding tanks could be composited, because the water in the tanks originated from a single source. Separate samples were collected from the top, middle, and bottom of each tank to allow for the possibility of stratification of the contaminants within the tank.

Potentially dye contaminated water encountered during cap construction, including decontamination wash water will be contained within either frac tanks or 55 gallon drums, with the selection of containers being made on the basis of actual or anticipated water volume. Samples of these particular containerized waters will be collected from the approximate middle sections of the tanks or drums. If multiple tanks or drums or used to containerize water encountered during one "event" or process, for example, runoff collected during one storm in one particular area of the cap, then samples from each container will be proportionally composited to form the required number of samples (as discussed in Section 4.2) to form a 4-liter sample volume.

The sample network and design for analysis of dyes is indicated in Table 1-1, below.

TABLE 1-1
SAMPLES TO BE COLLECTED FOR DYE ANALYSES - (HPLC & ABSORPTION SPECTROPHOTOMETRY)

SWMU Tank designation #	Analysis & Matrix Type	Number & type of 4 L investi-gational samples	Number of EPA Split investi-gational samples	Field Duplicate samples per analysis (Crane)	MS/MSD (per analysis) (Crane)	EPA Split Field duplicate samples	EPA Split MS/MSD (per analysis)
GS88EA	dyes/water	2 (1 top & 1 bottom)**	1 bottom	1 bottom	1 pair (bottom)	1 bottom	1 pair (bottom)
S650NEA	dyes/water	1 composite	1 composite	1 composite	1 pair composite	1 composite	1 pair composite
S879NSD	dyes/water	2 (1 top & 1 bottom)**	none	none	none	none	none
1001MEA	dyes/water	1 composite	none	1 composite	none	none	none
S47ST	dyes/water	2 (1 top & 1 bottom)**	none	none	none	none	none
S1647SD	dyes/water	1 composite	none	1 composite	none	none	none
GS522EA	dyes/water	2 (1 top & 1 bottom)**	none	none	none	none	none
GS505EA	dyes/water	2 (1 top & 1 bottom)**	none	none	1 pair (bottom)	none	none
S1885EA	dyes/water	1 composite	1 composite	none	none	none	none

**Note: Top samples should be collected prior to bottom samples in tanks GS88EA, S879NSD, S47ST, GS522EA, and GS505EA.

TABLE 1-2
SAMPLE PRESERVATION AND BOTTLE REQUIREMENTS

Analyte	Analytical method	Sample Container	Preservation
TOC	EPA 415.1	1 500-ml plastic	sulfuric acid to pH<2; ice to 4 degrees C
VOCs	8240	3 40-ml glass vials	HCL to pH<2; ice to 4 degrees C
TSS	EPA 160.2	1 500-ml plastic	ice to 4 degrees C
Ammonia	EPA 350.2	1 500-ml plastic	sulfuric acid to pH<2; ice to 4 degrees C
dyes & explosives	Navy method	1 4-liter glass	ice to 4 degrees C

SECTION 2
PROJECT ORGANIZATION AND RESPONSIBILITY

Table 2-1 lists the responsibilities of the team members who are involved in the tasks described in this QAPP. This table shows the complete reporting structure for site activities. Whereas all individuals shown below have an interest in ensuring that the specific data quality is achieved, certain individuals have specific quality responsibilities. Individuals with specific quality assignments include the USEPA Region V Project Coordinator who reviews and approves all phases of the remedial activities including work plans and analytical results and the NSWC Explosives Sciences Branch Project Chemist who documents analytical methods and reports analytical results. In addition, the Project Manager, Science Manager, and Site Quality Manager individually and collectively are responsible for ensuring that the quality goals are achieved.

Although not shown in the table below, a USEPA research laboratory will also contribute to the quality program by acting in an analytical auditing capacity by performing analysis of sample splits.

TABLE 2-1
PROJECT RESPONSIBILITIES

Team Members	Responsibilities
Southern Division NAVFAC Remedial Project Manager (RPM)	Overview of project execution and coordination between Contractor, NSWC Crane, USEPA, and other agencies.
Program Management Office (PMO)	Overall responsibility for all cleanup measures at all sites in the Southern Division of the Naval Facilities Engineering Command under Contract No. N62467-93-D-1106. The PMO is the point of contact for Southern Division.
USEPA Region V Project Coordinator (RPC)	Overview of all site activities to assure compliance with RCRA. The RPC reviews and approves all phases of remedial activities, including work plans, construction design, equipment, analytical results, etc.
NSWC Environmental Protection Department (EPD), Environmental Construction Representative (ECR)	Monitoring contractor performance for compliance with RCRA, the RCRA Corrective Action Part B Permit, and other environmental regulations as they apply to the approved Interim Measures Work Plans. Is the primary coordinator between the NSWC and the U.S. EPA. In the absence of NTR and in an environmental emergency, the ECR provides direction to Contractor and provide notification to appropriate parties.

TABLE 2-1
PROJECT RESPONSIBILITIES

Team Members	Responsibilities
NSWC Resident Officer in Charge of Construction (ROICC)	Southern Division's on-site representative and liaison between NSWC officials, the USEPA, and the Project Manager for the SWMUs at NSWC Crane.
NSWC Explosives Sciences Branch Project Chemist	Receives, stores, analyzes, and disposes of dye-contaminated runoff water samples. Also documents analytical methods used and reports analytical results.
Project Manager (PM)	Reports to the Field Operations Manager from the PMO. Overall responsibility for implementing work activities in support of release characterization. The PM controls all on-site forces to ensure completion of project tasks. The PM: • Serves as the single point of contact for U.S. Navy and USEPA liaison. • Coordinates the project resources to ensure compliance with the appropriate plans, procedures, and regulatory requirements. • Oversees all on-site personnel and coordinates with the PMO. • Overall responsibility for cost, schedule control, safety, and quality.
Science Manager	Reports to the PM. Establishes technical guidelines for data collection, evaluation, and reporting.
Site Safety and Health Officer (SSHO)	Reports to the PMO. Implements and ensures compliance with the Task-Specific Site Safety and Health Plan (SSHP). Tracks and reports on safety-related matters. The SSHO: • Conducts radiological surveys including instrument calibration and survey documentation. • Controls and eliminates existing and potential industrial hazards. • Implements and executes personnel surveillance program to ensure proper monitoring of internal and external exposures. • Provides site-specific training to personnel as required by the SSHP. • Tracks all personnel training requirements for heavy and light equipment operation, survey data, certifications, and records to ensure compliance with plans and regulations. • Assists in developing and implementing the SSHP. • Conducts audits as appropriate to ensure compliance. • Reviews and approves work permits for appropriate industrial hygiene and safety controls. • Provides monitoring to ensure the protection of project personnel, the public, and the environment. • Maintains an inventory of industrial hygiene and safety supplies as appropriate. • Maintains monitoring equipment and calibration records. • Stops work when necessary to ensure the safety of personnel and to prevent damage to the environment.

TABLE 2-1
PROJECT RESPONSIBILITIES

Team Members	Responsibilities
Site Quality Control Supervisor (SQCS)	Reports to the PMO. Verifies a consistently high level of quality for the project. The SQCO: • Reviews and checks MK documents, reports, and testing results. • Coordinates with the PM on all operations. • Provides surveillance of all field activities to ensure compliance with this QAPP.

SECTION 3
QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

3.1 DATA QUALITY OBJECTIVES

Data quality objectives (DQOs) are qualitative and quantitative statements specifying the quality and quantity of data to be collected for each intended use. This section describes the DQOs and the requirements necessary to meet the following objectives:

- Determine the presence of radiological contaminants through a radiological survey. Surface surveying and sampling and analysis methods will comply with U.S. Department of Energy (DOE) guidelines for radiological surveying and USEPA sampling and analysis guidelines.

- Accurately and precisely determine dye composition in the contaminated runoff contained in the existing ten storage tanks and any additional water that is collected and containerized on the basis of representative tank water samples.

- Tank characterization data must provide a basis for decision-making related to the treatment and disposal of the contents of the existing ten holding tanks and any additional water that is collected and containerized.

- The data must be of sufficient quality to allow decisions to be made regarding the subsequent site remediation tasks.

- Data collection must comply with all applicable federal, state and local regulations.

- The data must be of sufficient quality to support risk assessments. (As noted in Section 1.5, it is acknowledged that many of the possible dyes do not have associated toxicity data and that limited amounts of the actual dye remains for future testing that is representative of disposed dyes. It is further noted that the remaining dye is, in some cases, very old (40 years or more). The likely absence of historical toxicological data will complicate establishing toxicological discharge criteria or release of water, for example, to a wastewater treatment facility, establishing decontamination criteria, and contributing to a risk assessment supporting site closure. If toxicological data do not exist, treatment of treated effluent will need to emphasize risk-based discharge criteria.)

When developing the DQOs, the following tasks will be performed:

1. Radiological survey data will be obtained from the surface soil in the cap construction area to assess worker safety and support construction of the DBG cap.

2. Analytical data for the samples collected from the tanks will be provided by the NSWC Crane Project Chemist. These data will be evaluated to determine whether the objectives founded on laboratory data to be generated under this QAPP have been met, as well as the appropriate treatment and disposal options for the dye-contaminated runoff contained in the existing ten holding tanks at the DBG and any additional water that is collected and containerized. This assessment will include a review of associated quality control (QC) data to determine whether laboratory control limits or other acceptance criteria were met.

DQOs include identifying the need, use, quality, quantity, and type of data to be collected to ensure that project objectives are attained. These DQOs are summarized in Table 3-1.

As shown in Table 3-1, Field-level and NEESA Level C (or equivalent) criteria, will apply to data collected during radiological surface soil screening and tank water characterization. Field level involves the use of portable instruments to perform field screening. A sodium iodide detector for radiological screening of surface soil will be used to conduct field level screening.

NEESA Level C involves the use of an off-site analytical laboratory to analyze the samples. Level C allows the use of non-Contract Laboratory Program (CLP) methods, but does require that the methods be USEPA-approved or equivalent. Quality control documentation similar to CLP requirements will be generated to enable data verification and validation. NSWC methods to be employed will meet the NEESA Level C (or equivalent) criteria.

Level C-equivalent analyses are being performed on the tank water samples collected on April 18, 1997, by the NSWC Crane Prcject Chemist at the NSWC Explosive Sciences Branch. These analyses are being conducted using USEPA methods from the most recent edition of USEPA Methods for Chemical Analysis of Water and Wastes and Internal Laboratory Procedures. Identical (or optimally modified) analyses will be performed on additional water that may be collected and containerized.

TABLE 3-1
SUMMARY OF DATA NEEDS

Need	Use	Quality	Quantity	Analysis Type
Radiological field screening data for surface soil in the cap construction area	To identify the presence of Ra-226/228 and assess worker safety	Field Level	Survey lanes will be established over the cap construction area such that the entire area will be surveyed. Fixed point surveys will delineate areas of potential contamination.	Gamma scanning using a sodium iodide detector
Analytical data for containerized dye-contaminated runoff water	To characterize the runoff water constituents for identification of treatment and disposal options	NEESA Level C or equiv.	One set of three samples collected on April 18, 1997, by personnel from NSWC EPD. Each sample was a composite of the liquid from the top, middle, or bottom of all ten holding tanks.	TOC (USEPA 415.1); TSS (USEPA 160.2); NH_4 (USEPA 350.3); unidentified compounds by GC/MS, FT/IR, TLC, SEM, HPLC (explosives and dye), AS (UV/VIS)
Analytical data for any potential dye-contaminated water to be collected and containerized in the future	To characterize the constituents in this additional water for identification of treatment and disposal options	NEESA Level C or equiv.	Two sets of composite samples from the approximate middle of the holding tanks or drums	TOC (USEPA 415.1); TSS (USEPA 160.2); NH_4 (USEPA 350.3); unidentified compounds by GC/MS, FT/IR, TLC, SEM, HPLC (explosives and dye), AS (UV/VIS)

TOC = Total organic carbon
NH_4 = Ammonia
FT/IR = Fourier transform infrared spectroscopy
SEM = Scanning electron microscopy
HPLC = high pressure liquid chromatography
AS Absorption Spectrophotometry
TSS = Total suspended solids
GC/MS = Gas chromatography/mass spectrometry
TLC = Thin layer chromatography

3.2 DATA QUALITY REQUIREMENTS

Specific data quality requirements to meet the DQOs include precision, accuracy, representativeness, comparability, and completeness (PARCC parameters). These PARCC parameters will be evaluated during assessment of the data. Each parameter related to both radiological and chemical analysis is discussed below.

3.2.1 Precision

Radiological

There are no QC limits on precision for semi-quantitative Field Level radiological survey data from the soil.

Chemical

For Level C data, the QC limits for precision established by the USEPA- or Project Chemist-specified methods will be used to evaluate precision of the water analyses. Investigation and matrix sample duplicates will be used to determine the precision of the analytical process for the water samples. An evaluation will be performed during data validation and summarized in the data assessment for the water samples. A further check on laboratory protocols will be made by sending one of the two sets of water samples collected from each tank (or sample set) to a USEPA laboratory for analysis.

3.2.2 Accuracy

Radiological

There are no QC limits on accuracy for semi-quantitative Field Level radiological screening data for the soil.

Chemical

For Level C data, the QC limits for accuracy established by the USEPA- or Project Chemist-specified methods will be used to evaluate accuracy of the water samples. It is acknowledged that some of the proposed methods for the water analyses may not have associated accuracy and precision criteria. Matrix spike samples and laboratory control spike sample data will be used to evaluate laboratory accuracy of the water data. An evaluation will be performed during data validation and summarized in the data assessment.

3.2.3 Representativeness

Radiological

The cap construction area will be radiologically surveyed using 6-foot-wide parallel survey lanes. This width has been chosen to allow complete radiometric survey coverage of the site. Potential contamination detected during the area survey will be further delineated using a fixed-point survey.

Chemical

Representative samples of tank contents were collected on April 18, 1997, using the proper sampling equipment and techniques. The extent to which these samples are representative of the tank water is an outcome of the sampling procedure used (described in Section 4). A similar sampling procedure will be employed for any additional water encountered during cap construction and containerized.

3.2.4 Completeness

Radiological

The completeness goal for Field Level data is 80 percent, which is considered to be attainable using standard procedures for radiological surveying of the cap area.

Chemical

Since only three samples were analyzed for characterization of the runoff water, the completeness goal for this set of data is 100 percent. An incomplete data set will require additional sampling and analysis for completion. Since only one composite sample, for each laboratory, will be collected for any newly encountered water the completeness goal is 100%.

3.2.5 Comparability

Radiological

Comparability of data generated during radiological surveying of the soil will be achieved by using standard techniques and reporting the data in appropriate units.

Chemical

Comparability of data sets generated by the NSWC laboratory and the USEPA laboratory of the existing water samples or for any newly encountered water will be achieved by using standard operating procedures and reporting the analytical data in appropriate units.

SECTION 4
SAMPLING PROCEDURES

This section describes both the procedures used to conduct the previous sampling event, as well as those to be implemented for planned future sampling events. Information regarding the previous sampling activities is provided to document those procedures and to ensure that future sampling efforts will be carried out in a consistent manner.

4.1 RADIOLOGICAL SURVEY OF SURFACE SOIL

Radiological surveying of the surface soil of the DBG area will be performed by establishing 6-foot-wide survey lanes across the entire cap area to ensure complete coverage. The area survey will be performed by a technician walking the length of each survey lane and swinging the probe back and forth across the lane approximately 12 inches from the surface. Areas that show levels of radiation above background will be marked with a pin flag for a more concentrated fixed-point survey. The field standard operating procedures (SOPs) provided in Appendix C gives detailed procedures for performing the radiological screening of the surface soil.

4.2 TANK WATER CHARACTERIZATION SAMPLES

Samples of the dye-contaminated runoff in the holding tanks were collected on April 18, 1997, using the procedure described below.

There were six 22,000-gallon holding tanks (identification numbers S1885EA, 1001MEA, GS505EA, S650NEA, SDE1EA, and GS522EA). Each tank was accessed through a 10-inch by 10-inch opening at the top. Using one bailer, approximately 0.5 L was taken from the top of each of the six tanks and composited in a 1-gallon polyethylene container. This sample was labeled DBGFT-01-041897.

A separate sampler (a 16-foot by 1-inch length of plastic tubing) was used to collect approximately 0.5 L from the middle of each tank. These sub-samples were similarly composited into a 1-gallon container and labeled DBGFT-02-041897. String was tied to the sampler and measured with respect to the outside of the tank so that the bottom half of the bailer would be suspended halfway through the middle of the water column for sample collection. Because of the light weight of the sampler, the sampler was first inserted into the tank until it filled with water. The sampler was then raised about half-way out of the water, and then dropped (with a light push) back into the water. This was done so that the sampler's ball-valve (a cork) would open and water would flow through the sampler in order to get a more representative sample (rather than the sampler filling up at the top and sinking to the middle). Approximately half the volume of the sampler

was emptied into the container, the remainder was then discharged back into the tank. No decontamination of the sampler was performed during the sampling program. No preservatives were used for these samples.

The same procedure was used for sampling the bottom of all six tanks in order to produce a composite sample (DBGFT-03-041897). In this instance the sampler was lowered until the bottom of the sampler reached the bottom of the tank, as determined by a mark on the string, as well as hearing the sampler strike bottom.

The same sampler was used for a given horizon in all six tanks (i.e., one sampler collected the top samples from all tanks, another sampler collected the middle samples from all tanks, etc.). The samplers were returned to their plastic sleeves when transported from one tank to the next, to prevent dripping contaminated water onto surrounding surfaces. These samples were not collected for QC purposes. Consequently, a second round of sampling will occur once the preliminary data is complete and the first round results are confirmed.

Four additional 22,000 gallon frac tanks (identification numbers S879NSD and GS88EA) and two 10,000 gallon mud tanks (identification numbers MB280 and MB281) bring the total tank count for the area of interest to twelve.

If the water is drummed, appropriate sized samples will be collected from each drum to yield an identical suite of 4 liter composite samples discussed immediately above. If the bailer(s) is (are) decontaminated between sampling events, for example, if water from multiple "events" or areas are to be sampled, two 4 l decontamination wash water samples will be collected, with one provided for use by both the Navy and EPA laboratories. In the event that samples are sent to the EPA lab, one 4-l lab blank will be provided by the Navy laboratory. The EPA has agreed that no field or trip blank is required to support the data quality objectives for this program.

Split samples to be sent to the EPA lab for auditing purposes are found indicated in Table 1-1. (Depending on financial constraints, the samples may be analyzed after the date of the NSWC's split analysis.) The split procedure is described in this QAPP section.

The Navy lab has also requested that a 55 gallon drum of water representative of the "local" background conditions to the Dye Burial Grounds be collected from, for example, a local to-be-determined well or stream and retained for future use. The rationale for this request is to aid in the identification of "unusual" or previously unidentified compounds.

4.2.1 Quantitative Sampling

There are currently twelve tanks at the dye burial ground. Fluids were transferred to different tanks in September of 1997 to allow movement of the tanks away from the area of construction of the DBG cap. Nine tanks currently contain fluid and 3 have been drained. This section addresses sampling the fluid in the nine tanks.

Three methods will be used to extract samples:

- A top layer sample will be obtained by using a dip sampler at the 10" by 10" access port to fill bottles identified in tables 1-1 and 1-2 (or a larger mixing bottle).
- A bottom layer will be obtained using a weighted trip-cord-actuated sample bottle at the 10" by 10" access port to fill bottles identified in tables 1-1 and 1-2 (or a larger mixing bottle). The cord used to lower the bottle shall be marked to indicate when the sampler is ten feet below the surface of the water.
- A vertical composite will be compiled drawing 2 liters from the bottom and 2 liters from the top to produce bottles identified in tables 1-1 and 1-2 (or a larger mixing bottle).

The sampling equipment will be unused or decontaminated prior to use on a different tank or layer in a tank. The samplers will be wrapped in plastic or placed in a plastic bag while being moved from one tank to another to prevent dripping water onto surrounding surfaces. All sampling equipment which is not decontaminated (including carboys) shall be collected in and wrapped in plastic and disposed of per US Navy Crane Division Environmental Protection Department (EPD) procedures.

The TOC, VOC, TSS, and Ammonia bottles will be filled separately first. Fluid shall be drawn and placed directly into the bottles as identified in Table 1-2. For tanks 1001MEA, S650NEA, and S1647SD, fill the TOC, VOC, TSS and Ammonia bottles first with solutions drawn from the bottom profile (VOC VIALS MUST BE FILLED FIRST). The 4 Liter bottles shall be filled next. A 2 liter bottle shall be filled last for future testing which may have to be conducted.

The other parameters to be reported, indicated in Table 3-1, will be measured from the 4 liter aliquot (after allowing for sufficient quantities for dye analyses). The purpose of the additional sample is to have additional sample available for additional tests which may be useful to perform, although this is a matter of convenience and it is anticipated that this additional volume is not needed. (It shall be indicated in the Final Report which, if any, parameters were reported using the additional 2 liter sample.)

Each sample aliquot identified in Table 1-1 will consist of a 4 liter bottle. For the samples requiring only US Navy investigative sample analysis, the fluid shall be placed

directly in the bottles. For S1885EA and the bottom sample of GS505EA, collect 14 liters in a five gallon HDPE carboy or bucket, swirl and split into four 4-liter bottles and the remainder in a two liter bottle. For the bottom sample of GS88EA and one of the samples of S650NEA collect 34 and 30 liters respectively, place in a suitably sized HDPE carboy or bucket and swirl, and split into 8 and 7 4-liter bottles respectively with the remainder going into a two liter bottle. Use a fresh carboy for each tank. Samples to be delivered to the US Navy and to the U.S. EPA are identified in Table 1-1. All other sized bottles will be delivered to the Navy.

4.2.2 Sample Designation

Samples will be numbered DBGFT-A-XXXXXX. A is a sequential number for each tank investigational sample identified in Table 1-1 (1 to 9 respectively). XXXXXX is the date of the sampling event expressed as MMDDYY (MM being the two digit number of the month, DD being the two digit number for the day, and YY being the last two digits of the year). The sample number is used on the duplicates, matrix spikes, and non-dye analysis fractions collected with an investigative sample fraction.

Field sampling personnel are responsible for describing, documenting, labeling, packaging, holding, handling, and delivering samples obtained in the field to ensure that all samples can be readily identified through the use of a unique sampling identification number and to ensure the integrity of the samples from collection to data reporting. Sample designation parameters used for the April 18, 1997, tank water samples are described below. These same procedures will be used to collect future samples.

4.2.3 Sample Labels

All information and data for a sample are keyed to a unique sample designation. The sample designation on all sample containers and associated field data forms are used for data recall from a database system.

Field personnel label each sample container with an indelible pen immediately after filling the container. The sample label contains the following information:

- Location of sample collection
- Sample identification number
- Date of sample collection

Sample information is legibly printed using waterproof ink. The label contains information sufficient to ensure that the sample can be identified as required at the laboratory. The sample identification also reflects that split samples have been collected for analysis at multiple laboratories. The sampling code also designates field samples to be used for quality purposes, including decontamination wash samples, if collected.

4.2.4 Sample Containers

The April 18, 1997, tank water samples were collected and delivered to the NSWC Crane Project Chemist in 1-gallon low-density polyethylene (LDPE), capped containers. Aliquots of these samples were transferred to capped, 500-milliliter (ml) high-density polyethylene (HDPE) bottles for shipment to the USEPA laboratory. In the event that additional sampling is necessary for newly encountered and containerized water similar sample containers will be used.

4.2.5 Sample Packaging and Shipping

A waterproof, plastic cooler is used for packaging and shipping samples. Fresh gel ice is placed in the coolers with the samples to maintain shipping temperature at 4 degrees Celsius (°C) ±2°C. Chain-of-custody forms are completed for every sample cooler shipped, sealed in a polyethylene bag, and taped to the inside of the lid of the cooler. A minimum of two signed custody seals are placed on the outside of the coolers, one on the front and one on the rear of the cooler. Both seals are then covered with tape.

Sample packaging and shipping varies, depending upon sample media, contaminant concentration, preservation technique, and sample container. All samples are packaged and shipped in accordance with all state and federal regulations, including U.S. DOT requirements (49 CFR 171 through 177). All samples are hand-delivered or shipped by overnight delivery to the receiving laboratory.

The April 18, 1997, tank water samples were hand-delivered to the NSWC Crane Project Chemist on the day they were collected. The duplicate samples for the USEPA laboratory were packed into coolers with gel-ice packs and shipped by Federal Express.

The holding times and appropriate sample storage conditions in the laboratory will be identified in the analytical procedures, provided in Section 7 of this document.

SECTION 5
SAMPLE CUSTODY

Records generated as a result of analytical sampling activities are quality records and will be processed in accordance with the requirements of this QAPP. Documents such as sampling records, including those in the field logbook recorded at the time of sampling, chain-of-custody records, analytical testing results, and other required laboratory deliverables are essential for ensuring the integrity and defensibility of data used to make decisions in the remediation process. Quality records maintain sample integrity during field sampling activities and provide a record of events for all aspects of the remedial work, and their adequate generation, review, protection, and submittal is essential to the success of the project.

The following sections describe the chain-of-custody, sample delivery, and documentation procedures that were followed for the April 18, 1997, sampling event. If it is determined that additional samples should be collected from the holding tanks at a later date, the procedures outlined below will be used.

5.1 FIELD DOCUMENTATION

The following information will be recorded on the sampling record of the field at the time of sampling:

- Project name and location
- Sample locations
- Sample identification
- Date and time of sample collection
- Type of sample (characterization sample, QC, etc.)
- Type of preservative used (if any)
- Visual characteristics of the sample material or other observations
- Names of sampling personnel

5.2 CHAIN-OF-CUSTODY DOCUMENT

Chain-of-custody procedures are necessary to maintain and document sample possession. Elements of the chain include, at a minimum:

- Sampling record
- Sample seals
- Labels with identification numbers (including tags) to allow for sample tracking
- Chain-of-custody records

- Bills of lading and air bills

Field and laboratory sample custodians or their designated representatives are responsible for maintaining custody of samples. A sample is considered to be under a person's custody if one or more of the following conditions are met:

- It is in the person's physical possession
- It is in view of the person
- It is secured by the person so that no one can tamper with the sample without being detected
- It is secured by the person in an area that is restricted to authorized personnel

Chain of custody for the April 18, 1997 tank water samples was maintained in the field through use of the sampling record, chain-of-custody records, sample labels, custody seals, and airbills/bills of lading. All records generated through the field and laboratory efforts are part of the project QA records and will be maintained in the project evidence file.

The chain-of-custody record is initiated in the field for each sample by the person collecting the sample. Each sample will be assigned a unique identification number, and that number is entered on the chain-of-custody form. The chain-of-custody forms for samples hand-delivered to the NSWC Crane Project Chemist and shipped to the USEPA analytical laboratory should include the following:

- Appropriate project identification information
- Sample identification number
- Sample location
- Sample date
- Number of containers
- Analysis required/ type (or absence) of preservatives
- Sampler's name
- Release and acceptance information including date, location, and technician's signature

Custody is relinquished by using the signature blocks at the bottom of the custody form. The original chain-of-custody record accompanies the shipment, and a copy is retained in the Project Records Files. For samples shipped by commercial carrier, the waybill serves as an extension of the chain-of-custody record.

Upon receipt in the NSWC laboratory, all samples proceed through an orderly processing sequence (as defined in the laboratory quality assurance plan, page III-8 of Appendix E) specifically designed to ensure continuous integrity of both the sample and

other information pertinent to the analysis. All samples are carefully checked and verified for proper chain-of-custody records, preservation, broken, or leaking sample containers, proper label identification, and any associated discrepancies. If any samples arrive leaking or broken, or the custody seal on the shipment coolers is not intact, the QC manager is notified of the problem within 24 hours.

If no discrepancies are identified, the sample chain-of-custody record is signed, and the samples are subsequently assigned a unique laboratory identification number by the laboratory for tracking and filing. The laboratory QA system and the use of an internal chain-of-custody procedure ensures that the samples are appropriately tracked from receipt through completion of the analytical process.

Chain-of-custody information, along with all other sample-related information, will be retained in the final evidence files, which will be the central repository for all documents which constitute evidence relevant to sampling and analysis activities as described in this QAPP. Morrison Knudsen is the custodian of the evidence files and maintains the contents of the evidence files for the duration of the Delivery Order, including all relevant MK records, reports, logs, field notebooks, pictures, subcontractor reports, and data reviews in a secured, limited access area, under custody of Morrison Knudsen.

The final evidence files will include at a minimum:

- Field logbooks
- Field data and data deliverables
- Photographs
- Drawings
- Laboratory data deliverables
- Data validation reports
- Data assessment reports
- Progress reports, QA reports, interim project reports
- All custody documentation (tags, forms, air bills, etc.)

Upon completion of the Delivery Order these records will be turned over to Navy personnel.

5.3 LABORATORY SAMPLE CUSTODY

The April 18, 1997, tank water samples were either hand-delivered to the NSWC Crane Project Chemist or packaged and shipped with a separate custody record to the USEPA laboratory in accordance with DOT requirements. The analytical laboratories are required to maintain custody of samples to ensure sample integrity. The laboratory chain-of-custody procedures will be provided along with the detailed analytical procedures previously mentioned.

SECTION 6
CALIBRATION PROCEDURES AND FREQUENCY

6.1 RADIOLOGICAL SURVEY OF THE SURFACE SOILS

The sodium iodide gamma radiation detector used for the radiological survey of the surface soils will be calibrated according to the manufacturer's before use at the site. A performance check will be performed each day prior to use in accordance with the field SOPs contained in Appendix C to this QAPP. Performance checks will be documented on the Response Check Control Log, which is included with the Field SOP.

6.2 ANALYSIS OF THE CONTAINERIZED WATER SAMPLES

Laboratory instruments will be calibrated at prescribed intervals and/or as part of daily use as further discussed in Section 7.0. Frequency will be based upon the type of equipment, inherent stability, and manufacturer's recommendations. Equipment will be calibrated, whenever possible, using reference standards having known relationships to nationally recognized standards or accepted values of physical constants. If national standards do not exist, the basis for calibration will be documented.

The laboratory will be responsible for maintaining laboratory instruments and equipment. Instruments, and the measurements made as part of the analytical methodology, will be as specified in the method without modification. The laboratory's QA program ensures that only trained personnel perform routine maintenance on all major instruments and that repairs are performed by trained laboratory personnel or service technicians employed by the instrument manufacturer or representative. Instrument maintenance will be appropriately documented through the use of instrument logs, which will be included in the laboratory project file.

More detailed information is provided in Section 7.

SECTION 7
ANALYTICAL PROCEDURES

A description of the detailed analytical procedures to be employed is presented below.

It must be understood that assessment of the to-be-obtained analytical data could lead to further analysis of the water samples that yield undefined characteristics with methods that are not discussed within this QAPP. For example, additional analytical procedures may be employed to identify and quantify compounds not previously identified in the first analytical phase of dye analysis. This process will employ Infrared (IR) analysis which will be first used to identify "known" or previously identified dyes. If anomalous spectra are obtained, efforts will be directed at identifying these anomalous signatures, if through on-going laboratory research these signatures had not already been identified. This focused activity would be directed to recharacterize the sample within the holding time requirements.

Section 1 previously discussed the various levels of analytical work to be performed and the relationship of the various methods used to first qualitatively screen, and to ultimately quantify the various dyes and explosives that are present.

In general the analytical process used to research and develop the analytical procedures for the dye-contaminated water involves the evaporation of 900 ml of water to complete dryness under a dry nitrogen purge. From this evaporate derived from the first phase samples, it was determined that the major component in the residue was calcium sulfate. Further the dye contamination concentration was found to be quite low (in the parts per billion range).

In light of this low concentration that was found future analytical work will first use a sample obtained from the evaporation of at least 2 liters of contaminated water. (This results in the relatively large sample sizes previously specified.) The sample will be evaporated as before under a dry nitrogen purge. The residue will be extracted with ethanol for further quantification. To minimize experimental error and maximize the sensitivity of the analysis, a set of standards for the proper range of concentrations is required which will be developed to ultimately bracket the measured concentration. Based on analytical experience and professional expertise regarding explosives and pyrotechnic dyes, the losses of explosives and dyes due to volatilization are minimal.

The first phase analytical procedures involved screening for all of the Section 7 dyes. This resulted in the identification of two dyes types (3 total compounds). The future program will focus on the 3 previously identified dyes. If the resultant data can be explained by the presence of some or all of these dyes no further effort will be directed at trying to discern additional dye compounds. If otherwise unexplainable "anomalies" or

signatures uncharacteristic of the previously detected dyes are observed, then effort to relate these to the dyes and/or explosives listed in Section 7 will be performed. Clearly, if previously undetected dyes start to become "routinely" encountered, these "new" dyes would be included along with the dyes detected during the first analytical phase. One rationale for this approach is conservation of existing dye for use in the formulation of standards. Analysis for the more "rare" dyes only in screened samples that might have detectable concentrations of the rare dyes will conserve the consumption of the existing limited dye inventory.

As previously noted these data may be used to support a risk assessment. Consequently, the toxicology of the dyes becomes an important consideration in establishing the necessary sensitivities of the analytical methods to be employed. Appendix D provides a summary of the toxicological information related to the water-based dyes for which toxicological data could be obtained.

7.1 ANALYTICAL PROCEDURES

The following narrative discusses the identification process for analysis of the dye contaminated water containerized at the dye burial ground at the Naval Surface Warfare Center (NSWC) and the procedures to be used for analysis of the water to be collected in the future. These methods are applicable to the quantitative analysis of Disodium Fluorescein and Mil-D-16627, Blue Dye from the Dye Burial Ground Tank Water and associated contaminants. These methods cover the initial qualitative and final quantitative evaluation of the dye water. Since the dyes at the dye burial ground originated at Crane, it is very fortunate that NSWC Explosive Sciences Branch (ESB) has a large collection of samples from all the dyes used on the center in the formulation and manufacture of pyrotechnic compositions. The water from the dye burial ground will be evaluated for the dye content based on all possible dyes that could be present. All safety, chemical waste disposal and personnel protection requirements in the ESB laboratory facilities are covered in the Standard Operating Procedure (SOP) for Ordnance Evaluation by Explosive Sciences Branch (CR4052-2707-0003A). The Quality Assurance /Quality Control Plan for NPDES waste water analysis at NSWC Crane is attached as Appendix E.

Through the following procedures it will be noted that certain changes to the analytical protocols have been made from when the first phase of dye-contaminated water samples were examined to those procedures that will be applied. In general these changes relate to an additional number of standards being initially run, requirements that a sample concentration be bracketed by standards having concentrations both above and below the detected value, and specifications being established for degree of linearity and matrix spike recovery.

7.1.1 Application

These methods are applicable to ground and surface water samples where concentrations of marker dye contamination are very low. All particulates will be removed and evaluated separately for preliminary qualitative evaluation and final quantitative analysis as required. Quantitative analysis for dye contamination will involve the water samples as received with no filtration. The possibility that the particulates may contain trace levels of dye are considered using this technique.

7.1.2 General Method Description

All ESB reference samples of dyes were subjected to solubility tests in water to determine which dyes buried in the dye burial ground could be causing the discoloration of the water. A list of the ESB reference dyes is attached as Section 7. The majority of the dyes buried in the burial ground are smoke dyes which are not water soluble. Next, a flow chart was designed/formulated for the evaluation of the dye water. The chart is attached as Appendix F for reference. The analysis followed two distinct paths, water insolubles and water solubles. The water samples were analyzed as received for total organic carbon (TOC), ammonia-nitrogen analysis, toxicity, total suspended solids (TSS), volatile organic components (VOC), explosive contamination and inorganic and organic anions using ion exchange chromatography (IEC). Samples of the as-received dye water (100-milliliters aliquots) were evaporated to dryness using nitrogen purge at room temperature. Fourier Transform Infrared Spectroscopy (FT/IR) analysis of the residues after evaporation indicated that sulfate minerals were the major components present. The residues were extracted with ethanol (*) to remove colored components from the sulfate minerals. The alcohol extracted solutions were evaporated with nitrogen to dryness and extracted with methanol for chromatography evaluation. The methanol extract was subjected to thin-layer chromatography (TLC) analysis to determine the proper solvent phase for high pressure liquid chromatography (HPLC) quantitative analysis. Analysis using the spectrophotometer was used to determine the best wavelength for quantitative analysis. The absorption in the blue portion of the spectrum is the one characteristic of the dye mix that can be clearly defined. Absorption at 408 nanometers was used for quantitative analysis.

(*) It was later determined that methanol could be substituted for ethanol to simplify the analysis.

7.1.3 Sample Handling and Storage

Samples for this analysis should be collected in amber glass containers (with Teflon coated lids) and maintained in temperature controlled (4°C), dark environment. The holding time between sample collection and sample analysis is directly dependent on

the analysis to be performed. The following chart shows the standard hold times for each analysis:

TEST	PRESERVATIVE AND MAXIMUM HOLDING TIME
TOC	pH <2 HCl REFRIGERATE 14 DAYS
VOC	pH <2 HCl; NO VAPOR IN HEADSPACE; REFRIGERATE 14 DAYS
TSS	REFRIGERATE 7 DAYS
AMMONIA	pH <2 H_2SO_4 REFRIGERATE 28 DAYS
ION EXCHANGE CHROMATOGRAPHY	REFRIGERATE 48 HOURS
HPLC (dyes) and SPECTROPHOTOMETER	REFRIGERATE NO MAXIMUM LIMIT
HPLC (explosives)	Refrigerate 14 days; analyze within 40 days after extraction
FT/IR	REFRIGERATE NO MAXIMUM LIMIT
GC/MS	REFRIGERATE NO MAXIMUM LIMIT
SEM	REFRIGERATE NO MAXIMUM LIMIT
TOXICITY (MICROTOX)	REFRIGERATE NO MAXIMUM LIMIT
TLC	REFRIGERATE NO MAXIMUM LIMIT

7.1.4 Sample Preparation/Screening Procedures

Routinely, unknown samples are handled according to matrix type. In general, the samples are approached in the following manner based on the three states normally analyzed:

A. Water/Solvent Sample with Dissolved Material

1. Analyze sample as received.

2. Evaporate the sample (a 900 ml aliquot) without heat under dry nitrogen purge to complete dryness.

B. Solid/Soil Sample

1. Analyze sample as received.

2. Extract the sample with an appropriate solvent.

C. Particulates in Liquid

1. Filter out particulates. Analyze separately.
2. Analyze liquid after filtration.

Full details of the sample preparation for the dye water analysis are covered under each respective analytical procedure.

As stated previously, the Explosive Sciences Lab has a collection of dyes (dating back over 40 years) that were originally submitted for analysis during times when dyes were used in production at NSWC Crane.

The dyes were pulled from storage and screened for properties that were similar to the dyes found in the water from the dye burial ground. As previously noted, only two stored dye samples had the solubility and color that matched the dyes found in the containerized ground water.

A. The green fluorescent dye appears to be Disodium Fluorescein (uranine). Uranine dye is used for dyeing silk and wool yellow, tracing subterranean waters, marking water for air-sea rescues, and clinical test solution.

B. The blue dye components appear to match a blue dye mixture described in Mil-D-16627(BuOrd) for Dyes, Projectile-spotting (30 percent Alphazurine B and 20 percent Acid Fast Violet BG). The Mil-D-16627 blue dye mixture also contained 48 percent sugar and 2 percent Naccosol A (wetting agent) . Alphazurine is a trademark for triphenylmethane acid blue dyes. Acid Fast Violet BG is also a triphenylmethane dye with a Society of Dyers and Colourists Color Index number of 699.

C. A wet chemical technique was also applied to confirm the dyes found. When an ethanol solution of the known dye mixture is acidified with one percent acetic acid, the dye color changes from green to blue. The dye extract from the containerized water behaves the same way changing from green to blue when acidified with acetic acid.

7.1.5 Specific Method Procedures

The water samples as received, were properly containerized and preserved as required by the appropriate procedure. Listed below are the detailed procedures as required by the dye water for analysis. These procedures will also be employed for the to-be-collected water samples.

PROCEDURE FOR SCANNING ELECTRON MICROSCOPY: ENERGY DISPERSIVE X-RAY ANALYSIS ON UNKNOWN SAMPLES

PURPOSE

Use of this procedure will be focused on particulates and evaporated residues from water samples. The ultimate purpose of this technique is to develop elemental qualitative analysis to aid in the identification of precipitated and suspended inorganic and organic compounds.

SAMPLE PREPARATION

Solid Sample - No Preparation Required

Particulates in Liquid

Filter using appropriate filter paper

Examine the particulates under optical microscope and separate based on morphology. Take lab notes based on observations.

Water/Solvent Sample with Dissolved Material

Evaporate without heat under dry nitrogen purge to complete dryness.

Examine the particulates under optical microscope and separate based on morphology. Take lab notes based on observations.

SEM STUD SELECTION AND PREPARATION

The choices are copper, aluminum and carbon tape for sample analysis. If the sample is an unknown, keep in mind the tape material can cause interferences in the material ID.

Place sample on the tape/stud based on optical microscopic examination to separate potentially different components.

If uncertain of sample interferences, run several analyzes using different tapes for each analysis.

SEM CALIBRATION AND EVALUATION

Introduce sample into SEM chamber and evacuate chamber.

Following procedures (equipment handbooks) for each SEM (1600 or 3200) analyze sample at a minimum of 20 KeV for elemental identification (ID). Calibrate instrument with copper and aluminum standard for energy levels. No quantitative calibration is performed.

Both SEMs can ID down to and including carbon. If carbon is detected, use FT/IR to confirm the form of carbon found (organic or carbonate).

For quantitative purposes, SEM is only valid for polished metal surfaces. Use atomic absorption (AA), high pressure liquid chromatography (HPLC), gas chromatography mass spectrometry (GC/MS) or ultraviolet/visible absorbance for quantitative analysis as required.

DATA EVALUATION

Check all possible mismatches on the computer for elemental ID, i.e., Bromide vs Aluminum, Sulfur vs Molybdenum, etc. Use manual ID skills to confirm analysis.

Confirm the presence and quantity of any potential anions using ion exchange chromatography (IEC). See Appendix I.

If metals, confirm alloy and heat treatment by metallography (and other physical tests) if possible.

PROCEDURE FOR FOURIER TRANSFORM INFRARED SPECTROSCOPY (FT/IR)

PURPOSE

Samples to be processed by this method will have been selected based on a SEM analysis that revealed, for example, detectable amounts of inorganics or possibly evidence of oil-based dye compounds. The practical implication is though that all samples will be processed by this method.

SAMPLE PREPARATION AND ANALYSIS TECHNIQUES

Solid/Dry Sample

Sample may need to be ground using mortar and pestle.

KBr pellet - Disperse sample (0.7 milligrams) in 99 milligrams of Spectro-grade potassium bromide. Form into pellet for analysis.

Diamond Cell - For very small samples. Using optical microscope place sample on center of diamond on one half of diamond cell. Close the cell, apply pressure. Analyze using microscope attachment for FT/IR.

Dispersive - Grind sample using mortar and pestle. Distribute the powder on the surface of diamond powder using the dispersive attachment to the FT/IR.

Particulates in Liquid

Filter using appropriate filter paper.

Examine the particulates under optical microscope and separate based on morphology. Take lab notes based on observations. Analyze samples per solid sample suggestions.

Analyze the liquid portion of the sample using the ATR ("attenuated reflectance") circle cells, silver chloride plates or salt crystals.

Water/Solvent Sample with Dissolved Material

Analyze the liquid sample using the ATR circle cells, silver chloride plates or salt crystals.

Evaporate the liquid without heat under dry nitrogen purge to complete dryness.

Examine the particulates under optical microscope and separate based on morphology. Take lab notes based on observations. Analyze samples per solid sample suggestions.

FT/IR EVALUATION

The samples can be analyzed using the various attachments to the FT/IR or can be analyzed using the microscope portion of the FT/IR.

Using whichever attachment as required by the sample, always analyze a Styrene Standard film to insure that wavenumber resolution is within requirements (4 wavenumbers).

Following procedures (equipment handbooks) for each FT/IR (FTS 50 or FTS 60) analyze samples from 4000 to 200 wavenumbers.

Emphasize the areas of interest and plot the IR scans using wavenumber versus percent transmission.

DATA EVALUATION

Identify the compound (spectrum) using known standards and peak location markers, the system resolution is 4 wave numbers. All ESB reference dye samples will be characterized using this technique.

Always consider the possibility that a mixture may exist.

Separation techniques may be required to evaluate mixtures (i.e., high pressure liquid chromatography (fraction collection), thin layer chromatography, organic solvent separation, gas chromatography mass spectrometry, etc. These methods may be less commonly employed than those referenced in Section 6.2.1 A, B, and C.

QUANTITATIVE ANALYSIS

FT/IR can be used to quantify, but sensitivity will have to be evaluated for each application. No quantitative analyzes were performed on the dye water samples. The quantitative analysis of FT/IR requires 1-5% to be a valid technique.

Liquid samples are easier to quantify than solids.

Always consider other analytical techniques to confirm analysis.

PROCEDURE FOR QUALITATIVE THIN LAYER CHROMATOGRAPHY (TLC) FOR DYE ANALYSIS

PURPOSE

This procedure establishes the activities associated with performing thin-layer chromatography (TLC) analyses.

SAMPLE PREPARATION

Water/Solvent Sample with Dissolved Material

Evaporate the sample, a 900 ml aliquot, without heat under dry nitrogen purge to complete dryness.

Solid/Soil Sample

Extract the sample which typically is about 20 to 30 milligrams, with methanol.

A 100 ml aliquot to spot the TLC plate is recommended for water-based dyes.

(Note - Methanol works on water-based dyes. In the event that oil-based dyes are encountered, if necessary, additional effort will be directed toward identifying a more optimal solvent. For the forthcoming work, methanol is regarded as an appropriate solvent due to the prior identification of only water-based dyes. To characterize the potential presence of oil-based dyes a solvent matrix for TLC elution using one of the following solvents: dichloromethane, dichloroethane, or chloroform, will be used. This process will be employed for each sample. The typical 20 to 30 milligrams sample is reacted with 1 ml of one of the above solvents. A 100 μml aliquot is then recommended to spot the TLC plate for the analysis of oil-based dyes. The technique should provide resolution of the semi-quantitative presence of oil-based dyes, within the 100 μml aliquot to about 500 parts per billion.)

SEPARATION OF COMPONENTS

TLC Method

Dye extracts are spotted on a silica gel TLC plate. A mixture of organic solvents is used to develop the TLC plate.

Based on the completeness of separation, the solvent mixture polarity is adjusted to obtain better separation.

IDENTIFICATION OF COMPONENTS

Examination of Separated Components

The developed TLC plate is examined using visible and ultraviolet (UV) lamps to determine the number of dye components and their color characteristics.

Standards Analysis

Select reference dyes for comparison based on similarity of color and solubility characteristics.

Prepare sample of known reference dyes and use the same TLC procedure for qualitative comparison.

Mixtures of the known dyes gave a similar pattern of tailing TLC spots that had been observed for the dyes extracted from the burial ground samples.

HPLC ANALYSIS FOR RESIDUAL EXPLOSIVES

PURPOSE

The explosives analysis of the dye samples will be performed in accordance with the SW-846 Update II, September 1994, Method #: 8330, Title: Nitroaromatics And Nitroamines By High Performance Liquid Chromatography (HPLC).

SAMPLE PREPARATION

The procedure will be adapted in the following manner:

In paragraph 7.1.1.1 Low-Level Method (salting-out extraction), of the above reference, is proposed for use in the analysis of samples from the dye burial ground at NSWC, Crane. The "salting-out extraction" will be replaced with evaporation concentration of the water samples. The modification to the method was made because the water samples contain sediments. The explosives may be dissolved in the water or they may be attached to the particulates.

Measure out 900 ml of a shaken water sample (using a 1 L graduated cylinder) and transfer it to a 3000 ml beaker or equivalent glass container what gives a large liquid surface for evaporation. Attach a dry nitrogen supply (cook off from liquid nitrogen storage tank) line to the beaker. Adjust the nitrogen line position and flow rate so that it is directed on to the surface of the water and slightly moves liquid surface. Cover the container loosely with aluminum foil to protect it from light. Evaporate the water to dryness.

Add a 2 ml aliquot of acetonitrile to the beaker. Loosen the evaporite from the beaker surface and transfer the suspension to 15 ml vial. Add a second 2 ml aliquot of acetonitrile to the beaker continue to remove evaporite from the beaker and transfer to the vial. Repeat this process until 10 ml of acetonitrile had been used to clean all surfaces of the beaker where the water sample was evaporating and all acetonitrile has been transferred to the vial. Cap the vial with a Teflon-line cap, vortex swirl for one minute, and place in a cooled ultrasonic bath for between two to four hours.

Continue the analysis with paragraph 7.1.2.2.2 for soil and sediment samples. Samples were analyzed for explosives listed in the Method #8330. There was no evidence of these explosives in the sample. There were no peaks that could be integrated from the explosive HPLC column.

Nitroguanidine and Nitroglycerine are to be added to the list of explosives to be analyzed for. Additionally, the compounds indicated on page A-88 of Appendix E will also be present in all spiking solutions and calibration standards.

All samples will be analyzed using 5 standards as required by Method #8330 that blanket the samples.

A standard from Environmental Resource Associates (ERA) will be obtained for method #8330 for analysis in addition to required blanks, matrix spike samples and laboratory spiked samples. All will be analyzed in accordance with the prescribed procedures.

QUANTITATIVE ANALYSIS OF DISODIUM FLUORESCEIN BY HPLC

PURPOSE

This procedure establishes the activities associated with quantitative analysis of disodium fluorescein by HPLC.

SAMPLE PREPARATION

A sample, a 900-ml aliquot, is evaporated by a dry nitrogen purge to 5 ml.

APPARATUS AND REAGENTS

Anotec Syringe Filter, Catalog # 2001050U, 0.2 micrometers

5 ml volumetric flasks

1000 ml beakers

Shimadzu SIL-9A Auto Injector

LDC Model III Constametric Pump

Spectra-Physics SP4270 Integrator

Alltech 345 Solvent Recycler

Column Packing:	Alltech Econosil, C18, 10 micron
Column Size:	Length: 250 millimeter, Inside Diameter: 4.6 millimeter
Mobile Phase:	Isocratic, 50% Methanol, 50% Deionized Water and a Tetrabutylammonium Phosphate, 0.5 molar, pH 7.5, Kit from Alltech (1 kit per liter of mobile phase).
Flow Rate:	1.0 milliliter per minute

Detector: Ultraviolet at 254 nanometers

Injection Volume: 10 microliters

Standard: Disodium Fluorescein, Eastman Catalog # 735, Lot # AGA, (85% min. by spectro analysis, corrected for water). Disodium Fluorescein standards are prepared in methanol.

Methanol: All methanol used for extraction and analysis is Fisher Scientific, HPLC grade.

Water/Blank: All reagent water used in the analysis procedure is steam distilled and then filtered through a Millipore Model ZD40 (Analytical) Milli-Q-Plus Water System.

Nitrogen: Dry nitrogen gas is supplied by liquid nitrogen cook off.

Glassware: Glassware is rinsed with high quality distilled water.

Filter: Anotop 0.2 micron

Instrument Detection Limits

The limit of detection is dependant on the amount of concentration of the sample. Using a 900 milliliter aliquot of sample concentrated down to 5 milliliters, the limit of detection for Disodium Fluorescein is about 10 parts per billion.

The lowest calibration standard is 1.64 ppm. The reporting limit for the method of 10 ppb, is dependent on the amount of concentrating of the original sample (in this case 180 times). The spectrophotometer analyzes a concentrated water sample. This limit was used because, after concentration from 900 ml into 5 ml, satisfactory results were obtained.

CALIBRATION PROCEDURES

Disodium Fluorescein, Eastman Catalog # 735, Lot # AGA, (85% min. by spectro analysis, corrected for water) is used for reference. Disodium Fluorescein standards are prepared in Fisher Scientific, HPLC grade, methanol. A concentrated standard was prepared and diluted to the range of the sample concentrate (2 ppm, 4.5 ppm, and 9 ppm) in the analysis of the first two samples. For further samples, five standards will be prepared in the range that will blanket the sample values. These standards are in addition to the standard blank. The standards will be evaluated for linear correlation. The linear correlation factor will be at a minimum of 0.995.

The matrix spiking solution should consist of 15 ppb of blue dye standard and 25 ppb of Disodium Fluorescein standard after addition to the neat tank water sample, i.e., approximately double the concentration of each component. Recovery will be 100 +- 20%.

Initial calibration is performed at the start and at the end of a shift. Acceptable criteria for calibration is a stable baseline (correlation factor 0.995).

A laboratory reference standard is prepared independently of the calibration stock using de-ionized laboratory water. It is analyzed by the above procedure and must be within ± 10% of the true value. If the reference is not within ± 10% of the true value, it will be reanalyzed. If the reference is still outside the criteria, the reason will be determined and corrected.

Code 4052 will strive to obtain a certified standard dye sample solution will be obtained from an outside source for further calibration checks/recovery. Recovery will be +- 10% of true value.

INTERFERENCES AND CORRECTIVE MEASURES

Liquid Chromatography separation was used to avoid possible interferences.

ANALYTICAL PROCEDURE

Concentration

The sample bottle containing the dye contaminated water is shaken to put all solids into suspension. A 900 milliliter aliquot of sample is poured into a graduated cylinder. The aliquot is divided between three (1000-milliliter) beakers. A nitrogen line is attached to the lip of each beaker and the beakers are covered with aluminum foil. Nitrogen flow is adjusted to slightly move the surface of the sample liquid. The samples are evaporated to dryness under ambient conditions.

Extraction

The dry sample residues are each extracted with three or more 2-milliliter aliquots of methanol. Each beaker residue is extracted until there is no visible blue color left in the extract or the residue. The combined extracts are quantitatively filtered. The filtered methanol solution is evaporated to less than 2 milliliters. The concentrate is quantitatively transferred to a 5-milliliter volumetric flask and diluted to volume with methanol.

A high performance liquid chromatography (HPLC) procedure for separation of food dyes, found in the Hewlett Packard Catalog, was used on the known and unknown dye samples. The procedure gave a good separation for the Disodium Fluorescein standard and a peak with the same retention time (six minutes) was observed in the unknown sample. (The procedure uses a C18 column with a one milliliter per minute flow rate of 50/50 mixture of methanol and water. The solvent is buffered with, Tetrabutylammonium phosphate solution from Alltech. A 254 nanometer wavelength detector was used for data collection). This separation procedure can be used for quantitative analysis of the Disodium Fluorescein (uranine) dye. Also, an appropriate secondary confirmation column shall be used to confirm the identify of unknown peaks and all peaks associated with analytes of interest. However, it is the primary column which shall be used for quantitation purposes.

CALCULATIONS

Peak heights of the samples and standards are used for quantitative determination of Disodium Fluorescein. A response factor for the standards is determined from a plot of concentration and peak height of the dye. The peak height of the dye in the sample is multiplied by the response factor and in turn divided by the concentration factor. Results are reported in parts per billion of Disodium Fluorescein in the original water sample.

QUALITY CONTROL

The sample quality control will be handled by in accordance with the Crane NPDES QA/QC plan (Appendix E).

DATA REPORTING

The sample data reporting will be handled in accordance with the Crane NPDES QA/QC plan (Appendix E).

QUANTITATIVE ANALYSIS OF MIL-D-16627, BLUE DYE BY ABSORPTION SPECTROPHOTOMETRY

PURPOSE

This procedure establishes the activities associated with quantitative analysis of MIL-D-16627, Blue Dye by Absorption Spectrophotometry.

SAMPLE PREPARATION

Evaporate the sample, a 900-ml aliquot, without heat under a dry nitrogen purge to 10 ml.

APPARATUS AND REAGENTS

10 ml volumetric flasks

Perking-Elmer model 552 spectrophotometer

one centimeter path length cuvettes

pipettes

Acetic Acid, Fischer Scientific reagent grade

Reference standards are prepared from a sample of Mil-D-16627 dye in methanol. Mil-D-16627 contains only 50 percent dye according to specification. One drop of acetic acid is added to 10 milliliter of the final methanol standard.

Water/Blank: All reagent water used in the analysis procedure is steam distilled and then filtered through a Millipore Model ZD40 (Analytical) Milli-Q-Plus Water System.

INSTRUMENT DETECTION LIMITS

The limit of detection for the blue dye is 5 parts per billion but background interference could change the limit. The lowest standard is 1.6 ppm. The reporting limit for the method of 5 ppb, is dependent on the amount of concentrating of the original sample (in this case 90 times). The spectrophotometer analyzes a concentrated water sample. This limit was used because, after concentration from 900 ml into 10 ml, satisfactory results were obtained. This limit was used because, after concentration from 900 ml into less than 10 ml, interferences from sample background were too overwhelming for the instrument to analyze.

INTERFERENCES AND CORRECTIVE MEASURES

The acetic acid removes the Disodium Fluorescein absorption and slightly increases the blue dye absorption. One drop of acetic acid is added to 10 milliliter of the methanol standard.

CALIBRATION PROCEDURES

Peak heights of the samples and reference standards are used for quantitative determination of the Mil D-16627 blue dye. No attempt was made to distinguish

between the two blue dyes. A response factor for the standards is determined from a plot of concentration and peak height of the dye. The peak height of the dye in the sample is multiplied by the response factor and in turn divided by the concentration factor. Results are reported in parts per billion of blue dye in the original water sample.

A concentrated standard is prepared and diluted to the range of the sample concentrate 1.6 ppm 3.29, and 16.4 ppm for the blue dye in the analysis of the first two samples. For further samples, five standards will be prepared in the range that will blanket the sample values. These standards are in addition to the standard blank. The standards will be evaluated for linear correlation. The linear correlation factor will be at a minimum of 0.995.

The spiking solution should consist of 3 ppm of blue dye standard and 25 ppm of Disodium Fluorescein standard added to a 900 ml tank water sample aliquot before concentration and extraction steps are performed. Recovery will be 100 +- 20%.

Initial calibration is performed at the start and at the end of a shift. Acceptable criteria for calibration is a stable baseline (correlation factor 0.995).

A laboratory reference standard is prepared independently of the calibration stock using de-ionized laboratory water. It is analyzed by the above procedure and must be within ± 10% of the true value. If the reference is not within ± 10% of the true value, it will be reanalyzed. If the reference is still outside the criteria, the reason will be determined and corrected.

Code 4052 will strive to obtain a certified standard dye sample solution from an outside source for further calibration checks/recovery. Recovery will be +- 10% of true value.

ANALYTICAL PROCEDURE

The sample concentrate prepared for Disodium Fluorescein analysis was diluted by half to 90 times concentration using methanol. The background is too high at 180 times concentration. One drop of acetic acid is added to the 10 milliliter volumetric flask. The acetic acid removes the Disodium Fluorescein absorption and slightly increases the blue dye absorption. The Mil-D-16627 blue dye was scanned in the visible range with a spectrophotometer. The blue dyes have a maximum absorbance at 408 nanometer (nm) and a shoulder at 390 nm. The visible spectrophotometer can be used for quantitative analysis of the Mil-D-16627 dye.

CALCULATIONS

The blue dye reference standard weight is corrected for purity. Quantitation was based on the peak height at 408 nm. A response factor for the standards is determined from a

plot of concentration versus peak height of the dye. The peak height of the dye in the sample is multiplied by the response factor and in turn divided by the concentration factor. Results are reported in parts per billion of blue dye in the original water sample.

QUALITY CONTROL

The sample quality control will be handled in accordance with the Crane NPDES QA/QC plan (Appendix E).

DATA REPORTING

The sample data reporting will be handled in accordance with the Crane NPDES QA/QC plan (Appendix E).

TOTAL ORGANIC CARBON (TOC)

Appendix G covers the TOC analysis used in the evaluation of the dye water. The sample will be analyzed as received.

TOTAL SUSPENDED SOLIDS (TSS)

Appendix H covers the procedure for non-filterable residue in drinking or waste water. This test is commonly referred to as TSS. This method will be used for every sample and generate non-soluble particulate samples for FT/IR, SEM, GC-MS, and TLC analysis.

TOXICITY (MICROTOX)

Appendix B covers the procedure for toxicity analysis used in the evaluation of the dye water. The Microtox test is performed on as received samples and on samples representative of the water after treatment. The purpose of the data collection is to show relative toxicity before and after treatment without any correlation to human health toxicity data.

ION-EXCHANGE CHROMATOGRAPHY (IEC)

Appendix I covers the inorganic/organic anion analysis by IEC used in the evaluation of the dye water. Full analysis for all anions will be performed.

UNKNOWN MATERIALS ANALYSIS USING GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

Appendix J covers the volatile and pyrolysis analyzes on unknowns performed by GC/MS. Analysis of the filtration and dry residue are required to determine if the residue contained other compounds not yet identified. This method will not be used for quantification.

AMMONIA-NITROGEN ANALYSIS

Ammonia-Nitrogen Analysis procedure is attached as Appendix K. This analysis is routinely performed on waste water.

DYE	QTY. (GM)	DATE	MANUFACTURER	MIL-SPEC
1-8 DIPHENOX QUINON DRY GRD LA-6-209	20	11/56	GENERAL DYESTUFF CO.	
1,4-DIAMINO-2,3-DIHYDROANTHRAQUINONE, MIL-D-3668	40			MIL-D-3668
1,4-DI-METHYL AMINO ANTHRAQUINONE, MIL-D-21354,DISPERSE BLUE-14	30			MIL-D-21354
1,9-BENZ-10-ANTHRONE, MIL-D-50074C, BENZANTHRONE	15	08/81		MIL-D-50074C
3,4,8,9-DIBENZPYRINE-10-QUINONE, MIL-D-50029C, VAT YELLOW 4	15	08/81		MIL-D-50029C
ACCRAMINE HYDROCHLORIDE	6		GENERAL DYESTUFF CO.	
ACID BLUE 1 (3 EACH)	5	04/96	MCALLISTER	
ACID ORANGE 10	5	06/96	NTS	
ACID ORANGE 10	120	03/96		
ACID YELLOW 23 (3 EACH)	5	04/96	MCALLISTER	
ANTHRACENE, 480 LOT # 63	400		KODAK	
AZOSOL BRILLIANT YELLOW GGF DRY, LA-6-223	30	11/56	GENERAL DYESTUFF CO.	
BAGHOUSE TEST DYE	5			
BENZAN CRUDE B DRY GRD LA-6-207	50	11/56	GENERAL DYESTUFF CO.	

DYE	QTY. (GM)	DATE	MANUFACTURER	MIL-SPEC
BENZAN CRUDE B, DRY GROUND LA6-207	500	02/57	GENERAL DYESTUFF CO.	
BENZAN PURF DGRD LA-6-208	50	11/56	GENERAL DYESTUFF CO.	
BENZATHRONE, MIL-B-50074	20	07/70		MIL-B-50074
BLUE DYE MIL-D-16627 (1)	250			MIL-D-16627(1)
BLUE DYE, MIL-D-16627 (5),	350			MIL-D-16627(5)
BLUE DYE, MIL-D-21354	20	07/70		MIL-D-21354
BROMBENZANG GRD LA-6-224	30	11/56	GENERAL DYESTUFF CO.	
CALCO OIL SCARLET, 69493	200		AMERICAN CYANIAD	
CALCOZINE RHODAMINE BXP	40			
DUPONT - OIL BLUE A	20	01/26/56		
DUPONT OIL RED	50	03/52		
DUPONT OIL RED, REF. L4-A (5301), SER.5211	50	11/55		
DUPONT OIL YELLOW C-1904	30	10/55		
DYE MARKER, GREEN URANINE, CONTRACT N19514446, LOT 9721	40	11/62		
FEAA, LOT 22242583	300			
GREEN 6820 00 625 3503	250			
GREEN DYE, (1) ACID YELLOW 23, (2) ACID BLUE 1	5	06/96	NTS	
GREEN-ACID YELLOW 23, ACID BLUE 1	150	03/04/96		
HELIO FAST YELLOW 6 GL, LA 6-192	30	10/56	GENERAL DYESTUFF CO.	
HVT-YELLOW-GK IS INDANTHRENE YELLOW GKA POWDER, LA-6-191	30	10/56	GENERAL DYESTUFF CO.	
IND GOLD YEL GKAC, LA-6-211	30	11/56	GENERAL DYESTUFF CO.	

DYE	QTY. (GM)	DATE	MANUFACTURER	MIL-SPEC
MIL-D-16627 DYE	450			MIL-D-16627
MIL-D-16627 STD DYE, RED	30			MIL-D-16627
MIL-D-16627, DYE 146				MIL-D-16627
MIL-D-16627, RED DYE	50			MIL-D-16627
MIL-D-16627, RED, ?6820-624OR8-(3 OR 2)50(8OR3)	25			MIL-D-16627
MIL-D-16627, STD DYE 3PKGS 10g EACH				MIL-D-16627
MIL-D-16627, STD DYE, RED	40			MIL-D-16627
OIL SCARLET 1370, PEERLESS COLOR	500			
OIL SCARLET BL, ORDER # 1789	400			
ORANGE DYE	5		MCALLISTER	
ORANGE DYE, MIL-D-16627(3), ORANGE G	250			MIL-D-16627(3)
ORANGE MIL-D-16627	200			MIL-D-16627
PARA M LA-6-225	30	11/56	GENERAL DYESTUFF CO.	
PYRAZOLE ANTHRONE LA-6-228	15	11/56	GENERAL DYESTUFF CO.	
R1184 YELLOW DYE RDA 446, 744-443-505	450		DUPONT	
R1187 VIOLET DYE, DUPONT, RDA 435	300			
R5054 BENZANTHRANONE RDA 451 COMPOSITE	400			
RED 6820 00 624 3503	250			
RED DYE	5		MCALLISTER	
RED DYE MIL STD 713	20	07/70		MIL-STD 713
RED DYE, DISPERSE 9, MIL-D-003284	20	07/70		MIL-D-003284
RED DYE, MIL-D-16627 (2)	250			MIL-D-16627(2)

DYE	QTY. (GM)	DATE	MANUFACTURER	MIL-SPEC
RED DYE, MIL-STD 713	30			MIL-STD 713
REFERENCE STANDARD SAMPLE DYE, BENZATHRONE 99%, MIL-B-50074C, PARA 6.4	10			MIL-B-50074(C)
REFERENCE STANDARD SAMPLE DYE, DISPERSE RED 9, 99%, MIL-D-3284A, PARA 6.6	15			MIL-D-3284(A)
REFERENCE STANDARD SAMPLE DYE, DISPERSE RED 9, 99%, MIL-D-3718A, PARA 6.5	15			MIL-D-3718(A)
SMOKE YELLOW B-10	50	03/57	GENERAL DYESTUFF CO.	
SMOKE YELLOW B-11	50	03/57	GENERAL DYESTUFF CO.	
SMOKE YELLOW I IS ANTHRARUFIN DRY, LA-6-193	30	10/56	GENERAL DYESTUFF CO.	
SOLVENT YELLOW 33 DYE	20			
STEARATED YELLOW CHROME, FROM MK12 MARINE LOCATION MARKER	250			
SUDAN ORANGE RRA	500		GENERAL DYESTUFF CO.	
SUDAN SCARLET 6G SPECIAL, LA6-42	400	04/56	GENERAL DYESTUFF CO.	
TRANSKETON DRY LA-6-227	30	11/56	GENERAL DYESTUFF CO.	
VIOLET DYE PA2491, 74.52% PURE, 0.8% VOC @ 70 DEGREES C	300			
YELLOW DYE, MIL-D-50029	30	07/70		MIL-D-50029
Z4CR2O7 PIGMENT	5			

7.2 PRIMARY LABORATORY

The primary laboratory used to analyze the tank contents is the NSWC Crane Explosive Sciences Branch Laboratory. Sample analyses were in accordance with analytical methods published in the most recent edition of USEPA Methods for Chemical Analysis of Water and Wastes or with the NSWC Crane Explosive Sciences Branch Internal Laboratory Procedures, as summarized as appropriate in Section 7, above.

7.3 QUALITY ASSURANCE LABORATORY

Duplicates of the tank water samples were provided to the USEPA research laboratory in Athens, Georgia. The USEPA laboratory will analyze the duplicate samples using the same methods and procedures as the NSWC Crane Explosive Sciences Branch Laboratory and will prepare a data package. The USEPA data package will be evaluated during data validation and summarized in the data assessment.

SECTION 8
INTERNAL QUALITY CONTROL CHECKS

Internal quality control checks are performed through the collection and evaluation of field QC samples and laboratory QC samples. Field QC samples are the duplicate tank water samples collected on April 18, 1997, and sent to the USEPA laboratory. Lab QC samples include method blanks, laboratory duplicates, laboratory control samples, matrix spikes, and matrix spike duplicates, according to method requirements. Project samples are used for matrix spikes and matrix spike duplicates. Section 4.2 reports the specific samples that will be collected including those to provide QC support. Both field and laboratory QC data will be evaluated as part of the data assessment.

SECTION 9
DATA REDUCTION, VALIDATION, ASSESSMENT, AND REPORTING

9.1 DATA REDUCTION

9.1.1 Field Data Reduction Procedures

Field data reduction will consist of tabulating the raw data recorded in the field logbook from direct read instrumentation. Data will be recorded in the field logbook immediately after measurements are taken. If errors are made, the results will be legibly crossed out, initialed and dated by the field sampler, and corrected in a space adjacent to the original (erroneous) entry. Data from daily instrument performance checks will also be tabulated.

9.1.2 Laboratory Data Reduction Procedures

Raw analytical data from the NSWC Crane Explosive Sciences Branch laboratory and from the USEPA laboratory will be corrected into appropriate units of measurement, tabulated, and submitted to MK.

9.2 DATA VALIDATION AND ASSESSMENT

Data verification procedures will be performed for both field and laboratory operations, as described below.

9.2.1 Procedures Used to Evaluate Field Data

Procedures to evaluate field data for this project primarily include checking for transcription errors and reviewing field logbooks. This task is the responsibility of the QC Manager, who will not otherwise make any of the field measurements or add notes, data, or other information to the logbook.

9.2.2 Procedures to Verify and Assess Laboratory Data

MK representatives will perform independent validation of analytical data from the NSWC Crane Explosive Sciences Branch laboratory and the data from the split samples analyzed by the USEPA laboratory to determine data quality and to assess the usability of the data to meet the project DQOs. Validation of "new" data generated by the USEPA laboratory should not require independent validation, because this laboratory will be functioning in an audit capacity. Data will be validated by reviewing chain-of-custody forms, sample preservation records, analytical holding times, sample data as compared to QC sample data, and reporting requirements.

Data assessment will involve reviewing the results of the field and laboratory QC sample data, the validation report, evaluating the PARCC parameters, and evaluating whether the DQOs have been met. If project goals have not been achieved to satisfy DQOs, the MK Science Manager, SouthDiv RPM, USEPA RPC, and NSWC Crane EPD ECR will review the circumstances affecting the data usability and evaluate alternatives or resolutions. This may necessitate resampling with appropriate modifications to the analytical strategy.

9.3 DATA REPORTING

This section describes data reporting procedures for field and laboratory operations.

9.3.1 Field Data Reporting

Field data reporting will be conducted principally through the transmission of report sheets containing tabulated results of all measurements made in the field and documentation of all field calibration activities.

9.3.2 Laboratory Data Reporting

The task of reporting laboratory data begins after the validation activity has been concluded. Data from the NSWC Crane Explosive Sciences Branch laboratory and the USEPA laboratory will be reported in summary tables; copies of the laboratory results will be provided in an appendix. A quality control summary and assessment of the usability of the data to meet the project's DQOs will be included in the report. A final report will be available 120 days after final data validation.

APPENDIX A: HPLC EXPLOSIVES ANALYSIS

EXPLOSIVE SCIENCES BRANCH
CODE 4052
NAVAL SURFACE WARFARE CENTER
CRANE, INDIANA 47522

PROCEDURE FOR ANALYSIS USING THE HIGH PERFORMANCE LIQUID CHROMATOGRAPH

CR 4052-EOP-0022

PREPARED BY
MAROFF QURASHI

DATE
19 Aug 97

APPROVED BY
NANCEY J. MAEGERLEIN

DATE
19 Aug 97

TITLE: Quantitative Analysis Of Materials By High-Performance Liquid Chromatography (HPLC)

1..0 SCOPE AND APPLICATION

1.1 This method is intended for the separation and quantitative analysis of relatively non-volatile components that are soluble in solvents who's characteristic are suitable for HPLC. The method is primarily intended for solids and high boiling point liquids that are not corrosive samples. It is also useful as an exploratory tool for samples of unknown or uncertain composition. Making comparisons of samples to identify differences is also a use for the method.

1.2 The matrices applicable to the method are shown below:

Soluble Plastics
Lubricants
Components and Contaminants in Explosives
Rubber and Plastic Extracts
Paint Extracts
Soluble Residues on Metal Surfaces
Inclusions Taken From Samples that can be dissolved
Water Analysis

1.3 Contaminants in water samples may be concentrated with solid phase extractors prior to analysis by HPLC.

2.0 SUMMARY OF METHOD

2.1 A known weight of sample is extracted or dissolved and diluted to volume. Typically the solution concentration is kept to around 10 parts per million (ppm). The sample is injected into the carrier liquid and passes through the separation column and into the detector. The travel time through the column is an indicator of component identity. An integrator is used to measure the separation time and the component peak area or the peak height for quantitative analysis.

2.2 Larger sample concentrations may be required if the detector is not sensitive to the component.

3.0 PROCEDURE

3.1 Instrument Preparation

3.1.1 Prepare the filtered carrier solvent using HPLC grade solvents. Turn on the instrument and prime the liquid chromatograph pump. The HPLC unit is checked to determine if the correct operating programs are installed. Enclosure (1) shows the program parameters for the instruments

3.1.2 At a cold instrument start up it may take several hours to stabilize and give a straight base line on the integrator. During sample analysis, known compounds may be introduced into the sample if additional calibration checks are needed. Calibration of the instrument is performed using pure compound of known concentration

3.2 Sample Preparation

3.2.1 The weighed sample is dissolved in the carrier solvent or one of its components. The solution is diluted to volume prior to analysis.

3.2.2 The sample solution should be filtered before injection to avoid stopping up the separation column.

3.3 Calibration

3.3.1 A standard is weighed and dissolved in the carrier solvent. The solution is diluted to volume in a volumetric flask. The concentrated standard is used to make dilute standards in the concentration range of the sample. Three standards are prepared to bracket the sample concentration.

3.3.2 Once linearity of calibration is established, one standard will suffice for calibration of the instrument. A response factor is determined for the component based on the integrator peak areas and standard weights.

3.4 Quantitation

3.4.1 The sample Integrator peak area times the response factor and divided by sample weight are used to determine the component concentration. The sample weight is corrected for the dilution or concentration factor.

3.4.2 If the integrator peak area is distorted by baseline problems, the peak heights of the standards and the sample component may be used for quantitation.

INSTRUMENT PARAMETERS FOR THE HPLC SYSTEM

Enclosure (1)

Parameters for Waste Water Analysis HPLC

Pump Unit: Altex Model 110AS

Carrier Flow Rate: 1.1 milliliters per minute

Injector Unit: Rheodyne Model 7152

Injector Volume: 100 microliters
Filter: 0.45 microns

Detector: Beckman Model 153

Wavelength: 254 nanometer fixed
Cell Path length: 1 centimeter

Column: Alltech C-18

Particle Size: 10 microns
Length: 25 centimeters
Frit Pore Size: 2 microns
Inside Diameter: 4.6 millimeters
Column Temperature: 34 Celsius

Electronic Filter: Spectrum Model 1021A Electronic Filter and Amplifier

Cut off Frequency: 0.02
Output: 1

Integrator: Spectra Physics Model SP4270

Detection Limits:

HMX, RDX, Tetryl, DATB and TNT are all 0.1 milligrams/liter

Parameters for Failure Analysis HPLC

Pump Unit: LDC, Model III

Carrier Flow Rate: 1.0 milliliters per minute

Injector Unit: Shimadzu Auto Injector, Model SIL-9A

Injector Volume: 100 microliters
Filter: 0.45 microns

Detector: Linear, Model UV-106

Wavelength: 254 nanometer fixed
Cell Path length: 1 centimeter

Column: Alltech C-18

Particle Size: 10 microns
Length: 25 centimeters
Frit Pore Size: 2 microns
Inside Diameter: 4.6 millimeters
Column Temperature: 34 Celsius

Solvent Recycler: Alltech, Model 345

Integrator: Spectra Physics Model SP4270

Detection Limits:

HMX, RDX, Tetryl, DATB and TNT are all 0.1 milligrams/liter

Parameters for Ion Chromatograph HPLC

Pump Unit: Waters Model 590

Carrier Flow Rate: 0.6 milliliters per minute

Injector Unit: Shimadzu Auto Injector, Model SIL-9A

Injector Volume: 100 microliters
Filter: 0.45 microns

Detector: Waters Model 430 Conductivity Detector

Gain: 0.005
Range: 500(us x 10)

Column: Waters ICPak Anion, Part # 07355

Length: 5 centimeters
Inside Diameter: 4.6 millimeters
Column Temperature: Ambient

Integrator: Waters Model 740

Detection Limits:

Carbonate, Fluoride, Chloride, Nitrate, Nitrite, Sulfate and Phosphate Anions all 0.1 milligrams/liter

Parameters for Acetyl/Formal Analysis HPLC

Pump Unit: Beckman Model 110A

Carrier Flow Rate: 0.5 milliliters per minute
Solvent Carrier: Acetone with 13 % Water

Injector Unit: Rhedyn

Injector Volume: 100 microliters
Filter: 0.45 microns

Detector: Evaporative Light Scattering Detector, Varex Model ELSDIIA

Wavelength: 254 nanometer fixed wavelength
Cell Path Length: 1 centimeter

Column: Alltech C-18, 3 Columns in series

Particle Size: 10 microns
Length: 25 centimeters
Frit Pore Size: 2 microns
Inside Diameter: 4 6 millimeters
Column Temperature: Ambient

Integrator: Spectra Physics Model ChromJet

Detection Limits:

RDX and Acetyl/Formal are all 0 4 milligrams/liter

DOES NOT APPLY

Parameters for Organic Acid Analysis HPLC

Pump Unit: LDC Model III

Carrier Flow Rate: 0.5 milliliters per minute
Solvent Carrier: 0.013 Normal Sulfuric Acid

Injector Unit: Shimadzu Auto Injector, Model SIL-9A

Injector Volume: 100 microliters
Filter: 0.45 microns

Detector: Jasco, Model UVIDEC-100-IV

Wavelength: 220 nanometer fixed wavelength
Cell Path Length: 1 centimeter
Range: 0.02

Column: Phenomenex, Part # 00H-0138-K0

Packing: Rezex, 8% H. Organic Acid
Particle Size: 10 microns
Length: 30 centimeters
Frit Pore Size: 2 microns
Inside Diameter: 7.8 millimeters
Column Temperature: Ambient

Integrator: Spectra Physics Model SP4270

Detection Limits:

Oxalic, Citric, Tartaric, Succinic, Formic and Acetic Acid are all 10 milligrams/liter

DOES NOT APPLY

Parameters for Dye Analysis HPLC

Pump Unit: Altex Model 110A

Carrier Flow Rate: 1.0 milliliters per minute
Solvent Carrier: Water/Methanol 50/50 + PIC(A)

Injector Unit: Kratos Model 300 Auto Sampler

Injector Volume: 20 microliters
Filter: 0.45 microns

Detector: LDC UV Monitor Model 1205

Wavelength: 254 nanometer fixed wavelength
Cell Path Length: 1 centimeter

Column: Alltech C-18

Particle Size: 10 microns
Length: 25 centimeters
Frit Pore Size: 2 microns
Inside Diameter: 4.6 millimeters
Column Temperature: Ambient

Integrator: Spectra Physics Model SP4270

Detection Limits:

Dependent on the dye

APPENDIX B: TOXICITY PROCEDURE

EXPLOSIVE SCIENCES BRANCH
CODE 4052
NAVAL SURFACE WARFARE CENTER
CRANE, INDIANA 47522

PROCEDURE FOR THE ASSESSING OF MICROBIAL DETOXIFICATION OF CHEMICALLY CONTAMINATED WATER AND SOIL USING A TOXICITY TEST WITH A LUMINESCENT MARINE BACTERIUM

CR 4052-EOP-0033

PREPARED BY: SANDRA M. BISHOP

PREPARED BY: DATE

Sandra M Bishop 5-7-97

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Designation: D 5660 – 95

AMERICAN SOCIETY FOR TESTING AND MATERIALS
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If not listed in the current combined index, will appear in the next edition.

Standard Test Method for Assessing the Microbial Detoxification of Chemically Contaminated Water and Soil Using a Toxicity Test with a Luminescent Marine Bacterium[1]

This standard is issued under the fixed designation D 5660; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method (**1**)[2] covers a procedure for the rapid evaluation of the toxicity[3] of wastewaters and aqueous extracts from contaminated soils and sediments, to the luminescent marine bacterium *Photobacterium phosphoreum*,[4] prior to and following biological treatment. This test method is meant for use as a means to assess samples resulting from biotreatability studies. Sensitivity data for 1300 chemicals have been reported in the literature (**2**). The data obtained from this test method, when combined with respirometry, total organic carbon (TOC), biochemical oxygen demand (BOD), chemical oxygen demand (COD), or spectrophotometric data, can assist in the determination of the degree of biodegradability of a contaminant in water, soil, or sediment (**3**).

1.2 This test method is applicable to the evaluation of the toxicity (to a specific microbe) and its implication on the biodegradation of aqueous samples from laboratory research bio-reactors (liquid or soil), pilot-plant biological treatment systems, full-scale biological treatment systems, and land application processes (see Notes 1 and 2).

NOTE 1—If the biologically treated material is to be discharged in such a manner as to potentially impact surface waters and ground water, or both, then the user must consult appropriate regulatory guidance documents to determine the proper test species for evaluating potential environmental impact (**4**). Correlations between data concerning reduction in toxicity produced by this test method and by procedures for acute or short-term chronic toxicity tests, or both, utilizing invertebrates and fish (see Guides E 729 and E 1192), should be established, wherever possible.

NOTE 2—Color (especially red and brown), turbidity, and suspended solids interfere with this test method by absorbing or reflecting light. In these situations data are corrected for these effects by use of an absorbance correction procedure included in this test method (see 5.3, 6.1, and 6.2).[5]

1.3 The results of this test method are reported in terms of an inhibitory concentration (IC), which is the calculated concentration of sample required to produce a specific quantitative and qualitative inhibition. The inhibition measured is the quantitative reduction in light output of luminescent marine bacteria (that is, IC20 represents the calculated concentration of sample that would produce a 20 % reduction in the light output of exposed bacteria over a specified time).

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[6]

D 1193 Specification for Reagent Water[6]

D 3370 Practices for Sampling Water[6]

E 729 Guide for Conducting Acute Toxicity Tests with Fishes, Macroinvertebrates, and Amphibians[7]

E 943 Terminology Relating to Biological Effects and Environmental Fate[7]

E 1192 Guide for Conducting Acute Toxicity Tests on Aqueous Effluents with Fishes, Macroinvertebrates, and Amphibians[7]

2.2 *Other Standards:*

Standard Methods For The Examination Of Water And Wastewater, 18th Edition[8]

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[1] This test method is under the jurisdiction of ASTM Committee D-34 on Waste Management and is the direct responsibility of Subcommittee D34.09 on Treatment.

Current edition approved Feb. 15, 1995. Published April 1995.

[2] The boldface numbers in parentheses refer to the list of references at the end of this standard.

[3] Toxicity measured as toxic inhibition of bacterial light output.

[4] Microbics Corp. is currently the only known supplier of the reagents (test organism *Photobacterium phosphoreum* strain NRRL B-11177) specific to this test method. There are two known manufacturers of analyzers that can be used to measure bioluminescence under temperature control: Microbics Corp., 2232 Rutherford Road, Carlsbad, CA 92008 (Microtox Model 500 and Model 2055 Analyzers), and Pharmacia LKB 9319 Gaither Road, Gaithersburg, MD 20877 (LKB Wallac Model 1250 and Model 1251 Luminometers). Other instruments would be considered when they become available. Please notify ASTM Subcommittee D34.09 if you are aware of any additional systems or instruments capable of performing this testing.

[5] At present (1993) use of the color correction scheme described in this procedure is known to be effective only with the Microbics Corporation's toxicity analyzers, due to the fact that the correction mathematics involve the detailed geometry of both the ACC and the light meter. Please notify ASTM Subcommittee D34.09 if you are aware of any other source of equipment capable of providing color or turbidity correction, or both, for the *P. phosphoreum test*. Data validating the absorbance correction procedure are available from Microbics Corp.

[6] *Annual Book of ASTM Standards*, Vol 11.01.

[7] *Annual Book of ASTM Standards*, Vol 11.05.

[8] Available from American Public Health Association, 1015 15th Street, NW, Washington, DC 20005.

3. Terminology

3.1 *Definitions*—The IC20 is defined in terms of a modification of the definition of IC50 as it appears in Terminology E 943. The terms turbidity and volatile matter are defined in accordance with Terminology D 1129. These terms are as follows:

3.1.1 *color*—that is, the presence of dissolved matter that absorbs the light emitted by *P. phosphoreum* (that is, wavelength of 490 ± 100 nm).

3.1.2 *IC20*—a statistically or graphically estimated concentration of test material that, under specified conditions, is expected to cause a 20 % inhibition of a biological process (such as growth, reproduction, or bioluminescence) for which the data are not dichotomous.

3.1.3 *turbidity*—reduction of transparency of a sample due to the presence of particulate matter.

3.1.4 *volatile matter*—that matter that is changed under conditions of the test to the gaseous state.

4. Summary of Test Method

4.1 This test method covers the determination of acute toxicity of aqueous samples to luminescent marine bacteria, *P. phosphoreum*.

4.2 Wastewater samples are osmotically adjusted to the appropriate salinity for the test species *P. phosphoreum*. A sodium chloride (NaCl) concentration of 2 % has been found optimal for this test organism for freshwater tests, or about 3.4 % NaCl for seawater samples. This provides the necessary osmotic protection for the bacteria, which are of marine origin.

4.3 Samples should not be pH adjusted unless the user is not concerned about toxic effects related directly to pH. Altering the sample pH will usually alter the solubility of both organic and inorganic constituents of the sample. Altering the pH can also cause chemical reactions that will change the integrity of the sample, and greatly alter the exhibited toxicity of the sample. If sample pH is considered secondary to organism response, then the optimal pH for the bacterium *Photobacterium phosphoreum* is 6.7.

4.4 Comparison of inhibitory concentrations (IC20s) for untreated wastewater (or extracts of untreated soils) versus those for biologically treated wastewater (or extracts of treated soils), calculated from measured decreases in light output of exposed bacteria, allows for an assessment of the reduction in toxicity to the marine bacterium *P. phosphoreum* (see 1.1, 1.2, and Note 1).

4.5 Samples that are highly colored, or contain solids that can not be removed without seriously compromising sample integrity, can be analyzed using an absorbance correction procedure. This procedure determines the amount of light absorbed by the wastewater at a concentration near the nominal IC20 versus the baseline light output established by measuring the light absorbed by the clear diluent.

5. Significance and Use

5.1 This test method provides a rapid means of determining the acute toxicity of an aqueous waste, or waste extract, prior to and following biological treatment, and contributes to assessing the potential biodegradability of the waste (see 1.1, 1.2, and Note 1). The change in toxicity to the marine bacterium *P. phosphoreum* with respect to time may serve as an indication of the biodegradation potential. Sample analyses are usually obtained in 45 to 60 min, with as little as 5 mL of sample required (5).

5.2 Samples with high suspended solids concentrati may test nontoxic to the bacteria, while still exhibiting significant toxicity to freshwater organisms, due to those suspended solids.

5.3 The absorbance correction procedure included in this test method allows for the analysis of highly colored light-absorbing samples, by providing a means for mathematically adjusting the light output readings to account for light lost due to absorption.[5]

6. Interferences

6.1 Some test samples that are highly colored (especially red and brown) interfere with this test method, but the absorbance correction procedure can be used to correct for this interference.[5]

6.2 Turbidity due to suspended solids interferes with this test method. The absorbance correction procedure can be used to correct for this interference and is preferable to other alternatives. Pressure filtration, or centrifuging and decanting, will also remove this interference. Some toxics may be lost through adsorption and volatilization during filtration or centrifugation, thus impacting the exhibited toxicity.[5]

7. Apparatus

7.1 *Fixed or Adjustable Volume Pipetter*, 10 µL, with disposable tips.

7.2 *Variable Volume Pipetter*, 10 to 1000 µL, with dispo able tips.

7.3 *Variable Volume Pipetter*, 1 to 5 mL, with dispos. tips.

7.4 *Timer or Stopwatch*.

7.5 *Glass Cuvettes*, 11.75 mm OD, 10.5 mm ID by 50 mm height, 4-mL volume.

7.6 *Absorbance Correction Cuvettes (ACC)*—Optional item, but required to analyze highly colored samples or those containing suspended particulates.[5]

7.7 *Variable Voltage Chart Recorder (optional)*—Useful when using some types of light meters.

7.8 *Computer (optional)*—Useful with some light meters, for which software is also available, to facilitate data capture and reduction.

7.9 *Light Meter*, for cuvettes listed in 7.5.[4,5]

7.10 *Temperature Control Devices*, (temperature-controlled room, water bath, refrigerators, or other device—One capable of maintaining 5.5 ± 1°C and one capable of maintaining 15 ± 0.5°C).

8. Reagents and Materials

8.1 *Test Reagents:*

8.1.1 For purposes of this test method, test reagents are defined as the reagents actually used in performance of the test method. The necessary requirement with regard to qualification of test reagents is that this test method provide acceptable results when reference toxicants are tested using the test reagents.

8.1.2 *Microbial Reagent*—Freeze-dried *Photobac phosphoreum*. This is the only test reagent that is cur (1993) available from only one source.[4] While other accept-

able means of preservation may become available in the future, freeze-dried *P. phosphoreum* is specified in this test method because a large number of users concur in the opinion that the strain is well standardized by this method of preservation, and that the same strain does not provide comparable response to reference toxicants when preserved by other methods, or when freshly cultured and harvested at the user's laboratory, as described by Anthony A. Bulich et al (1). Another consideration is that a large body of published results, for which freeze-dried *P. phosphoreum* was used, has accumulated since about 1980, increasing the relevance of results obtained with this test method (1, 2, 3, 5, 6).

8.1.3 *Reconstitution Solution*—Nontoxic water.

8.1.4 *Diluent*—Nontoxic 2 % sodium chloride (NaCl), or 3.4 % NaCl, reconstituted seawater or sea water (depending upon the type of sample and purpose of the test). The *P. phosphoreum* test has been performed at osmotic pressures equivalent to 1 to 6 % NaCl, but has long been standardized at 2 % for freshwater samples. The major requirement is that the osmotic pressure be held constant within each test, to minimize transient variations in luminescence due to variations in osmotic pressure. The higher salinity (and osmotic pressure) of marine samples dictate the use of a diluent other than 2 % NaCl. Both reconstituted seawater and clean seawater have been used as diluent. A procedure for preparing reconstituted seawater is given in Table 8010:III of Standard Methods For The Examination of Water And Wastewater. Actual seawater has also been collected at remote sites and used as diluent for testing aqueous samples of marine origin. The most important requirement is that the diluent must be qualified for use with this test method (see 8.1.1).

8.2 *Reagent Chemicals*—Reagent grade chemicals are recommended for use in preparation of test reagents and reference toxicants. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.[9] Other grades may be used, but there will be more risk that the resulting test reagents will fail to qualify (see 8.1.1).

8.2.1 *Sodium Chloride (NaCl)*—Used in preparation of diluent, and for adjusting the osmotic pressure of samples to that of the chosen diluent.

8.2.2 *Phenol, or Other Common Organic Toxicant*—Used as a reference toxicant.

8.2.3 *Zinc Sulfate Heptahydrate, or Other Common Inorganic Toxicant*—Used as reference toxicant.

8.3 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specifications D 1193, Reagent Water, Type I or II, Subtype A. Test reagents prepared from reagent water are to be qualified for use with this test method (see 8.1.1).

8.4 When this test method is used in conjunction with other tests employing higher organisms, appropriate dilution water for bulk samples should meet the acceptability criteria established in Section 8 of Guide E 729. In addition, all such dilution water used for comparative testing with this test method and invertebrates and fish, is to be assayed on *P. phosphoreum* (minimally once per month).

9. Hazards

9.1 The handling of wastewaters entails potential hazards due to exposure to chemical and biological contaminants. Appropriate safety measures, such as the wearing of protective clothing (gloves, apron, face shield, respirator, etc.) and maintaining proper hygiene, are utilized to minimize the chance of exposure. This test method is to be performed in a well-ventilated area.

9.2 Appropriate, environmentally safe procedures prescribed by regulatory agencies are utilized in the disposal of used waste samples.

9.3 Due to the presence of aqueous samples and electrical instrumentation in close proximity, care must be taken to prevent electrical shock.

10. Technical Precautions

10.1 Osmotic adjustment of freshwater test samples, to 2 % sodium chloride concentration, is required due to the use of a marine bacterium as a test organism. Osmotic adjustment may make some components of a wastewater less soluble, reducing concentrations in solution and altering exhibited toxic inhibition.

10.2 Samples containing highly volatile components are to be handled as little as possible to reduce losses due to stripping. Mixing procedures (see 13.8.4) are modified by performing only one pipet mixing per sample dilution versus the usual five pipet mixings. Volatile samples, which can be analyzed by UV spectrophotometry, allow the investigator to measure the average sample concentration of volatiles over the actual test period.

10.3 The addition of any preservative or other chemical agent, including acid or base to alter pH, will in all likelihood impact the exhibited toxicity of the sample. These practices should be avoided in most cases, unless the user is specifically testing to determine the effects of these sample modifications.

10.4 The use of a reference toxicant, such as phenol or zinc sulphate, is recommended for validation of data produced with different lots of test reagents (that is, bacteria, reconstitution solution, and diluent) or for individual lots used over an extended period of time. A good practice is to perform a reference toxicant analysis with each new lot of bacterial reagent received and new lots of test reagents prepared (or purchased). Under normal conditions, with reagent in good condition, tests on phenol produce an IC50 (5 min) between 13 and 26 mg phenol/L, and tests of zinc sulfate heptahydrate produce an IC50 (15 min) between 5 and 12 mg $ZnSO_4 \cdot 7H_2O$/L (or, 1.1 to 2.7 mg Zn/L). The corresponding nominal ranges are IC20 (5 min) = 3 to 6 mg phenol/L and about 1.5 to 4.5 mg $ZnSO_4 \cdot 7H_2O$/L (or, 0.34 to 1.02 mg Zn/L).

10.5 In order to verify that changes in observed toxicity are due to treatment, it is essential to have control samples for biodegradation test systems. Typical controls would be sterilized (autoclaved) waste samples. These samples undergo

[9] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

toxicity assessment for comparison with the treated samples; that is, they undergo the same physical manipulations and testing as the inoculated or nutrient-enhanced treatment systems, but all microbial action has been terminated by sterilization at the outset of the test series. Autoclaving of samples for use as control samples requires special consideration and sample handling techniques. The following procedure is recommended:

10.5.1 Completely fill new borosilicate jars with sample, and seal them with autoclavable caps having TFE-fluorocarbon liners, to minimize loss of volatile toxicants during autoclaving.

10.5.2 Soil and sediment samples are to be moist, for optimal effectiveness of autoclaving.

10.5.3 Bring the autoclave to 121°C and hold the sample jars there for one to two hours, then turn off the heat and allow the autoclave to cool very slowly, to avoid large transient positive pressure inside the jars, which might cause them to fracture.

10.5.4 It is recommended that the autoclaving be repeated 24 h later as a precaution against survival of spores. In addition, or alternatively, commercially available spore strips or preparations may be added to a jar of soil and included in the autoclave load as a direct means of validating the effectiveness of the autoclave cycle.

11. Sampling

11.1 Collect aqueous samples in accordance with Practice D 3370. Soil and other solid material samples, for aqueous extraction, should be sampled in such a way as to reduce the risk of loss of volatile components.

11.2 All sample containers (vials or bottles) should be made of borosilicate glass that has been thoroughly cleaned using a nontoxic soap wash, HCl wash, and water rinse (twice). All sample containers should be sealed with TFE-fluorocarbon-lined caps.

11.3 Prepare all dilutions required for a single toxicity evaluation from the same treated or untreated wastewater sample. Portions of the sample shall be stored, until needed, at a temperature of 2 to 4°C in completely filled, tightly stoppered borosilicate-type glass containers. TFE-fluorocarbon-lined caps are used to seal collection bottles to minimize adsorption or sample contamination.

11.4 Uniformly disperse (by mild agitation), any undissolved material present in a wastewater sample, before withdrawing a measured portion for osmotic adjustment and subsequent analysis. Undissolved material, which will interfere with light transmission during analysis, should be adjusted for or removed as described in Section 6. Avoid violent agitation and unnecessary exposure of the sample to the atmosphere.

12. Calibration and Standardization[10]

12.1 Use the procedure specified by the manufacturer of whatever light-measuring instrument is being utilized. The procedure should include a mechanism for zeroing the instrument for no light production and a procedure for setting the output range.

12.2 If a chart recorder is being used, it should be calibrated against either the digital reading of the photometer or the voltage output of the photometer to the recorder.

13. Procedure[11]

13.1 Samples taken from a treatment process are collected using an ASTM acceptable sampling procedure (see Section 11).

13.2 For aqueous samples, visually evaluate the sample for suspended particulates and color. Both of these factors can interfere with measured light output readings. If either of these conditions is present use one of the methods described in 6.2 to remove or account for the interference.

13.3 For solid phase samples prepare the test sample as follows:

13.3.1 Wet sediment should be centrifuged to separate the pore water. Centrifuge 50 to 100 g of sediment at 2000 to 4000 g, for 10 to 20 min at 4°C. Decant the pore water and use the resulting pellet of solids as if it were a soil sample.

13.3.2 Homogenize 10 to 50 g of representative soil sample by hand mixing with a spatula for 10 min.

13.3.3 Weigh a representative 3 to 5-g portion of the homogenized sample to the nearest 0.01 g, then air dry at 20 to 25°C for 16 h. After drying, reweigh the dried sample.

13.3.4 Take a 2-g sample from the homogenized soil or sediment and add 20 mL of the appropriate diluent.

13.3.5 Mix the soil/diluent mixture for 16 h using an orbital shaker set at 200 rpm.

13.3.6 Centrifuge the sample at 2000 to 4000 g, for 10 to 20 min at 4°C.

13.3.7 Decant 10 to 15 mL of the aqueous phase for in the analysis of toxic inhibition.

13.4 Positive pressure filtration (through a prerinsed, glass-fiber filter) can be used to remove suspended solids, while minimizing loss of volatile organics. Rinsing the filter with nontoxic water, prior to sample filtration, reduces organic leaching from the filter. Note the potential sample alterations mentioned in 6.2.

13.5 Take 5 mL of the aqueous sample from 13.2 to 13.3 and measure the pH, dissolved oxygen (DO), conductivity, and salinity.

13.6 Adjust the sample salinity to either 2 % NaCl or 3.4 % NaCl (for samples of marine origin) by adding sodium chloride to 10 mL of sample. Adjust the pH and DO only if those factors are not concerns in the process under investigation. Be aware of the potential changes in overall sample chemistry as noted in 6.2.

13.7 If the user is adjusting the sample pH to determine the effect thereof, the acid or base, or both, used for the adjustment should be noted, and the quantity required in the adjustment should be recorded. Sample dilution and chemical species changes must be taken into account if pH adjustment is necessary.

13.8 Samples of unknown toxicity are screened, prior to definitive testing, using the following range finding procedure:

[10] Calibration and standardization procedures will vary depending on the instrument being used to measure the bacterial light output.

[11] This is a generic procedure that will require modification dependin particular instrument being used to measure microbial light output.

13.8.1 Prepare a cuvette of bacterial reagent (*Photobacterium phosphoreum*) by adding 1 mL of reconstitution solution at 5.5 ± 0.5°C to a bottle of lyophilized luminescent bacteria and transferring the reconstituted bacteria to a cuvette maintained at 5.5 ± 0.5°C.

13.8.2 Prepare 10 test cuvettes, by adding 0.5 mL of diluent and 10 µL of reconstituted bacteria. Maintain the test cuvettes at 15 ± 0.5°C.

13.8.3 Without waiting the normal 15-min temperature acclimation period, place one of the test cuvettes of bacteria into the photometer, and measure the light output for 10 to 20 s. If the instrument used allows the output value to be adjusted, adjust the output to read 90 units. Otherwise record the output value as it is.

13.8.4 Add 10 µL of the unknown sample to the cuvette being measured. Mix the contents with a 250-µL pipet by aspirating and dispensing its full volume five times, or as an alternative, mix the contents by briskly flicking the cuvette with a finger (cuvette flicking method).

13.8.5 Measure the light output of the exposed bacteria for 10 to 20 s.

13.8.6 If the loss of light output is greater than 20 % within several minutes, dilute the sample ten-fold, and repeat 13.8.3 through 13.8.5 with one of the unused cuvettes prepared in 13.8.2 using the diluted sample. Repeat this procedure until a sample dilution produces a loss of light of less than 20 % during the first few minutes after sample addition. Observe the bacterial response for 5 min, and then estimate graphically the 5-min toxic response. This information gives the tester a good indication of the sample concentration range which will produce a statistically sound IC20, if the sample is toxic to that extent.

13.9 The procedure for running a toxicity test using *Photobacterium phosphoreum* is as follows:

13.9.1 Place 20 clean cuvettes in a temperature-controlled area at 15 ± 0.5°C, and one additional clean cuvette at 5.5 ± 1°C. Set the cuvettes in two rows of ten, and use a labeled test tube rack or other device to identify the cuvettes as A1–A10 and B1–B10.

13.9.2 Add 1 mL of reconstitution solution (nontoxic water) to the cuvette being held at 5.5°C.

13.9.3 Add the appropriate amount of diluent to Cuvettes A1–A9 (being maintained at 15°C) to obtain the desired concentrations after serial dilution (for example, for a 2:1 serial dilution, 1.5 mL of diluent is added to A1–A9). Cuvette A10 is left empty for the primary sample concentration.

13.9.4 Add 0.5 mL of diluent to Cuvettes B1–B10 (which serve as the test cuvettes).

13.9.5 Add 1.5 mL of the osmotically adjusted primary sample concentration (diluted or not) to Cuvette A10, and an appropriate amount to A9. Mix the diluted contents of A9 by aspirating and dispensing, by pipette, 500 µL of sample five times; or by briskly flicking the cuvette with a finger. Complete the serial dilution of the test sample by transferring an appropriate volume of A9 to A8 and A8 to A7 . . . A3 to A2, using one of the mixing methods previously described. In the example of a 2:1 serial dilution scheme, the dilution would be performed as follows: 1.5 mL of 100 % sample (note that the actual concentration is 91 to 100 % depending on the need for and method of salinity adjustment) added to Cuvettes A10 and A9 and mix A9, 1.5 mL of A9 to A8 and mix, 1.5 mL of A8 to A7 and mix, 1.5 mL of A7 to A6 and mix, 1.5 mL of A6 to A5 and mix, 1.5 mL of A5 to A4 and mix, 1.5 mL of A4 to A3 and mix, 1.5 mL of A3 to A2 and mix, and remove and discard 1.5 mL of A2.

13.9.6 Allow 5 to 10 min for samples to reach thermal equilibrium, then check to verify that the temperature of the reconstitution solution is 5.5 ± 1°C and that the test cuvettes have reached 15 ± 0.5°C.

13.9.7 While the prepared test cuvettes are temperature equilibrating, remove a vial of lyophilized bacteria from refrigeration and rapidly add the precooled 1-mL volume of reconstitution solution into the vial, swirl the vial to mix, and return the reconstituted bacteria to the cuvette which is replaced at a temperature of 5.5 ± 1°C. Mix the reconstituted bacteria by aspirating and dispensing 0.5 mL of solution, by pipet, 20 times. The reagent dilution is started within 5 min of bacterial reconstitution, in order to maintain maximum sensitivity.

13.9.8 Transfer 10 µL of reconstituted bacterial reagent to each Cuvette B1 through B10. Wipe the pipet tip of excess reagent before each transfer. Mix the contents of each cuvette using a 250-µL pipet to aspirate and dispense the solution five times, or by the cuvette flicking method.

13.9.9 Allow the bacteria in the test cuvettes to achieve a stable light output level by remaining undisturbed at 15°C for 15 min. This allows the bacteria to recover from the shocks of reconstitution, shift in temperature, and dilution of nutrients.

13.9.10 Cycle the cuvettes through the photometer, and adjust the light output levels to read between 80 and 100 units if possible (some units will automatically perform this task with the initial I_0 light readings). Cuvette output reading is performed in the order of B1, B2, B3 . . . B10.

13.9.11 Take the initial (I_0) readings by cycling the cuvettes, one cuvette every 25 s, and recording the light output of each cuvette (B1 through B10) for 5 s. Record the time with each reading so that the 5, 15, and 30-min exposure periods are accurately timed.

13.9.12 Start the addition of the test samples (Cuvettes A1–A10) to the test cuvettes (Cuvettes B1–B10) immediately following the reading of the light output of Cuvette B10, the last cuvette in the cycle. The addition starts with 0.5 mL of A1 (the nontoxic blank) added to Cuvette B1, mixing the sample by the pipet technique or flicking technique. The sample additions proceed from low concentration to high concentration, adding 0.5 mL of A2 to B2 and continuing up to A10 to B10, allowing 25 s between each sample addition. The time of each addition is recorded so that the light output of each challenged test cuvette can be measured 5, 15, and 30 min after the sample addition.

13.9.13 The test cuvettes (B1 through B10) are cycled through the photometer 5 min after the sample additions and the light output of the bacteria is recorded for each cuvette. This procedure is repeated at 15 and 30 min to observe any time-dependent increases in toxic inhibition (that is, toxicity due to metals).

13.9.14 The recorded light outputs are used to calculate IC values by plotting or mathematical determination.

13.10 The procedure used to correct for absorbance in

highly colored aqueous samples, as described in 6.1, is as follows:

13.10.1 Pipet 1.5 mL of diluent into the outer chamber of a clean absorbance correction cuvette (ACC) and place it in the photometer.

13.10.2 Pipet 1.0 mL of diluent into a standard cuvette (A1) and place it at 15°C.

13.10.3 Pipet 2.0 mL of sample of chosen concentration C_c (the concentration closest to the nominal ICxx) into each of two standard cuvettes (A2 and A3), and place them at 15°C.

13.10.4 Allow 10 min for the solutions to reach thermal equilibrium.

13.10.5 Pipet 50 µL of reconstituted bacterial reagent into Cuvette A1. Mix five times with a 500-µL pipet or flick the cuvette briskly.

13.10.6 Remove the ACC from the photometer long enough to transfer a sufficient amount of bacterial solution from cuvette A1 into the inner chamber of the ACC to get a volume level equal to that of the diluent level in the outer chamber.

13.10.7 Return the ACC to the photometer. Adjust the light output reading of the ACC to 90 units (if possible), then record the light output for 10 to 20 min until a stable baseline or steady drift baseline is established.

13.10.8 Using a clean aspirator, remove the diluent from the outer chamber of the ACC while the ACC remains in the photometer.

13.10.9 Remove as much of the diluent as possible with an aspirator. Transfer 1.5 mL of test sample from Cuvette A3 into the outer chamber of the ACC.

13.10.10 Record the light output for 10 min or more. The light levels recorded for the sixth through tenth minute will be used in data reduction.

14. Calculation

14.1 The following equations are used to determine 20 % inhibitory concentrations (IC20s) from light output readings produced using the methods described in Section 13:

14.1.1 Calculate the blank ratios (which will be used to normalize the Γ responses calculated in 14.1.2) for 5, 15, and 30 min, using the following equations:

$$R(t) = I(t)b/I(0)b \quad (1)$$

where:

$R(t)$ = blank ratio for time t,
$I(0)b$ = initial light reading for the blank cuvette (zero time, just before transferring toxicants), and
$I(t)b$ = final light reading for the blank cuvette (t min after transferring toxicants).

14.1.2 Calculate the 5, 15, and 30-min gamma responses, $\Gamma(t)$, for each of the eight test cuvettes, normalized for reagent pipetting errors and normal drift of luminescence with time, using the following equation:

$$\Gamma(t) = \text{Light Lost/Light Remaining} = [R(t)I(0) - I(t)]/I(t) = [R(t)I(0)/I(t)] - 1 \quad (2)$$

where:

$I(0)$ = initial light reading for any given test cuvette at zero time, just before challenging the organisms,
$I(t)$ = light reading for the corresponding test cuvette at time (t),
$R(t)$ = blank ratio for time (t) as defined in 14.1.1, and
$\Gamma(t)$ = Γ effect calculated for each exposure time (t); that is, at 5, 15, and 30 min.

It should be noted that $\ln \Gamma(t) = \ln (D/(1 - D))$, (see 14.1.4) is identical to Berkson's logit P/Q = logit $P/(1 - P)$ (7). The method described in this test method is, therefore, a [illegible] analysis.

14.1.3 Use linear regression[12] of $\ln \Gamma(t)$ on $\ln C$, with $\ln \Gamma(t)$ as the dependent variable, to obtain the $\ln$-$\ln$ regresssion equation,

$$\ln \Gamma(t) = b(\ln C) + \ln a \quad (3)$$

then solve this equation for $\ln C$ to obtain the estimating equation,

$$\ln C = 1/b[\ln \Gamma(t)] - 1/b[\ln a] \quad (4)$$

where:

C = concentration of sample,
$\ln a$ = intercept of the $\ln$-$\ln$ regression line with the ordinate $\ln C = 0$, which will be a constant number, but different for each exposure time (5, 15, and 30 min),
b = slope of the $\ln$-$\ln$ regression line, which will also be a constant number, but different for each exposure time (5, 15, and 30 min), and
$\Gamma(t)$ = toxic responses for corresponding concentrations, for each exposure time (5, 15, and 30 min).

14.1.4 In order to find IC20s, solve the above estimating equation for C when $\Gamma(t) = 0.25$, corresponding to 20 % reduction of light output (see 1.3), for 5, 15, and 30-min data. These concentrations (Cs) are the IC20s for 5, 15, and 30 min, respectively. The relationship between Γ and percent reduction of light output (% D) is:

$$\Gamma = \% D/(100\ \% - \% D) \quad \text{or} \quad \% D = 100\ \% \times \Gamma/(1 + \Gamma)$$

It may be easily seen that IC20 (that is, % D = 20 %) corresponds to Γ = 20 %/(100 % − 20 %) = 20 %/80 % = 0.25. The estimating equation must be satisfied by these corresponding values of C and Γ. Substituting these specific values into the estimating equation results in the following:

$$\ln(\text{IC20}) = 1/b \ln(0.25) + 1/b \ln a = 1/b(-1.3863) + 1/b \ln a \quad (6)$$

Once the right side of the equation is reduced to a single number, say N, IC20 is the antiln of N. The antiln (N) is simply e^N, where e = 2.7182818...; that is, the base of the natural logarithms.

14.2 The following equations use data obtained in 13.9 and 13.10 to determine corrected light loss when a sample is highly colored and light absorbing or highly turbid, or both.[13]

14.2.1 Considerable labor can be saved when it is possible to calculate the values of A_c for all sample concentrations (C)

[12] Standard regression analysis should be used, with care given to make certain that the quality of the data warrants the conclusions drawn. The estimating equation reserves the variables compared to the conventional dose response curve to facilitate solution of the equation for C for a specified Γ. This estimating equation is simply the regression equation rearranged to make $\ln C$ a function of $\Gamma(t)$.

[13] In samples where absorbance due to concentration does not behave in accordance with Beer's Law or the samples causing significant Γ responses (0.02 or larger) are turbid, or both, it is necessary to directly measure the absorbance in the ACC for each sample concentration toxicity tested that gave a significant response, by this test method.

based upon measurement of only one concentration (C_c) in the ACC, using the equation given in 14.2.2. When the sample is such that this approach is not applicable,[13] determine A_c for each concentration that yielded a significant Γ (that is Γ between 0.02 and 100) by direct measurement with each such concentration in the ACC. The equation in 14.2.2 must then be solved for each set of ACC data, I_0/I_F, with $C/C_C = 1$ in each case. It should be noted that A_C is considered to be zero for concentrations having Γ responses of 0.02 or less.

14.2.2 When applicable (see 14.2.1),[13] calculate absorbance due to color (A_C) for the ACC for all concentrations (C) of sample tested in the toxicity cuvettes which gave significant Γ responses, using the following equation:

$$A_C = (C/C_C)\,[3.1\ ln(I_0/I_F)] \quad (7)$$

where:

A_C = calculated absorbance expected if concentration C were to be measured in the ACC, for each concentration tested in the toxicity test which gave a significant Γ.[13] (Alternatively, each A_C is calculated using I_0 and I_F results from direction measurements in the ACC.)

I_0 = initial light level, measured in the ACC (for diluent),

I_F = final light level, measured in the ACC (for C_C),

C_C = chosen concentration measured in the ACC (in 13.10),

C = each sample concentration tested in the toxicity cuvette, which gave a significant Γ (that is, 0.02 or larger), and

3.1 = composite factor for the ACC which corrects for geometrical differences between it and the standard test cuvette.[5]

14.2.3 Calculate the transmittance (T_C) of the toxicity cuvette for each sample concentration tested that gave a significant Γ, using the following formula:

$$T_C = (1 - e^{-A_C})/A_C \quad (8)$$

where:

T_C = unity (that is, 1.00) for concentrations having insignificant Γ responses, corresponding to A_C = zero.

14.2.4 Calculate the corrected gamma responses ($\Gamma_C(t)$) for 5, 15, and 30-min data for each concentration tested, using the following equation:

$$\Gamma_C(t) = T_C(1 + \Gamma(t)) - 1 \quad (9)$$

where:

$\Gamma(t)$ = Γ response observed for each concentration (C) in the test, at each test time (5, 15, and 30 min), and

$\Gamma_C(t)$ = color-corrected toxic response for each test time (5, 15, and 30 min).

14.2.5 Determine the color-corrected IC20 ($IC20_C$) for 5, 15, and 30-min data as described in 14.1.3, using the $\Gamma_C(t)$ values determined in 14.2.3 for each exposure time.

14.3 The following equation is used to correct the IC20s determined for soil and sediment samples in either 14.1.3 or 14.2.4 (if color/turbidity corrected) to dry-weight basis. The wet and dry weights of a representative soil/sediment sample were determined in 13.3.3.

$$IC20(t)_{DRY} = IC20(t)_{WET} \times (\text{dry weight})/(\text{wet weight}) \quad (10)$$

15. Data Interpretation

15.1 *Choice of Exposure Time*—the exposure time of choice is, in general, that which provides the greatest sensitivity. However, the IC20 having the smallest 95 % confidence interval may be preferred in cases in which the confidence interval varies appreciably with time of exposure. Consistency of choice between control samples and treated samples is of major importance for comparative studies. Finally, it should be noted that organics generally cause fast (5 to 10 min) response, while some metals continue to affect the luminescence of *P. phosphoreum* beyond 30 min. The changes in relative IC20 for the various exposure times as treatment progresses may, therefore, provide some additional information with regard to progress of treatment or further treatability, or both.

15.2 Compare the IC20 values (calculated concentration at Γ = 0.25) for the treated and untreated sample. Any toxicity reduction of 20 % or more, compared to the untreated system control sample or the raw starting material, is considered to be significant and a potential indication of biodegradability (see 1.1, 1.2, and Note 1).

15.3 Care must be taken to account for toxicity reduction that is not due to biodegradation (that is, adsorption, volatilization, and sample preparation errors). Control samples not exposed to biodegradation are essential as part of the data validation process (see 10.5).

16. Report

16.1 The record of the test and published reports of the results of the test should contain the following information:

16.1.1 Name of test, investigator, and laboratory; and the date the test was conducted;

16.1.2 Detailed description of the test sample including its source (detail biodegradation system used), composition (identity and concentration of major ingredients and major impurities), known physical and chemical properties, and identity and concentration of any solvents or other additives used;

16.1.3 The source of the dilution water, its chemical characteristics, and a description of any pretreatment;

16.1.4 Detailed information about the reagents used, including lot number, date received, reference toxicant data for the reagent lot, and any noted abnormalities;

16.1.5 A detailed description of the toxic inhibition analysis performed on the sample, including the test date, exposure times, test temperature, pH of sample before and after testing, all parametric data about sample, observations during test, and data reduction results (see 1.1, 1.2, and Note 1).

17. Precision and Bias

17.1 Quality data are produced when test procedures are followed as stated. The greatest source of error will be due to operator error. Errors are most likely to occur during sample preparation, salinity adjustment, filtration (if required), sample dilution, reagent dilutions, sample transfer and mixing steps, and data interpretation and resulting calculations. Use of the proper equipment and development of the appropriate skills required for using the test equipment are necessities in producing quality data.

17.2 Precision of the data may be improved by running a split sample duplicate analysis, repeating the procedures listed in 13.9 with the duplicate sample. Duplicate analyses can be performed simultaneously, or the duplicate sample

can be analyzed separately. The duplicate sample must be protected from incurring further biodegradation or other physical/chemical changes. The results of the duplicate analyses are compared for any irregularities (obvious differences) in response versus exposure concentration. If such irregularities are noted, the sample should be retested if at all possible.

17.3 The raw data generated by the test procedures will determine whether an IC20 can be calculated with reasonable accuracy.

17.4 The determination of 95 % confidence intervals, using an acceptable procedure, will assist the investigator in determining the quality of generated IC20s (computer programs are available to perform these calculations).

17.5 An interlaboratory comparison study (5) was conducted on the toxic inhibition procedure described in this test method. The study involved 18 laboratories in fo round robins, during which a total of six blind samples (fi toxic and one nontoxic) were analyzed. The coefficient variation (CV) ranged from 14.29 to 18.57 for the pooled data set, while the overall CV (regardless of sample) was calculated to be approximately 17.8 %.

17.6 The lack of an internal standard for this test method makes it impossible to determine the bias.

18. Keywords

18.1 bioluminescence; bioremediation; contaminated soil; contaminated water; detoxification; marine bacterium; toxicity

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8050 B. Bacterial Bioluminescence Test

1. General Discussion

Principle: Certain strains of luminescent bacteria divert up to 10% of their respiratory energy into a specific metabolic pathway that converts chemical energy into visible light. This pathway is intrinsically tied to respiration; any change in cellular respiration or disruption of cell structures results in a change in respiration with a concurrent change in the rate of bioluminescence.

In the BBT, the light output of test organisms is measured under standard conditions, the organisms are exposed to the test sample for a specified time, and their light output is measured again. Reduction in light output between the first and second measurements is essentially proportional to the toxicity of the test sample.

2. Test Procedures

Several milliliters of sample are required. Standard organisms and equipment are available commercially.* When serial dilutions of the sample are tested, suitable controls are used, and appropriate data reduction methods are applied, a dose/response curve is produced, which allows identification of an inhibition concentration (i.e., 20%, 50%) with good precision.

Standardization is achieved by providing the test cells in lyophilized form, designed to capture and maintain their optimum physical state. This method of cell preservation assures consistent sensitivity and stability of the test cells. Data reported in the literature were produced in tests using standard, commercially available, freeze-dried strains of the bacterium *Photobacterium phosphoreum*,[1,2] allowing meaningful comparison of results from tests from different laboratories.[3-5]

* Microtox®, Microbics Corp., Carlsbad, Calif., or equivalent.

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8110 ALGAE

Algae are unicellular to multicellular plants that occur in fresh water, marine water, and damp terrestrial environments. All algae possess chlorophyll, the green pigment essential for photosynthesis. Algae may contain additional pigments such as fucoxanthin (brown) or phycoerythrin (red), which can mask the green color of chlorophyll. The life cycle of algae may be simple, involving cell division, or complex, involving alternation of generations. Algae are primary producers of organic matter upon which animals depend either directly or indirectly through the food chain.

Test procedures using algae are valuable for determining the primary productivity of a water and for testing the toxicity of chemicals present in a water. Section 8111, Biostimulation (algal productivity), measures the response of a cultured species of algae to the nutritional condition of the water.

Section 8112, Phytoplankton, measures the response of an algal species to materials that interfere with its normal metabolism.

Together, the tests allow the assessment of the effects of point or nonpoint discharges in fresh and marine waters.

8111 BIOSTIMULATION (ALGAL PRODUCTIVITY)*

8111 A. General Principles

The algal assays consist of three steps: (*a*) selection and measurement of appropriate factors or conditions during the assay (for example, biomass indicators such as total cell carbon); (*b*) presentation and statistical evaluation of measurements; and (*c*) interpretation of results.

Interpretation of results involves assessment of receiving water to determine its nutritional status and its sensitivity to change, potential effects of materials on algal growth in receiving waters, effects of changes in waste treatment processes on algal growth in receiving waters, impact of nutrients in tributary waters on algal growth in lakes and receiving waters, and effects of measures such as those used in lake restoration.

The maximum specific growth rate and the maximum standing crop are responses that can be estimated from growth measurements. The maximum specific growth rate is related to concentration of rate-limiting nutrient present. The maximum standing crop is proportional to the initial amount of limiting nutrient available.

The algal test procedure for determining primary productivity

* Approved by Standard Methods Committee, 1993.

Failure to demonstrate mutagenic activity with one or more *Salmonella* tester strains does not amount to proof that the sample contains no mutagenic material. The individual strains have certain mutagens to which they are sensitive, the concentration of S9 may be critical, and some mutagens and carcinogens are not mutagenic for any commonly used strain. Therefore, qualify conclusions regarding mutagenic activity on the basis of the characteristics of the tester strains used as well as the test conditions.[2-4,8]

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8050 BACTERIAL BIOLUMINESCENCE

8050 A. Introduction

The bacterial bioluminescence test (BBT) is a metabolic inhibition test that uses a standardized suspension of luminescent bacteria as test organisms under standardized conditions. This test method provides a rapid, reliable, and convenient means of determining the toxicity of waste material. The BBT has been validated for a variety of environmental applications including effluent monitoring, groundwater testing, sediment testing, hazardous wastes testing, assessing the efficiency of bioremediation processes, and general biomonitoring.

Luminescent bacteria possess several attributes that support their use for toxicity testing. Their small size (less than 1 μ in diameter) provides a very high surface-to-volume ratio. This feature, as well as the relatively simply morphology and lack of membrane-sided compartmentalization of internal functions, provides many target sites at or near the cytoplasmic membrane.

In bacteria, many metabolic pathways that function in respiration, oxidative phosphorylation, osmotic stabilization, and transport of chemicals and protons into and out of the cell are located within, or very near, the cytoplasmic membrane. The luciferase pathway, which functions as a shunt for electrons directly to oxygen at the level of reduced flavin mononucleotide, also is located within the cell membrane complex.

These cellular characterizations, coupled with the fact that bacterial respiration is 10 to 100 times greater than that of mammalian cells, provide for a dynamic metabolic system that can be quantitated easily and accurately by measuring the rate of light output from a bacterial suspension. Typically, the suspension contains approximately 10^6 individual organisms. The light intensity is substantial (well within the operating range of common light sensors), and the number of organisms compensates for variations among individuals that may influence results of tests on statistically limited numbers of individuals.

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APPENDIX C: OPERATING PROCEDURES FOR RADIOLOGICAL SCREENING OF SURFACE SOILS FOR RADIUM 226/228

FIELD STANDARD
OPERATING PROCEDURE
TITLE: RADIOLOGICAL SCREENING OF SURFACE SOIL FOR RADIUM-226/228

1.0 PURPOSE

This procedure describes the method for daily use of the Ludlum Model 44-10 Probe with the Ludlum Model 2220 or 2221 Scaler/Ratemeter. This procedure assigns an operating voltage to the probe and provides guidance on usage under field conditions using this instrument combination.

2.0 SCOPE

This procedure applies to the Model 44-10/Model 2220 or 2221 instrument combination for gamma radiation monitoring. Typically, the Model 44-10 shall be used for in-situ radiation measurements, rather than as a personnel/equipment monitoring device. The instrument is intended to be used as a qualitative device for detecting contamination, not for quantifying the magnitude of contamination. The procedure is also written for personnel involved with the annual calibration. Every time the NaI crystal is replaced or the probe is otherwise dismantled and adjusted in such a way that the assigned background is affected, the probe shall be recalibrated.

3.0 REFERENCES

- *Ludlum Model 44-10 Instruction Manual*
- *Ludlum Model 2220/2221 Instruction Manual*

4.0 EQUIPMENT AND MATERIALS

- Ludlum Model 44-10 2X2 NaI probe
- Ludlum Model 2220 or 2221 Scaler/Ratemeter or equivalent
- Earphones, as necessary
- Radioactive game check source

5.0 PROCEDURE

5.1 Operating Procedure

5.1.1 Performance Check

Instruments operated in accordance with this procedure shall be performance-checked daily or within 24 hours before operation. The following steps shall be taken to conduct a performance check on instruments. Note that the instrument will be factory calibrated prior to shipment to site.

FIELD STANDARD
OPERATING PROCEDURE
TITLE: RADIOLOGICAL SCREENING OF SURFACE SOIL FOR RADIUM-226/228

STEP	ACTION
1	Inspect the probe, scaler, and cable for damage and dirt. The instruments should be clean before being placed in service. The scaler and the probe shall have valid and current calibration labels. If the probe or ratemeter is dismantled or adjusted so that the calibration parameters are affected, the item must be recalibrated before use. Any repairs made to the instrument should be noted in the comment section of Form 2.0.1.3 prior to check-in.
2	Turn the scaler on and depress the battery check button to verify that the batteries are charged to at least 5.00 volts. If they are not, turn the scaler off, replace them with fresh batteries, and repeat the battery check.
3	Leave the window out and set the scaler high voltage and threshold to the levels indicated on the probe calibration label. If the probe is not already attached, turn off the scaler power and attach the probe to the scaler.
4	Put the probe on a desk or table in an upright position. Place the radioactive source under the probe, and perform a 1-minute count.
5	The display lighting, count hold, speaker, and zeroing functions of the scaler/ratemeter should also be checked at this stage.
6	Post the results from Steps 2 through 4 on the instrument's Response Check Control Log Sheet, Form 2.8.1.3. The efficiency and background columns do not require completion.
7	If the instrument does not check to within ±20 percent of the posted source count rate on two consecutive occasions of the same daily check, remove the instrument from service. Any repairs or maintenance to the detector in the comment section of Form 26.1.3 prior to use.

5.1.2 Operation

1. The NaI 2X2 detector is used for making different kinds of gamma radiation measurements. The four most common applications of this detector are fixed point measurement, area surveys, downhole logging, and count rate measurement. The probe background should be checked in the field, in an area not affected by above-background concentrations of radionuclides before performing any measurements.

2. For the fixed-point survey, the NaI detector is held as close as possible to the surface being measured, and a count is made for a time interval (generally 1 minute).

3. The area survey involves screening for presence of above-background levels of gamma radiation over a large area. The probe is suspended in front of the

surveyor and swung back and forth over the ground while walking. The level of above-background gamma radiation is determined by comparing the ratemeter, scaler, and/or audio response to a predetermined background response.

4. When performing area surveys for formal characterization or verification, personnel should walk at a rate of approximately 1 foot per second. Approximate swinging rate is one swing of the probe for every step taken by the surveyor. The probe should stay within 12 inches from the ground while being swung. To better delineate potentially contaminated areas, surveyors will reduce their walking and swinging rates as necessary when they encounter areas exhibiting count rates which exceed a predetermined level.

5. The areas should be walked in straight lines. Stakes or markers may be used to aid in field walkovers over rough terrain. Marker point may be used to indicate small areas exceeding predetermined levels. Earphones may be used as necessary if working in noisy environments. Additional QC walkovers may be conducted as necessary by a different team of personnel in order to better characterize areas. It is also often helpful to use a map that includes current topographical lines and physical features or landmarks.

7. The count rate measurement is made with the NaI detector usually held 1 meter above the ground surface and is made for a certain time interval (generally one minute).

6.0 RECORDS

Permanent quality assurance records generated by this procedure are:

- Response Check Control Log Sheets.

7.0 EXHIBITS

Exhibit 1 Response Check Control Log (2.6.1.3.)

Dete and Serial # _____
Back.ound _____
Efficiency _____

RESPONSE CHECK CC ROL LOG
Form ES&H 2.6.1.3. Re.. 7, 02/96

MONTH _____

Cal 2 Calibration Due _____
Meter Cal Due _____
Detector Cal Due _____
Source Used _____
Serial # _____
Source DPM _____

Date	Time	Source (cpm)	Background (cpm)	Efficiency (cpm/DPM)	HV	Battery	Chkd. By	Meter	Comments

APPENDIX D: TOXICOLOGICAL INFORMATION

INTRODUCTION

Although not typically part of a QAPP, EPA requested that toxicological information be provided on the dyes anticipated to be found at the site under investigation. This Appendix provides the available information readily obtainable within the TOMES database. The available information is reported for the three dyes of concern and consists of: Substance Identification; Synonyms/Trade Names; Health Hazard Data and; References, when available.

Topic: Fluorescein, disodium salt

1.0 SUBSTANCE IDENTIFICATION

RTECS NUMBER: LM5425000
CHEMICAL NAME: Fluorescein, disodium salt
CAS NUMBER: 518-47-8
MOLECULAR FORMULA: C20-H10-O5.2Na
MOLECULAR WEIGHT: 376.28
WISWESSER NOTATION: T C666 BO EVJ IR BVQ& MQ &-NA- 2

2.0 SYNONYM(S) / TRADE NAME(S)

1. Aizen uranine
2. Calcocid uranine B4315
3. 9-o-Carboxyphenyl-6-hydroxy-3-isoxanthone, disodium salt
4. Certiqual fluoresceine
5. C.I. 766
6. C.I. Acid Yellow 73
7. C.I. 45350 disodium salt
8. C.I. 45350 sodium salt
9. D&C Yellow No. 8
10. Disodium 6-hydroxy-3-oxo-9-xanthene-o-benzoate
11. Fluorescein sodium
12. Fluorescein sodium B.P
13. Fluorescein, soluble
14. Fluor-I-strip A.T.
15. Ful-Glo
16. Funduscein
17. Furanium
18. Hidacid uranine
19. NCI-C54706
20. Resorcinol phthalein sodium
21. Sodium fluorescein
22. Sodium fluoresceinate
23. Sodium salt of hydroxy-o-carboxy-phenyl-fluorone
24. Soluble fluorescein
25. Soluble fluoresceine
26. Spiro(isobenzofuran-1(3H),9'-(9H)xanthen)-3-one, 3',6'-dihydroxy-, disodium salt
27. Uranin

28. Uranine
29. Uranine A extra
30. Uranine O
31. Uranine SS
32. Uranine USP XII
33. Uranine WSS
34. Uranine Yellow
35. 11824 Yellow
36. 12417 Yellow

3.0 HEALTH HAZARD DATA

3.1 ACUTE TOXICITY

3.1.1 TDLO/TCLO - LOWEST PUBLISHED TOXIC DOSE/CONC

A. MAN

1. TDLo; ROUTE: Intravenous; DOSE: 14 mg/kg/10M-I; TOXIC EFFECTS: CARDIAC - Arrythmias (including changes in conduction); REFERENCE: Anesthesia and Analgesia 66:283, 1987.

2. TDLo; ROUTE: Intravenous; DOSE: 7142 ug/kg; TOXIC EFFECTS: SENSE ORGANS AND SPECIAL SENSES - Hemorrage; GASTROINTESTINAL - Nausea or vomiting; REFERENCE: American Journal of Ophthalmology 103:111, 1987.

3.1.2 LDLO/LCLO - LOWEST PUBLISHED LETHAL DOSE/CONC

A. GUINEA PIG

1. LDLo; ROUTE: Intraperitoneal; DOSE: 1 gm/kg; REFERENCE: Chemical Warfare Laboratories Technical Memorandum #47-6,59.

3.1.3 LD50/LC50 - LETHAL DOSE/CONC 50% KILL

A. RAT

1. LD50; ROUTE: Oral; DOSE: 6721 mg/kg; TOXIC EFFECTS: BEHAVIORAL - Change in motor activity (specific assay); BEHAVIORAL - Ataxia; LUNGS, THORAX, OR RESPIRATION - Dyspnea; REFERENCE: Journal of Periodontology 48:228, 1977.

2. LD50; ROUTE: Intravenous; DOSE: 1 gm/kg; TOXIC EFFECTS: BLOOD - Other changes; REFERENCE: Toxicology and Applied Pharmacology 29:97, 1974.

B. MOUSE

1. LD50; ROUTE: Oral; DOSE: 4738 mg/kg; TOXIC EFFECTS: BEHAVIORAL - Change in motor activity (specific assay); BEHAVIORAL - Ataxia; LUNGS, THORAX, OR RESPIRATION - Dyspnea; REFERENCE: Journal of Periodontology 48:228, 1977.

2. LD50; ROUTE: Intravenous; DOSE: 1 gm/kg; REFERENCE: Toxicology and Applied Pharmacology 29:97, 1974.

C. DOG

1. LD50; ROUTE: Intravenous; DOSE: 1 gm/kg; TOXIC EFFECTS: GASTROINTESTINAL - Changes in structure or function of salivary glands; REFERENCE: Toxicology and Applied Pharmacology 29:97, 1974.

3.3 REPRODUCTIVE EFFECTS

A. RABBIT

1. ROUTE: Intravenous; DOSE: 933 mg/kg; DURATION: female 5-8D of pregnancy; TOXIC EFFECTS: MATERNAL EFFECTS - Postpartum; EFFECTS ON NEWBORN - Viability index; REFERENCE: American Journal of Ophthalmology 84:847, 1977.

3.4 GENETIC EFFECTS

3.4.1 DNA ADDUCT

A. BACTERIA - E COLI

1. DOSE: 15 umol/L; REFERENCE: Mutation Research 89:95, 1981.

3.4.2 MUTATIONS IN MAMMALIAN SOMATIC CELLS

A. MOUSE

1. CELL TYPE: lymphocyte; DOSE: 200 mg/L; REFERENCE: Science 236:933, 1987.

3.4.3 SISTER CHROMATID EXCHANGE

A. HAMSTER

1. CELL TYPE: ovary; DOSE: 50100 ug/L; REFERENCE: Science 236:933, 1987.

3.5 TUMORIGENIC EFFECTS

A. RAT

1. ROUTE: Subcutaneous; DOSE: 19 gm/kg/79W-I; TOXIC EFFECTS: TUMORIGENIC - Equivocal tumorigenic agent by RTECS criteria; TUMORIGENIC - Tumors at site of application; REFERENCE: Gann. Japanese Journal of Cancer Research 45:446, 1954.

2. ROUTE: Subcutaneous; DOSE: 16 gm/kg/1Y-I; TOXIC EFFECTS: TUMORIGENIC - Equivocal tumorigenic agent by RTECS criteria; SKIN AND APPENDAGES - Tumors; TUMORIGENIC - Tumors at site of application; REFERENCE: Gann. Japanese Journal of Cancer Research 47:51, 1956.

3.6 OTHER MULTIPLE DOSE TOXICITY DATA

A. RAT

1. ROUTE: Intravenous; DOSE: 4 gm/kg/28D-I; TOXIC EFFECTS: BLOOD - Pigmented or nucleated red blood cells; REFERENCE: Toxicology and Applied Pharmacology 29:97, 1974.

B. DOG

1. ROUTE: Intravenous; DOSE: 4 gm/kg/28D-I; TOXIC EFFECTS: GASTROINTESTINAL - Nausea or vomiting; BIOCHEMICAL - Transaminases; DEATH; REFERENCE: Toxicology and Applied Pharmacology 29:97, 1974.

4.0 REFERENCES

1. National Occupational Hazard Survey 1974: Hazard Code M1436; Number of Industries 18; Total Number of Facilities 2278; Number of Occupations 21; Total Number of Employees 14785.

2. National Occupational Exposure Survey 1983: Hazard Code M1436; Number of Industries 76; Total Number of Facilities 5145; Number of Occupations 69; Total Number of Employees 94491; Total Number of Female Employees 21830.

Topic: Ammonium, ethyl(4-(p-(ethyl(m-sulfobenzyl)amino)-alpha-(o-sulfophenyl) benzylidene)2,5-cyclohexadien- 1-ylidene)(m-sulfobenzyl)-, hydroxide, inner salt, diammonium salt

1.0 SUBSTANCE IDENTIFICATION

RTECS NUMBER: BQ4550000
CHEMICAL NAME: Ammonium, ethyl(4-(p-(ethyl(m-sulfobenzyl)amino)-alpha-(o-sulfophenyl)benzylidene)2,5-cyclohexadien-1-ylidene) (m-sulfobenzyl)-, hydroxide, inner salt, diammonium salt
CAS NUMBER: 2650-18-2
MOLECULAR FORMULA: C37-H36-N2-O9-S3.2H3-N
MOLECULAR WEIGHT: 783.01
WISWESSER NOTATION: L6Y DYJ AUYR BSWQ&R DN2&1R CSWQ&& DUK2&1R CSWQ &Q &ZH 2

2.0 SYNONYM(S) / TRADE NAME(S)

1. Acid Blue 9
2. Acilan Turquoise Blue AE
3. A.F. Blue No. 1
4. Aizen Brilliant Blue FCF
5. Alphazurine
6. Alphazurine B
7. Alphazurine FG
8. Alphazurine FGND
9. Alphazurine (indicator)
10. Amacid Blue FG Conc
11. Bleu Brilliant FCF
12. 11388 Blue
13. Brilliant Blue
14. Brilliant Blue FCF
15. Bucacid Azure Blue
16. Calcocid Blue EG
17. Calcocid Blue 2 G
18. C.I. 671
19. C.I. 42090
20. C.I. Acid Blue 9
21. C.I. Acid Blue 9, diammonium salt
22. C.I. Direct Brown 78
23. C.I. Direct Brown 78, diammonium salt
24. C.I. Food Blue 2
25. D and C Blue No. 4
26. Disulphine Lake Blue EG
27. Edicol Supra Blue E6
28. Erioglaucine
29. Erioglaucine A
30. Erioglaucine E

31. Eriosky Blue
32. Fenazo Blue XR
33. Food Blue 1
34. Hidacid Azure Blue
35. H.K. Formula No. K. 7117
36. Kiton Blue AR
37. Kiton Pure Blue L
38. Maple Brilliant Blue FCF
39. Neptune Blue Bra
40. Neptune Blue Bra Concentration
41. Patent Blue AE
42. Patent Blue 2Y
43. Peacock Blue X-1756
44. Schultz No. 770
45. Triantine Light Brown 3RN
46. Xylene Blue VSG

3.0 HEALTH HAZARD DATA

3.1 ACUTE TOXICITY

3.1.2 LDLO/LCLO - LOWEST PUBLISHED LETHAL DOSE/CONC

A. HUMAN

1. LDLo; ROUTE: Intravenous; DOSE: 33 ug/kg; TOXIC EFFECTS: BEHAVIORAL - Muscle contraction or spasticity; LUNGS, THORAX, OR RESPIRATION - Dyspnea; REFERENCE: "Toxicology of Drugs and Chemicals," Deichmann, W.B., New York, Academic Press, Inc., 1969 -:87, 1969.

3.2 GENETIC EFFECTS

3.2.1 UNSCHEDULED DNA SYNTHESIS

A. RAT

1. VELL TYPE: liver; DOSE: 200 umol/L; REFERENCE: Environmental Mutagenesis 7:101, 1985.

2. ROUTE: Oral; DOSE: 500 mg/kg; REFERENCE: Environmental Mutagenesis 7:101, 1985.

3.2.2 MUTATIONS IN MICROORGANISMS

A. MOUSE

1. CELL TYPE: lymphocyte; DOSE: 571 mg/L (+S9); REFERENCE: Mutation Research 189:223, 1987.

B. BACTERIA - S TYPHIMURIUM

1. DOSE: 3333 ug/plate (-S9); REFERENCE: Mutation Research 189:223, 1987.

3.2.3 CYTOGENETIC ANALYSIS

A. HAMSTER

1. CELL TYPE: fibroblast; DOSE: 5 gm/L; REFERENCE: Food and Chemical Toxicology 22:623, 1984.

3.3 TUMORIGENIC EFFECTS

A. RAT

1. ROUTE: Subcutaneous; DOSE: 10 gm/kg/77W-I; TOXIC EFFECTS: TUMORIGENIC - Neoplastic by RTECS criteria; TUMORIGENIC - Tumors at site of application; REFERENCE: Toxicology and Applied Pharmacology 8:29, 1966.

Topic: Benzyl violet

1.0 SUBSTANCE IDENTIFICATION

CHEMICAL NAME: Benzyl violet
CAS REGISTRY NUMBER: 1694-09-3
MOLECULAR FORMULA: C39-H41-N3-O6-S2.Na
WISWESSAR LINE NOTATION: L6Y DYJ AUYR DN &1&R DN2&1R CSWQ&& DUK2&IR CSNO &-NA- & 38/47

2.0 SYNONYM(S) / TRADE NAME(S)

1. 11386 Violet
2. Acid Fast Violet 5BN
3. Acid Violet
4. Acid Violet 49
5. Acid Violet 4BNS
6. Acid Violet 5 B
7. Acid Violet 5BN
8. Acid Violet 6B
9. Acid Violet S
10. Acilan Violet S4BN
11. Af Violet No 1
12. Aizen Acid Violet 5BH
13. Benzenemethanaminium, N-(4-((4-(Dimethylamino)phenyl)(4-(Ethyl((3-sulfophenyl)methyl)amino)phenyl)methylene)-2,5-Cyclohexadien-1-ylidine)-n-ethyl-3-sulfo-,Hydroxide, Inner Salt, Sodium Salt
14. Benzyl Violet 3B
15. Benzyl Violet 4B
16. Ci 42640
17. Ci Acid Violet 49
18. Ci Acid Violet 49, Sodium Salt
19. Ci F Food Violet 2
20. Cogilor Violet 411.12
21. Coomassie Violet
22. D and C Violet No 1
23. Dispersed Violet 12197
24. Fast Acid Violet 5BN
25. Fd and C Violet 1
26. Fd and C Violet No 1
27. Food Violet 2
28. Formyl Violet S4BN
29. Hidacid Wool Violet 5B
30. Intracid Violet 4BNS
31. Kiton Violet 4BNS
32. Pergacid Violet 2B
33. Pergacid Violet 3B
34 Polaxal Violet 6B

35. Solar Violet 5BN
36. Tertracid Brilliant Violet 6B
37. Violet 6B
38. Violet No 1
39. Wool Violet 4BN
40. Wool Violet 5BN

3.0 HEALTH HAZARD DATA

3.1 TOXICITY VALUES

IARC Summary and Evaluation:

1. No data are available in humans. Sufficient evidence of carcinogenicity in animals. OVERALL EVALUATION: Group 2B:The agent is possibly carcinogenic to humans. REFERENCE: [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-PRESENT. (Multivolume work).,p. S7 58 (1987)

3.2 TOXICITY EXCERPTS

Human Toxicity Excerpts:

1. There is little concern with the acute and subchronic toxicity of the food colors currently in use, but there is considerable concern in some groups about their chronic toxicity. Several of the colors approved for use by the Color Amendments have been delisted since 1971, including .. Violet 1. Their delisting occurred owing to concerns over their chronic toxicity, especially carcinogenicity.REFERENCE: [Amdur, M.O., J. Doull, C.D. Klaasen (eds). Casarett and Doull's Toxicology. 4th ed. New York, NY: Pergamon Press, 1991. 839

2. In..patients, iv admin of /fast acid violet..used/ to aid diagnosis & study of pathology of ocular fundus by vital staining..to differentiate pathologic from normal.. No toxicity to ocular structures..as a result..of dyes. REFERENCE: [Grant, W. M. Toxicology of the Eye. 2nd ed. Springfield, Illinois: Charles C. Thomas, 1974. 440

3.2 NON-HUMAN TOXICITY EXCERPTS:

1. Groups of 20 male or 20 female sprague-dawley rats..7-wk old fed diet containing 5% benzyl violet 4b (89.1% pure)..364 days. Nine of 18 treated female rats that survived more than 70 days developed tumors: 5 mammary carcinomas between 138 and 345 days. In 10 untreated control females, 1 mammary fibroadenoma was seen at day 338; no tumors were observed in 15 treated and 10 control males that survived more than 70 days. The average survival times were 187 (males) and 210 (females) days in the treated groups and 228 (males) and 315 (females) days in control groups. REFERENCE: [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer, 1972-PRESENT. (Multivolume work).,p. V16 157 (1978)

2. ..48 male & 50 female spf-derived ash-cs1 mice..fed diets containing 70, 700 or 3500 mg/kg of diet benzyl violet 4b (90% pure) for 80 wk. .. In treated female groups, 1/43, 5/42, & 4/48 animals @ 3 dose levels, respectively, had thymic lymphosarcomas, compared with 1/42 mice of untreated female controls. REFERENCE: [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-PRESENT. (Multivolume work).,p. V16 157 (1978)

3. Group of 35 female 6-wk-old sprague-dawley rats..fed diet containing 1% benzyl violet 4b (91.9% pure) for 1 wk, then 3% for 1 week and thereafter a diet containing 5% of the dye for 12 months. During this period, 11 rats developed mammary carcinomas, 4 had squamous cell carcinomas, and 7 animals had both types of tumor. The majority of the squamous cell carcinomas developed at the ear duct but also appeared at the buccal and axillary regions of the skin. The times of appearance of the first mammary carcinoma and the first squamous cell carcinoma were 13 and 27 weeks, respectively. REFERENCE: [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-PRESENT. (Multivolume work).,p. V16 158 (1978)

4. ..20 male & 20 female 3 wk old wistar rats had continual skin/fur contact with benzyl violet 4b (food grade) for 100 wk: tray of cage was sprinkled with 3 g of dye, & rats were placed directly on tray; the tray was cleaned twice weekly, and the same amount of dye was added after each cleaning. Malignant skin tumors were not observed in treated or control rats. The increase incidence of benign mammary tumors in the test group (8/14) compared with that in controls (1/14) was statistically significant ($p<0.05$). REFERENCE: [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-PRESENT. (Multivolume work).,p. V16 158 (1978)

5. ..18 young osborne-mendel rats of both sexes, received weekly sc injections of 20 mg benzyl violet 4b (food grade) as a 2% aq soln for 2 yr. Fibrosarcomas @ site of injection were seen in 14 rats. REFERENCE: [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-PRESENT. (Multivolume work).,p. V16 158 (1978)

6. In rabbits..iv admin of /fast acid violet..used/ to aid diagnosis & study of pathology of ocular fundus by vital staining...to differentiate pathologic from normal... No toxicity to ocular structures...as a result...of dyes. REFERENCE: [Grant, W. M. Toxicology of the Eye. 2nd ed. Springfield, Illinois: Charles C. Thomas, 1974. 440

7. Neurotoxic effects of chemicals as listed in major secondary REFERENCE: sources. Chemical: Acid Violet S; Subchronic neurotoxic effect: neuromuscular excitability changes reported in animals. /From table/ REFERENCE: [O'Donoghue, J. L. (ed.). Neurotoxicity of Industrial and Commercial Chemicals. Volume I. Boca Raton, FL: CRC Press, Inc., 1985. 72

8. Arylmethane dyes were tested in the Salmonella/mammalian microsome mutagenicity assay. The food color Benzyl Violet 4B CI 42640, was mutagenic in frameshift mutation detector strains TA1538 and required metabolic activation. Most of these compounds gave weak mutagenic responses with Salmonella and only within narrow dose ranges. Since conflicting results were obtained using dyes from different sources, minor dye components may have been responsible for their mutagenicity.
REFERENCE: [Bonin AM et al; Mutat Res 89 (1): 21-34 (1981)

APPENDIX E: NSWC CRANE NPDES QA/QC PLAN

SECTION THREE

Explosive Sciences Branch Laboratory Quality Assurance/ Quality Control Manual

Prepared for:
Environmental Protection Department
Explosive Sciences Branch

Prepared by:
COMARCO, Engineering Services Division
Bloomfield, IN

It is recommended that the Crane Explosive Sciences Branch laboratory QA/QC Manual be reviewed and updated at least annually by the Crane Quality Assurance Officer at Code 095. This should be accompanied by a quality system review of the laboratory's quality system and its standard operating procedures.

Section Three

Explosive Sciences Branch
Laboratory Quality Assurance/Quality Control Manual

for

Naval Surface Warfare Center Crane

300 Highway 361

Crane, Indiana 47522-5001

(812) 854-5500

August 1, 1997

Approvals:

Name: Jim Hunsicker Date:_____
Title: Environmental Protection Dept. Manager
Signature: _____

Name: Jim Market Date:_____
Title: QC Coordinator
Signature: _____

Name: Nancey Meagerlein Date:_____
Title: Explosive Sciences Branch Manager
Signature: _____

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Standard Operating Procedures

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Appendix A
Standard Operating Procedures

References:
EPA Method 335.3 Colorimetric Method
552 Perkin Elmer Spectrophotometer Manual

Rev: Original
Effective Date: 8/1/97

TOTAL CYANIDE

I. SCOPE AND APPLICATION.

This method covers the determination of cyanide in drinking, ground, surface, and saline waters, domestic and industrial wastes.

The colorimetric procedure is used for concentrations below 1 mg/l and is sensitive to about 0.005 mg/l.

DOES NOT APPLY to PROJECT

II. SUMMARY OF METHOD.

The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a manual reflux-distillation operation and absorbed in a scrubber containing a sodium hydroxide solution. The cyanide ion in the absorbing solution is converted to cyanogen chloride by reactions with chloramine-T, which subsequently reacts with pyridine and barbituric acid to give a red-colored complex.

Reduced volume versions of this method that use the same reagents and molar ratios are acceptable provided they meet the quality control and performance requirements stated in the method.

Limited performance-based method modifications may be acceptable provided they are fully documented and meet or exceed requirements expressed in Quality Control.

III. INTERFERENCES.

Several interferences are encountered with this method. Some of the known interferences are aldehydes, nitrate-nitrite, sulfide, and oxidizing agents such as chlorine, thiocyanate, and thiosulfate. Multiple interferences may require the analysis of a series of laboratory fortified sample matrices (LFM) to verify the suitability of the chosen treatment. Some interferences are eliminated or reduced by the distillation.

Sulfides adversely affect the procedure by producing hydrogen sulfide during distillation. If a drop of the sample on lead acetate test paper indicates the presence of sulfide, treat 25 ml more of the stabilized sample (pH ≥ 12) than that required for the cyanide determination with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper.

Filter the solution through a dry filter paper into a dry beaker, and from the filtrate, measure sample to be used for analysis. Avoid a large excess of cadmium and a long contact tin minimize cyanide loss on the precipitated material.

High results may be obtained for samples that contain nitrate or nitrite. During the distillation nitrate and nitrite will form nitrous acid that will react with some organic compounds to form oximes. These oximes will decompose under test conditions to generate HCN. The interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid.

Oxidizing agents, such as chlorine, decompose most of the cyanides. Test a drop of the sample with potassium iodide-starch paper (KI-starch paper) at time of collection; a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper; then add an additional 0.06 g of ascorbic acid for each liter of sample volume.

Other compatible procedures for the removal or suppression of interferences may be employed provided they do not adversely effect the overall performance of the method.

Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus.

IV. APPARATUS.

Balance -- Analytical, capable of accurately weighing to the nearest 0.0001 g.

Glassware -- Class A volumetric flasks and pipets as required.

Midi reflux distillation apparatus including boiling flask condenser, and absorber.

Heating mantle or heating block as required.

Data recording device Perkin Elmer Model 552 Spectrophotometer @ 570 nm

V. SAMPLE HANDLING AND PRESERVATION.

Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. Volume collected should be sufficient to insure a representative sample, allow for replicate analysis (if required), and minimize waste disposal.

If the sample contains chlorine or hydrogen sulfide provide treatment.

Samples must be preserved with sodium hydroxide pH $\geq$ 12 and cooled to 4°C at the time of collection.

Samples should be analyzed as soon as possible after collection. If storage is required, prese samples are maintained at 4°C and may be held for up to 14 days.

VI. REAGENTS.

Reagent water: Distilled or deionized water, free of the chemical of interest. ASTM type II or equivalent.

Ascorbic acid: Crystal (CASRN-50-81-7)

Chloramine-T: Dissolve 2.0 g of chloramine-T (CASRN-127-65-1) in 500 ml of reagent water.

Magnesium chloride solution: Weight 510 g of $MgCl_2$ $6H_20$ (CASRN-7786-30-3) into a 1000 ml flask, dissolve and dilute to 1 L with reagent water.

Pyridine Barbituric Acid Reagent: Place 15 g of barbituric acid (CASRN-67-52-7) in a 1 L beaker. Wash the sides of the beaker with about 100 ml of reagent water. Add 75 ml of pyridine (CASRN-110-86-1) and mix. Add 15 ml of conc. HC1 (CASRN-7647-01-0) and mix. Dilute to 900 ml with reagent water and mix until all the barbituric acid has dissolved. Transfer the solution to a I L flask and dilute to the mark.

Sodium dihydrogenphosphate buffer, 1 M: Dissolve 138 g of NaH_2PO_4 H_20 (CASRN-10049-21-5) in 1 L of reagent water. Refrigerate this solution.

Sodium Hydroxide Solution, 1.25 N: Dissolve 50 g of NaOH (CASRN-1310-73-2) in reagent water, and dilute to 1 L with reagent water.

Silver nitrate, 0.0192 N: Prepare by crushing approximately 5 g $AgNO_3$ (CASRN-7761-88-8) crystals and drying to constant weight at 40°C. Weight out 3.2647 g of dried $AgNO_3$, dissolve in reagent water, and dilute to 1000 ml (1 ml - 1 mg CN).

Stock Cyanide Solution: Dissolve 2.51 g of KCN (CASRN-151-50-8) and 2 g KOH (CASRN-1310-58-3) in 900 ml of reagent water. Standardize with 0.0192 N $AgNO_3$. Dilute to appropriate concentration so that 1 ml = 1 mg CN.

Standard Cyanide Solution, intermediate: Dilute 10.0 ml of stock (1 ml = 1 mg CN) to 100.0 with reagent water (1 ml = 100.0 mg CN).

Working Standard Cyanide Solution: Prepare fresh daily by diluting 20.0 ml of intermediate cyanide solution to 200.0 ml with reagent water and store in a glass stoppered bottle. 1 μL = 10.0 mg CN.

Sulfamic Acid: (CASRN-212-57-3)

Sulfuric Acid, 18 N: slowly add 500 ml of concentrated H_2SO_4 (CASRN-5329-14-6) to 500 ml of reagent water.

VII. CALIBRATION

Prepare a series of at least 3 standards, covering the desired range, and a blank by pipetting suitab. volumes of working standard solution into 100 ml volumetric flasks. To each standard (except those to be distilled) add 20 ml of 1.25 N sodium hydroxide and dilute to 100 ml with reagent water.

It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) and a blank be distilled and compared to similar values on the standard curve to insure that the distillation technique is reliable. If distilled standards do not agree within ± 10% of the undistilled standards the analyst should find the cause of the apparent error before proceeding. Before distillation, standards should contain 4 ml 0.25 N NaOH per 50 ml.

Set up the manifold in a hood or a well-ventilated area.

Allow the instrument to warm up as required. Pump all reagents, with 0.25 N NaOH in the sample line, until a stable baseline is achieved.

Place appropriate standards in the sampler in order of decreasing concentration and perform analysis.

Prepare standard curve by plotting instrument response against concentration values in a Lotus spreadsheet. A calibration curve may be fitted to the calibration solutions concentration/response data using computer or calculator based regression curve fitting techniques. Acceptance or contro' limits should be established using the difference between the measured value of the calibrati' solution and the "true value" concentration.

After the calibration has been established, it must be verified by the analysis of a suitable Quality Control Standard (QCS). If measurements exceed ± 10% of the established QCS value, the analysis should be terminated and the instrument recalibrated. The new calibration must be verified before continuing analysis. Periodic reanalysis of the QCS is recommended as a continuing calibration check.

VIII. CALCULATIONS

Prepare a calibration curve by plotting instrument response against standard concentration. Compute sample concentration by comparing sample response with the standard curve. Multiply answer by appropriate dilution factor.

Report only those values that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

Report results in mg/L.

IX. PROCEDURE

Samples and Standards are distilled in Andrews Glass Midi-Dist, Model 110-04R, System as per instruction manual.

Distillate (0.25 N NaOH) 50 ml, is transferred to 100 ml volumetric flasks. The impinge tube is rinsed three times with 5 ml portions of distilled water for quantitative transference.

For color development of the cyanide in distillate the following reagents are added in this order:

1. 15 ml of sodium phosphate solution mix.
2. 2 ml of chloramine-T solution mix, let stand for two minutes.
3. 5 ml of pyridine-barbituric acid solution mix, take to 100 ml mark with distilled water mix. Let stand for 8 minutes and read absorbance within 15 minutes at 578 nm.

Enter absorbance values in Lotus spreadsheets. Also enter any dilution factors and sample information. Spreadsheet will calculate analysis result.

X. ALLOWABLE LIMITS.

The NPDES effluent limit is 0.005 mg/l for Total Cyanide.

XI. QC CHECKS.

One spiked blank and one spiked sample will be run with every 20 sample determinations. The spike concentration be near the average cyanide concentration found in a typical sample. Code 4052 laboratory will obtain or prepare the standard solutions.

Duplicate analysis on one sample after every ten samples are analyzed shall be performed for each parameter if enough sample volume is available.

One reagent blank shall be analyzed each day an analysis is performed for each parameter.

Split samples shall be analyzed quarterly by a control laboratory.

Code 095 will obtain performance evaluation samples from a vendor and these will be analyzed by the Code 4052 laboratory every three months.

The Code 4052 laboratory will use Windowchem™ Software's ControlChart!™ software to generate quality control charts for the spectrophotometer. A separate control chart will be prepared for each concentration range represented in the outfall data. Duplicate sample range results will be charted to monitor the spectrophotometer's precision. Spiked blank and spiked sample percent recovery data will be charted to monitor the spectrophotometer's accuracy. Procedures for preparing and using control charts are in section 1, chapter 6 of this QA/QC manual.

XII. REFERENCES

Methods for Chemical Analysis of Water and Wastes, USEPA, EPA 600/4-79-020, Revised Marc 1983.

Perkin-Elmer, Model 552 UV-VIS Spectrophotometer operators manual, Oak Brook, IL June 1979.

References:	Rev: Original
EPA Method 300.0 Waters Ion Chromatography Manual Determination of Inorganic Anions by Ion Chromatography.	Effective Date: 8/1/97

NITRATE

I. SCOPE AND APPLICATION.

The Crane Code 4052 laboratory analyzes nitrate using the ion chromatography method.

The matrices applicable to each method are shown below:

A. Drinking water, surface water, mixed domestic and industrial wastewater, groundwater, reagent waters, solids, and leachates (when no acetic acid is used).

B. Drinking water and reagent waters.

Method A is recommended for drinking and waste water. The multi laboratory ranges tested for nitrate is as follows:

Ion	mg/L
Nitrate-N	0.42 - 14.0

This method is recommended for use only by, or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatograms. When this method is used to analyze unfamiliar samples nitrate identification should be supported by the use of a fortified sample matrix covering nitrate.

Users of the method data should state the data-quality objectives prior to analysis. Users of the method must demonstrate the ability to generate acceptable results with this method.

II. SUMMARY OF METHOD.

A 100 microliter (μL) sample is introduced into an ion chromatograph. Nitrate is separated and measured, using a system comprised of a guard column, analytical column, and conductivity detector.

Limited performance-based method modifications may be acceptable provided they are fully documented.

III. INTERFERENCES.

Samples that contain particles larger than 0.45 microns and reagent solutions that contain particl. larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

Interferences can be caused by substances with retention items that are similar to and overlap those of nitrate. Large amounts of one anion can interfere with the peak resolution of nitrate. Sample dilution or fortification can be used to solve most interference problems associated with retention times.

Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to unknown peaks or elevated baseline in ion chromatograms.

The acetate anion will elute early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetate buffers are used for pH adjustment.

IV. APPARATUS.

Glassware -- Class A volumetric flasks and pipets as required.

Waters Millipore Ion Liquid Chromatograph Model 430 or 490

V. SAMPLE HANDLING AND PRESERVATION.

Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. The volume collected should be sufficient to insure a representative sample, allow for replicate analysis, if required, and minimize waste disposal.

Glass or polyethylene 250 ml bottles will be used to collect samples. Samples should be cooled to 4°C and will be analyzed for nitrate within 48 hours of collection.

VI. REAGENTS.

Reagent water: Distilled or deionized water, free of the anions of interest. Water should contain particles no larger than 0.20 microns.

Stock standard solutions, 1000 mg/L (1 mg/ml): Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade materials (dried at 105°C for 30 min) as listed below.

VII. CALCULATIONS

The linear calibration range must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected. The calibration range must be determined using enough nitrate standard concentration points to insure the calibration range is linear. A blank and at least three standard nitrate concentrations must be used verify the linear calibration range.

The method detection limit for nitrate must be established. A blank is fortified with enough stock solution to be two to three times the estimated instrument detection limit. The estimated detection limit is the concentration where the instrument's signal to noise ratio is between 2.5 to 5. Perform seven replicate analyses of the blank and using the entire method and calculate the standard deviation of the results. Multiply the standard deviation by the student's t test value for a 99% confidence level to arrive at the method detection limit. The nitrate method detection limit should be determined every six months, when the analyst changes, or when there is a change in the instrument response.

Report sample concentrations from the linear calibration range curve in mg/l.

VIII. PROCEDURE

Check system calibration daily and, if required, recalibrate.

Load and inject 100 µL of well mixed sample. Flush injection loop thoroughly, using each new sample. Use the same size loop for standards and samples. Record the resulting peak size in area units. An automated constant volume injection system may also be used.

The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for nitrate. However, the experience of the analyst with the sample matrix should weigh heavily in the interpretation of chromatograms.

If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, fortify the sample with an appropriate amount of standard and reanalyze.

> **NOTE:** Retention time is inversely proportional to concentration. Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. In some cases this peak migration may produce poor resolution or identification.

The following extraction should be used for solid materials. Add an amount of reagent water equal to ten times the weight of dry solid material taken as a sample. This slurry is mixed for ten minutes using a magnetic stirring device. Filter the resulting slurry before injecting using a 0.45 micron

membrane type filter. This can be the type that attaches directly to the end of the syringe. Care should be taken to show that good recovery and identification of peaks is obtained with the user' matrix through the use of fortified samples.

It has been reported that lower detection limits for bromate (≈7 μg/L) can be obtained using a borate based eluent. The use of this eluent or other eluents that improve method performance may be considered as a minor modification of the method and as such still are acceptable.

Should more complete resolution be needed between peaks the eluent can be diluted. This will spread out the run but will also cause the later eluting anions to be retained longer. The analyst must determine to what extent the eluent is diluted. This dilution should not be considered a deviation from the method.

IX. ALLOWABLE LIMITS.

The NPDES effluent limit for outfalls 107, 201 and 301 is 90 ppm.

X. QC CHECKS.

One blank spike and one spiked sample will be run with every 20 sample determinations. The spike concentration shall consist of at least 1 time the average concentration found in a typical sample for each determined parameter. Code 4052 laboratory will obtain or prepare the standard solutions.

Duplicate analysis on one sample after every ten samples are analyzed shall be performed for eac parameter if enough sample volume is available.

One reagent blank shall be analyzed each day an analysis is performed for each parameter.

Split samples shall be analyzed quarterly by a control laboratory.

Code 095 will obtain performance evaluation samples from a vendor and these will be analyzed by the Code 4052 laboratory every three months.

The Code 4052 laboratory will use Windowchem™ Software's ControlChart!™ software to generate quality control charts for each ion liquid chromatograph. A separate control chart will be prepared for each concentration range represented in the outfall data. Duplicate sample range results will be charted to monitor each ion liquid chromatograph's precision. Spiked blank and spiked sample percent recovery data will be charted to monitor each ion liquid chromatograph's accuracy. Procedures for preparing and using control charts are in section 1, chapter 6 of this QA/QC manual.

XI. REFERENCES

Methods for Chemical Analysis of Water and Wastes, USEPA, EPA 600/4-79-020, Revised March 1983.

Waters, Waters Innovative Methods for Ion Analysis, Milford, Massachusetts, 1989.

References:
EPA Method 218.4 Chelation Extraction with MIBK
Perkin Elmer Model 5000 Atomic Absorption Manual

Rev: Original
Effective Date: 8/1/97

HEXAVALENT CHROMIUM

I. SCOPE AND APPLICATION.

This method covers the determination of dissolved hexavalent chromium in drinking, surface and saline waters. This method may also be applicable to certain domestic and industrial wastes after filtration provided that no interfering substances are present.

The detection limit of this method is 1.0 microgram of chromium per liter and the range of analysis is 1.0 to 25 micrograms per liter.

II. SUMMARY OF METHOD.

This method is based on the chelation of hexavalent chromium with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into the flame of a Atomic Absorption Spectrophotometer (AA).

III. INTERFERENCES.

THIS DOES NOT APPLY

High concentration of other reactive metals, as may be contained in industrial waste waters, may interfere. Knowledge of sample characteristics obtained from past analytical experience will indicate if interferences are a problem. Samples from new sources should be tested by Atomic Absorption Spectrophotometry for high concentrations of other reactive metals. The method is free from interferences from elements normally occurring in fresh water.

IV. APPARATUS.

Glassware -- Class A volumetric flasks and pipets as required. Procedures found to provide clean labware include washing with a detergent solution, rinsing with tap water, soaking for 4 hours in a mixture of dilute acids (10% HNO_3, 10% HCl, and 80% distilled water), rinsing with reagent water and storing clean. Ideally, ground glass surfaces should be avoided to eliminate a potential source of random contamination. When this is impractical, particular attention should given to all ground glass surfaces during cleaning. Chromic acid cleaning solutions must be avoided because the chromium concentration is being determined.

Perkin Elmer Atomic Absorption Spectrophotometer Model 5000

V. SAMPLE HANDLING AND PRESERVATION.

The water samples should be collected in glass or plastic containers and cooled to 4°C as soon as possible. The samples should be transported and stored at this temperature. Stability of hexavalent chromium is such that the analysis must to be completed within 24 hours of sample collection.

VI. REAGENTS.

Ammonium pyrrolidine dithiocarbamate (APDC) solution. Dissolve 1.0 gram APDC in distilled water and dilute to 100 ml. Prepare the APDC solution each day of analysis.

Bromophenol blue indicator solution: Dissolve 0.1 gram bromophenol blue in 100 ml of 1:1 ethanol distilled water mixture. Prepare once a year.

Chromium standard solution I, 1.0 ml = 100 microgram chromium. Dilute the purchased 1000 mg/l chromium AA stock standard solution by a factor of 10 (1:10). This solution is equivalent to the chromium stock solution described in EPA method 218.4. This solution is stable for six months.

Chromium standard solution II, 1.0 ml = 10.0 microgram chromium. Dilute chromium standard solution I by a factor of 10 (1:10). Prepare every month.

Chromium standard solution III, 1.0 ml = 0.10 microgram chromium. Dilute chromium standard solution II by a factor of 100 (1:100). Prepare each day of analysis.

Methyl isobutyl ketone (MIBK) CAS # 108-10-1.

Sodium hydroxide solution, 1 M: Dissolve 40 gram NaOH in distilled water and dilute to 1 liter. Prepare once a year or when needed.

Sulfuric acid, 0.12 M: Slowly add 6.5 ml concentrated sulfuric acid to distilled water and dilute to 1 liter. Prepare once a year or when needed.

VII. CALCULATIONS

Calibration Curve. The instrument's calibrated software package calculates the Cr^{+6} concentration in milligrams/liter for each sample. The software package is incorporated into the instrumentation and results are displayed either digitally or printed to paper and saved to disk.

Reporting Results. The NPDES permit for outfall 001 at the NSWC Crane Sewage Treatment Plant has a hexavalent chromium detection limit requirement of 0.005 milligram/liter. Triplicate analyses of the sample will be completed with three aliquot volumes of 100, 50 and 25 milliliters. The reported result is the largest aliquot volume analyzed that, after accounting for the dilution factor, falls within the calibration curve range. The hexavalent chromium detection limit for this procedure is 0.001 milligrams/liter, as stated in the EPA hexavalent chromium procedure 218.4. Any result less then 0.005 milligrams/liter, should be reported as < 0.005 milligrams/liter.

III. PROCEDURE

Three analyses shall be performed on each water sample. Filter at least 200 ml of sample through a 0.45 micron cellulose membrane filter into a 500 ml vacuum flask. Pipette three aliquots, 100 ml, 50 ml and 25 ml of filtered water sample into three different 200 ml volumetric flasks, and adjust the volume to approximately 100 ml with distilled water. These volumes allow sample concentration to fall within the range of analysis. If sample concentration of hexavalent chromium is above range of analysis on the 25 ml aliquot flask dilute sample 10 times and rerun.

Prepare a blank in a 200 ml volumetric flask containing the indicated amounts of the reagents APDC, Bromophenol blue indicator, 1.0 N Sodium Hydroxide solution or 0.12 N Sulfuric acid and MIBK. Also, prepare standards containing 0.25, 0.50, 1.0, 2.5 micrograms of hexavalent chromium by pipetting the correct amount of chromium standard solution III into 4 different 200 ml volumetric flasks. The volumes to be pipetted are as follows: 2.5 ml for the 0.25 microgram standard, 5.0 ml for the 0.5 microgram standard, 10.0 ml for the 1.0 microgram standard and 25.0 ml for the 2.5 microgram standard. A new set of standards must be prepared with each new set of samples.

Place a Teflon coated magnetic stirring bar in each 200 ml volumetric flask.

Add 2 drops of bromphenol blue indicator solution to each sample and standard flask. (The pH adjustment to 2.4 may also be made with a pH meter instead of an indicator).

For each sample and standard flask adjust the pH by addition of 1 M NaOH solution a drop at a time with agitation until a blue color persists. Add 0.12 M sulfuric acid a drop at a time until the blue color just disappears in both the standards and samples. Then add 2.0 ml of 0.12 M sulfuric acid in excess. The pH at this point should be 2.4.

To each sample and standard flask add 5.0 ml APDC solution and mix. The pH should then be approximately 2.8 as measured by a calibrated pH meter.

To each sample and standard flask add 10.0 ml MIBK and place flask on multiple electrical magnetic stirrer and adjust the stirring rate so that the flask contents are stirred vigorously for three minutes.

Allow the flask phases to separate and add distilled water until the MIBK top layer is completely in the neck of the volumetric flask. Having the MIBK layer in the neck of the flash makes it easer to separate it from the water layer and easer to aspirate into the AA. Samples and standards are ready to be aspirated into AA flame.

Set up the AA as follows: Wavelength 357.9 nm, acetylene as fuel, air as oxidant, with a fuel rich flame.

Optimize AA chromium absorbance with 4 milligrams/liter aqueous chromium standard as described in AA operating manual. Set AA burner control fuel flow-oxidant flow settings to fuel 30 and oxidant 40. Then reset zero while aspirating MIBK. While aspirating MIBK turn the aspirating adjust knob counter clockwise until bubbles come out of the aspirating tube, then slightly clockwise until bubbles stop. Then place the aspirating tube in the highest hexavalent chromium standard

MIBK layer in neck of volumetric flask (2.5 microgram hexavalent chromium standard). Very slowly turn the aspirating adjust knob clockwise until the absorbance increases to it's highest obtainable value. Check zero by aspirating MIBK. Them aspirate reagent blank and set instrumen zero while aspirating reagent blank. Them aspirate standards and samples. Recheck zero by aspirating MIBK between every standard and sample. Record absorbance values in laboratory notebook.

IX. ALLOWABLE LIMITS.

The NPDES effluent limit for hexavalent chromium is 0.008 mg/l.

X. QC CHECKS.

One spiked blank and spike sample will be run with every 20 sample determinations. The spike concentration shall consist of at least the average concentration found in a typical sample for each determined parameter. Code 4052 laboratory will obtain or prepare the standard solutions.

Duplicate analysis on one sample after every ten samples are analyzed shall be performed for each parameter if enough sample volume is available.

One reagent blank shall be analyzed in each batch, each day an analysis is performed for each parameter.

Split samples shall be analyzed quarterly by a control laboratory.

The Code 4052 laboratory will use Windowchem™ Software's ControlChart!™ software to generate quality control charts for the atomic absorption spectrophotometer. A separate control chart will be prepared for each concentration range represented in the outfall data. Duplicate sample range results will be charted to monitor the atomic absorption spectrophotometer's precision. Spiked blank and spiked sample percent recovery data will be charted to monitor its accuracy. Procedures for preparing and using control charts are in section 1, chapter 6 of this QA/QC manual.

XI. REFERENCES

Methods for Chemical Analysis of Water and Wastes, USEPA, EPA 600/4-79-020, Revised March 1983.

Perkin Elmer, Flame AA, Analytical Methods for Atomic Absorption Spectrophotometry, Norwalk, Connecticut, Jan, 1982.

References:
EPA Method 289.1 AA, Direct Aspiration
EPA Method 3015, Microwave Assisted Acid Digestion of Aqueous Samples and Extracts

Rev: Original
Effective Date: 8/1/97

ZINC

I. SCOPE AND APPLICATION.

This method provides procedures for the determination of dissolved and total recoverable zinc in groundwater, storm runoff, drinking water, surface water, industrial and domestic waste water, and saline waters. This method may also be applicable to certain domestic and industrial wastes after filtration provided that no interfering substances are present.

The detection limit of this method is 20 microgram of zinc per liter and the range of analysis is 50 to 1000 micrograms per liter.

II. SUMMARY OF METHOD.

In direct aspiration atomic absorption spectroscopy a sample is aspirated and atomized in a flame. A light beam from a hollow cathode lamp whose cathode is made of zinc is directed through the flame into a monochromator, and onto a detector that measures the amount of light absorbed. Absorption depends upon the presence of free unexcited ground state atoms in the flame. Because the light beam's wavelength is specific to zinc, the light absorbed in the flame is a measure of the zinc concentration in the sample.

The method is limited to metals in solution. The microwave assisted acid digestion method is used to facilitate total metal determination in samples that contain suspended solids.

III. INTERFERENCES.

Several interference sources may cause inaccuracies in the determination of trace elements by direct aspiration atomic absorption. Chemical interferences are caused by a lack of absorption of atoms bound in molecular combinations in the flame. This can occur when the flame is not sufficiently hot to dissociate the molecule or when the dissociated atom is immediately oxidized to a compound that will not dissociate at the flame temperature. High levels of silicon may interfere with zinc determination. The presence of high levels of dissolved solids in the sample may result in interference from non-atomic absorbance such as light scattering. Ionization interferences may occur when the flame temperature is high enough to generate the removal of an electron from a neutral atom, giving a positive charged ion. Finally, spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the zinc absorption line.

Use of the microwave assisted digestion method can introduce interferences if high pressure develops in the digestion vessel causing venting. Venting can result in either a loss of the metal of interest or sample.

IV. APPARATUS.

Glassware -- Class A volumetric flasks and pipets as required. Procedures found to provide clean labware include washing with a detergent solution, rinsing with tap water, soaking for 4 hours in a mixture of dilute acids (10% HNO_3, 10% HCl, and 80% distilled water), rinsing with reagent water and storing clean. Ideally, ground glass surfaces should be avoided to eliminate a potential source of random contamination. When this is impractical, particular attention should given to all ground glass surfaces during cleaning. Chromic acid cleaning solutions must be avoided because the chromium concentration is being determined.

Cem Corporation, Microwave Digestion System, Model MDS-81D

Perkin Elmer Atomic Absorption Spectrophotometer Model 300 or 5000

V. SAMPLE HANDLING AND PRESERVATION.

For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods Manual. All sample bottles and laboratory glassware should be thoroughly washed with detergent and tap water; rinsed with 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water and finally deionized distilled water in that order. Dissolved metal determination requires the sample be filtered through a 0.45 micron membrane before preserving the filtrate with nitric acid. For total metal determination the sample is preserved with nitric acid without filtering. The pH of the preserved samples should be <2. Before determining total metal concentrations the sample is digested using the microwave assisted acid digestion method.

VI. REAGENTS.

Deionized distilled water: Prepared by passing distilled water through a series of cation and anion exchange resins.

Nitric acid concentrated and (1:1): Dilute acid prepared by adding the concentrated acid to an equal volume of water.

Hydrochloric acid (1:1): Prepare a 1:1 solution of reagent grade hydrochloric acid and water.

Stock standard solutions and calibration standards: Commercially available stock standard solutions are diluted to make calibration standards to cover the concentration range desired. To make a stock solution weigh 1.00 gram of zinc metal and dissolve in 10 ml of nitric acid. Make 1 liter of stock with water (1 ml = 1 mg zinc).

VII. CALCULATIONS

Calibration Curve. The instrument's calibrated software package calculates the zinc concentration in milligrams/liter for each sample. The software package is incorporated into the instrumentation and results are displayed either digitally or printed to paper and saved to disk.

VIII. PROCEDURE

For the microwave assisted digestion method procedures see sections 1 through 10 of the SW-846 method 3510. For the analysis procedure and the calculation, see "direct aspiration" part 9.1 of the Atomic Absorption Methods Manual.

Notes:

1. High levels of silicon may interfere.

2. The air-acetylene flame absorbs about 25% of the energy at the 213.9 nm line.

3. The sensitivity may be increased by the use of low-temperature flames.

4. Some sample container cap liners can be a source of zinc contamination. To circumvent or avoid this problem, the use of polypropylene caps is recommended.

5. For concentrations of zinc below 0.01 mg/L, either the Special Extraction Procedure given in part 9.2 of the Atomic Absorption Methods section or the furnace procedure, Method 289.2, is recommended.

IX. ALLOWABLE LIMITS.

The NPDES effluent limit is 0.132 mg/l for zinc.

X. QC CHECKS.

One spiked blank and spiked sample will be run with every 20 sample determinations. The spike concentration shall consist of at least 1 time the average concentration found in a typical sample for each determined parameter. Code 4052 laboratory will obtain or prepare the standard solutions.

Duplicate analysis on one sample after every ten samples are analyzed shall be performed for each parameter if enough sample volume is available.

One reagent blank shall be analyzed each day an analysis is performed for each parameter.

Split samples shall be analyzed quarterly by a control laboratory.

Code 095 will obtain performance evaluation samples from a vendor and these will be analyzed by the Code 4052 laboratory every three months.

The Code 4052 laboratory will use Windowchem™ Software's ControlChart!™ software to generate quality control charts for the atomic absorption spectrophotometer. A separate control chart will b prepared for each concentration range represented in the outfall data. Duplicate sample range resu will be charted to monitor the atomic absorption spectrophotometer's precision. Spiked blank and spiked sample percent recovery data will be charted to monitor its accuracy. Procedures for preparing and using control charts are in section 1, chapter 6 of this QA/QC manual.

XI. REFERENCES

Methods for Chemical Analysis of Water and Wastes, USEPA, EPA 600/4-79-020, Revised March 1983.

Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, USEPA, SW-846, Update II, September 1994.

Perkin Elmer, Flame AA, Analytical Methods for Atomic Absorption Spectrophotometry, Norwalk, Connecticut, Jan, 1982.

References:
EPA Method 218.1 AA, Direct Aspiration
EPA Method 3015, Microwave Assisted Acid Digestion of Aqueous Samples and Extracts

Rev: Original
Effective Date: 8/1/97

CHROMIUM

I. SCOPE AND APPLICATION.

This method provides procedures for the determination of dissolved and total recoverable chromium in groundwater, storm runoff, drinking water, surface water, industrial and domestic waste water, and saline waters. This method may also be applicable to certain domestic and industrial wastes after filtration provided that no interfering substances are present.

The detection limit of this method is 0.25 milligram of chromium per liter and the range of analysis is 0.5 - 10 milligrams per liter.

II. SUMMARY OF METHOD.

In direst aspiration atomic absorption spectroscopy a sample is aspirated and atomized in a flame. A light beam from a hollow cathode lamp whose cathode is made of chromium is directed through the flame into a monochromator, and onto a detector that measures the amount of light absorbed. Absorption depends upon the presence of free unexcited ground state atoms in the flame. Since the wavelength of the light beam is characteristic of chromium, the light energy absorbed by the flame is a measure of the chromium concentration in the sample.

The method is limited to metals in solution. The microwave assisted acid digestion method is used to facilitate total metal determination in samples that contain suspended solids.

III. INTERFERENCES.

Several interference sources may cause inaccuracies in the determination of trace elements by direct aspiration atomic absorption. Chemical interferences are caused by a lack of absorption of atoms bound in molecular combinations in the flame. This can occur when the flame is not sufficiently hot to dissociate the molecule or when the when the dissociated atom is immediately oxidized to a compound that will not dissociate at the flame temperature. The presence of high levels of dissolved solids in the sample may result in interference from non-atomic absorbance such as light scattering. Ionization interferences may occur when the flame temperature is high enough to generate the removal of an electron from a neutral atom, giving a positive charged ion. Finally, spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the chromium absorption line.

Use of the microwave assisted digestion method can introduce interferences if high pressure develops in the digestion vessel causing venting. Venting can result in either a loss of the metal of interest or sample.

IV. APPARATUS.

Glassware -- Class A volumetric flasks and pipets as required. Procedures found to provide clean labware include washing with a detergent solution, rinsing with tap water, soaking for 4 hours in a mixture of dilute acids (10% HNO_3, 10% HCl, and 80% distilled water), rinsing with reagent water and storing clean. Ideally, ground glass surfaces should be avoided to eliminate a potential source of random contamination. When this is impractical, particular attention should given to all ground glass surfaces during cleaning. Chromic acid cleaning solutions must be avoided because the chromium concentration is being determined.

Cem Corporation, Microwave Digestion System, Model MDS-81D

Perkin Elmer Atomic Absorption Spectrophotometer Model 3300 or 5000

V. SAMPLE HANDLING AND PRESERVATION.

For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods Manual. All sample bottles and laboratory glassware should be throughly washed with detergent and tap water; rinsed with 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water and finally deionized distilled water in that order. Dissolved metal determination requires the sample be filtered through a 0.[illegible] micron membrane before preserving the filtrate with nitric acid. Total metal determination [illegible] sample is preserved with nitric acid without filtering. The pH of the preserved samples should be <2. Before determining total metal concentrations the sample is digested using the microwave assisted acid digestion method.

VI. REAGENTS.

Deionized distilled water: Prepared by passing distilled water through a series of cation and anion exchange resins.

Nitric acid concentrated and (1:1): Dilute acid prepared by adding the concentrated acid to an equal volume of water.

Hydrochloric acid (1:1): Prepare a 1:1 solution of reagent grade hydrochloric acid and water.

Stock standard solutions and calibration standards: Commercially available stock standard solutions are diluted to make calibration standards to cover the concentration range desired. To make a stock solution dissolve 1.923 grams of chromium trioxide in deionized distilled water. When the solution is complete, acidify with nitric acid and dilute to one liter with deionized distilled water. (1.000 ml = 1.000 mg Cr)

VII. CALCULATIONS

Calibration Curve. The instrument's calibrated software package calculates the chromium concentration in milligrams/liter for each sample. The software package is incorporated into the instrumentation and results are displayed either digitally or printed to paper and saved to disk.

VIII. PROCEDURE

For the microwave assisted digestion method procedures see sections 1 through 10 of the SW-846 method 3510. For the analysis procedure and the calculation, see "direct aspiration" part 9.1 of the Atomic Absorption Methods Manual.

Notes:

1. The following wavelengths may also be used:
   359.3 nm relative sensitivity 1.4
   425.4 nm relative sensitivity 2
   427.5 nm relative sensitivity 3
   428.9 nm relative sensitivity 4

2. The fuel rich air-acetylene flame provides greater sensitivity but is subject to chemical and matrix interference from iron, nickel, and other metals. If the analysis is performed in a lean flame the interference can be lessened but the sensitivity will also be reduced.

3. The suppression of both Cr(III) and Cr(VI) absorption by most interfering ions in fuel rich air-acetylene flames is reportedly controlled by the addition of 1% ammonium bifluoride (CAS# 1341-49-7) in 0.2% sodium sulfate (CAS # 7757-82-6). A 1% oxine (CAS # 148-24-3) solution is also reported to be useful.

4. For levels of chromium between 50 and 200 µg/l where the air-acetylene flame can not be used or for levels below 50 µg/l, either the furnace procedure (218.2) (USEPA 1983) or the extraction procedure (218.3) (USEPA 1983) is recommended.

IX. ALLOWABLE LIMITS.

The NPDES effluent limit is 0.254 mg/l for chromium

X. QC CHECKS.

One spiked blank and spiked sample will be run with every 20 sample determinations. The spike concentration shall consist of at least 1 time the average concentration found in a typical sample for each determined parameter. Code 4052 laboratory will obtain or prepare the standard solutions.

Duplicate analysis on one sample after every ten samples are analyzed shall be performed for each parameter if enough sample volume is available.

One reagent blank shall be analyzed each day an analysis is performed for each parameter.

Split samples shall be analyzed quarterly by a control laboratory.

Code 095 will obtain performance evaluation samples from a vendor and these will be analyzed by the Code 4052 laboratory every three months.

The Code 4052 laboratory will use Windowchem™ Software's ControlChart!™ software to generate quality control charts for the atomic absorption spectrophotometer. A separate control chart will be prepared for each concentration range represented in the outfall data. Duplicate sample range results will be charted to monitor the atomic absorption spectrophotometer's precision. Spiked blank and spiked sample percent recovery data will be charted to monitor its accuracy. Procedures for preparing and using control charts are in section 1, chapter 6 of this QA/QC manual.

XI. REFERENCES

Methods for Chemical Analysis of Water and Wastes, USEPA, EPA 600/4-79-020, Revised March 1983.

Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, USEPA, SW-846, Update II, September 1994.

Perkin Elmer, Flame AA, Analytical Methods for Atomic Absorption Spectrophotometry, Norwalk, Connecticut, Jan. 1982.

References:	Rev: Original
EPA Method 272.2 AA, Graphite Furnace Technique EPA Method 3015, Microwave Assisted Acid Digestion of Aqueous Samples and Extracts	Effective Date: 8/1/97

SILVER

I. SCOPE AND APPLICATION.

This method provides procedures for the determination of dissolved and total recoverable elements by graphite furnace atomic absorption (GFAA) in ground water, surface water, drinking water, storm runoff, industrial and domestic wastewater.

For reference where this method is approved for use in compliance monitoring programs [e.g., Clean Water Act (NPDES) or Safe Drinking Water Act (SDWA)] consult both the appropriate sections of the Code of Federal Regulation (40 CFR Part 136 Table 1B for NPDES, and Part 141 & 141.23 for drinking water), and the latest Federal Register announcements.

Dissolved metals can be determined in aqueous samples after suitable filtration and acid preservation. The microwave assisted acid digestion method is used to facilitate total metal determination in samples that contain suspended solids and is required for silver determinations.

For the determination of total recoverable metals in aqueous and solid samples a digestion/extraction is required prior to analysis when the elements are not in solution (e.g., soils, sludges, sediments and aqueous samples that may contain particulate and suspended solids). Aqueous samples containing suspended or particulate material ≥ 1% (w/v) should be extracted as a solid type sample. The microwave assisted acid digestion method is used to facilitate total metal determination in samples that contain solids.

Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples, fortified sample matrices and even fortified blanks if determined as a dissolved metal or by "direct analysis" where the sample has not been processed using the microwave assisted acid digestion method. For this reason it is recommended that samples be digested prior to the determination of silver. The microwave assisted acid digestion method is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, succeeding smaller volume, well mixed aliquots should be prepared until the analysis solution contains < 0.1 mg/L silver.

The method's optimum concentration range is 1-25 µg/L and the detection limit is 0.2 µg/L. These are intended as a guide and are typical of a system optimized for the element employing commercial instrumentation. However, actual method detection limits and linear working ranges will be dependent on the sample matrix, instrumentation and selected operating conditions.

The sensitivity and limited linear dynamic range (LDR) of GFAA often implies the need to dilute a sample prior to analysis. The actual magnitude of the dilution as well as the cleanliness of the labware used to perform the dilution can dramatically influence the quality of the analytical result. Therefore, sample types requiring large dilutions (>50:1) should be analyzed by an another approved test procedure which has a larger LDR or which is inherently less sensitive than GFAA.

II. SUMMARY OF METHOD.

An aliquot of a well mixed, homogeneous aqueous or solid sample is accurately weighed or measured for sample processing. For total recoverable analysis of a solid or an aqueous sample containing undissolved material, metals are first solubilized using the microwave assisted acid digestion method. After cooling, the sample is made up to volume, is mixed and centrifuged or allowed to settle overnight prior to analysis. For the determination of dissolved metals in a filtered aqueous sample aliquot, or for the "direct analysis" total recoverable determination of metals where sample turbidity is < 1 NTU, the sample is made ready for analysis by the appropriate addition of nitric acid, and then diluted to a predetermined volume and mixed before analysis.

The metals listed in this method are determined by stabilized temperature platform graphite furnace atomic absorption (STPGFAA). In STPGFAA, the sample and the matrix modifier are first pipetted onto the platform or a device which provides delayed atomization. The furnace chamber is then purged with a continuous flow of a premixed gas (95% argon - 5% hydrogen) and the sample is dried at a relatively low temperature (about 120°C) to avoid spattering. Once dried, the sample is treated in a char or ash step which is designed to minimize the interference effects caused by the contaminant sample matrix. After the char step the furnace is allowed to cool prior to atomization. The atomization cycle is characterized by rapid heating of the furnace to a temperature where the metal is atomized from the pyrolytic graphite surface into a stopped gas flow atmosphere of argon containing 5% hydrogen. (Only selenium is determined in an atmosphere of high purity argon.) The resulting atomic cloud absorbs the element specific atomic emission produced by a hollow cathode lamp (HCL) or an electrode-less discharge lamp (EDL). Following analysis the furnace is subjected to a clean out period of high temperature and continuous argon flow. Because the resulting absorbance usually has a nonspecific component associated with the actual metal absorbance, an instrumental background correction device is required to subtract from the total signal the component which is nonspecific to the metal. In the absence of interferences, the background corrected absorbance is directly related to the concentration of the metal. Interferences relating to STPGFAA must be recognized and corrected. Suppressions or enhancements of instrument response caused by the sample matrix must be corrected by the method of standard addition.

II. INTERFERENCES.

Several interference sources may cause inaccuracies in the determination of trace elements by GFAA. These interferences can be classified into three major subdivisions, namely spectral, matrix, and memory.

Spectral interferences are caused by the absorbance of light by a molecule or atom which is not the metal of interest, or broad spectrum or emission black body radiation.

Spectral interferences caused by an element only occur if there is a spectral overlap between the wavelength of the interfering element and the metal of interest. Fortunately, this type of interference is relatively uncommon in STPGFAA because of the narrow atomic line widths associated with STPFAA. In addition, the use of appropriate furnace temperature programs and high spectral purity lamps as light sources can minimize the possibility of this type of interference. However, molecular absorbencies can span several hundred nanometers producing broadband spectral interferences. This type of interference is far more common in STPGFAA. The use of matrix modifiers, selective volatilization, and background correctors are all attempts to eliminate unwanted nonspecific absorbance. The nonspecific component of the total absorbance can vary considerably from sample type to sample type. Therefore, the effectiveness of a particular background correction device may vary depending on the actual metal wavelength used as well as the nature and magnitude of the interference. The background correction device to be used with this method is not specified, however, it must provide an analytical condition that is not subject to the occurring inter-element spectral interferences of palladium on copper, iron on selenium, and aluminum on arsenic.

Spectral interferences are also caused by the emissions from black body radiation produced during the atomization furnace cycle. This black body emission reaches the photomultiplier tube, producing erroneous results. The magnitude of this interference can be minimized by proper furnace tube alignment and monochromator design. In addition, atomization temperatures which adequately volatilize the metal of interest without producing unnecessary black body radiation can help reduce unwanted background emission during analysis.

Matrix interferences are caused by sample components which inhibit the formation of free atomic metal atoms during the atomization cycle.

Matrix interferences can be of a chemical or physical nature. In this method the use of a delayed atomization device which provides stabilized temperatures is required. These devices provide an environment which is more conducive to the formation of free metal atoms and thereby minimize this type of interference. This type of interference can be detected by analyzing the sample plus a sample aliquot fortified with a known concentration of the metal. If the determined concentration of the metal addition is outside a designated range, a possible matrix effect should be suspected.

The use of nitric acid is preferred for GFAA analyses in order to minimize vapor state anionic chemical interferences, however, in this method hydrochloric acid is required to maintain stability in solution containing antimony and silver. When hydrochloric acid is used, the chloride ion vapor state interferences must be reduced using an appropriate matrix modifier. In this method a combination modifier of palladium, magnesium nitrate and a hydrogen (5%)-argon (95%) gas mixture is used for this purpose.

The palladium used in the modifier preparation may have elevated levels of Ag which will cause elevated blank absorbencies.

Memory interferences result from analyzing a sample containing a high concentration of an element (typically a high atomization temperature element) which cannot be removed quantitatively in one

complete set of furnace steps. The metal which remains in the furnace can produce false positive signals on the subsequent sample(s). Therefore, the analyst should establish the metal concentration which can be injected into the furnace and adequately removed in one complete set of furnace cycles. If this concentration is exceeded, the sample should be diluted and a blank analyzed to assure the memory effect has been eliminated before reanalyzing the diluted sample.

Use of the microwave assisted digestion method can introduce interferences if high pressure develops in the digestion vessel causing venting. Venting can result in either a loss of metals or sample.

IV. APPARATUS.

Cem Corporation, Microwave Digestion System, Model MDS-81D

Perkin Elmer Graphite Furnace Atomic Absorption Spectrophotometer Model 3300

The GFAA spectrometer must be capable of programmed heating of the graphite tube and the associated delayed atomization device. The instrument must be equipped with an adequate background correction device capable of removing undesirable non-specific absorbance over the spectral region of interest and provide an analytical condition not subject to the occurrence of inter-element spectral overlap interferences. The furnace device must be capable of utilizing an alternate gas supply during specified cycles of the analysis. The capability to record relatively fast (<1 s) transient signals and evaluate data on a peak area basis is preferred. In addition, a recirculating refrigeration bath is recommended for improved reproducibility of furnace temperatures.

Single element hollow cathode lamps or single element electrode-less discharge lamps along with the associated power supplies.

Argon gas supply (high-purity grade, 99.99%) for use during the atomization of silver, for sheathing the furnace tube when in operation, and during furnace clean out.

Alternate gas mixture (hydrogen 5% - argon 95%) for use as a continuous gas flow environment during the dry and char furnace cycles.

Auto-sampler capable of adding matrix modifier solutions to the furnace, a single addition of metal, and completing methods of standard additions when required.

Analytical balance, with capability to measure to 0.1 mg, for use in weighing solids, for preparing standards, and for determining dissolved solids in digests or extracts.

A temperature adjustable hot plate capable of maintaining a temperature of 95°C.

(optional) A temperature adjustable block digester capable of maintaining a temperature of 95°C and equipped with 250-ml constricted digestion tubes.

(optional) A steel cabinet centrifuge with guard bowl, electric timer and brake.

A gravity convection drying oven with thermostatic control capable of maintaining 180°C ± 5°C.

(optional) An air displacement pipette capable of delivering volumes ranging from 100 to 2500 μL with an assortment of high quality disposable pipet tips.

Mortar and pestle, ceramic or nonmetallic material.

Polypropylene sieve, 5-mesh (4 mm opening).

Labware - All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives. Procedures found to provide clean labware include washing with a detergent solution, rinsing with tap water, soaking for 4 hours in a mixture of dilute acids (10% HNO_3, 10% HCl, and 80% distilled water), rinsing with reagent water and storing clean. Ideally, ground glass surfaces should be avoided to eliminate a potential source of random contamination. When this is impractical, particular attention should given to all ground glass surfaces during cleaning. Chromic acid cleaning solutions must be avoided because chromium is an metal.

Glassware - Volumetric flasks, graduated cylinders, funnels and centrifuge tubes (glass and/or metal-free plastic).

Assorted calibrated pipettes.

Conical Phillips beakers, 250-ml with 50-mm watch glasses.

Griffin beakers, 250-ml with 75-mm watch glasses and (optional) 75-mm ribbed watch glasses.

(optional) PTFE and/or quartz Griffin beakers, 250-ml with PTFE covers.

Evaporating dishes or high-form crucibles, porcelain, 100 ml capacity.

Narrow-mouth storage bottles, FEP (fluorinated ethylene propylene) with screw closure, 125-ml to 1-L capacities.

One piece stem FEP wash bottle with screw closure, 125-ml capacity.

V. SAMPLE HANDLING AND PRESERVATION.

Prior to the collection of an aqueous sample, consideration should be given to the type of data required, (i.e., dissolved or total recoverable), so that appropriate preservation and pretreatment steps can be taken. The pH of all aqueous samples must be tested immediately prior to dividing for processing or "direct analysis" to ensure the sample has been properly preserved. If properly acid preserved, the sample can be held up to 6 months before analysis.

For the determination of the dissolved elements, the sample must be filtered through a 0.45-μm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. (Glass or plastic filtering apparatus are recommended to avoid possible contamination.) Use portion of the filtered sample to rinse the filter flask, discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1:1) nitric acid immediately following filtration to pH < 2.

For the determination of total recoverable elements in aqueous samples, samples are not filtered, but acidified with (1:1) nitric acid to pH < 2 (normally, 3 ml of (1:1) nitric acid per liter of sample is sufficient for most ambient and drinking water samples). Preservation may be done at the time of collection, however, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination it is recommended that the samples be returned to the laboratory within two weeks of collection and acid preserved upon receipt in the laboratory. Following acidification, the sample should be mixed, held for sixteen hours, and then verified to be pH < 2 just prior withdrawing an aliquot for processing or "direct analysis". If for some reason such as high alkalinity the sample pH is verified to be > 2, more acid must be added and the sample held for sixteen hours until verified to be pH < 2.

> NOTE: When the nature of the sample is either unknown or is known to be hazardous, acidification should be done in a fume hood.

Solid samples usually require no preservation prior to analysis other than storage at 4°C. There is no established holding time limitation for solid samples.

For aqueous samples, a field blank should be prepared and analyzed as required by the data us Use the same container and acid as used in sample collection.

VI. REAGENTS.

Reagents may contain elemental impurities which might affect analytical data. Only high-purity reagents that conform to the American Chemical Society specifications should be used whenever possible. If the purity of a reagent is in question, analyze for contamination. All acids used for this method must be of ultra high-purity grade or equivalent. Suitable acids are available from a number of manufacturers. Redistilled acids prepared by sub-boiling distillation are acceptable.

Hydrochloric acid, concentrated (sp.gr. 1.19) - HCl.

> Hydrochloric acid (1:1) - Add 500 ml concentrated HCl to 400 ml reagent water and dilute to 1 L.
>
> Hydrochloric acid (1:4) = Add 200 ml concentrated HCl to 400 ml reagent water and dilute to 1 L.

Nitric acid, concentrated (sp.gr. 1.41) - HNO_3.

> Nitric acid (1:1) - Add 500 ml concentrated HNO_3 to 400 ml reagent water and dilute to

Nitric acid (1:5) - Add to 50 ml concentrated HNO_3 to 250 ml reagent water.

Nitric acid (1:9) - Add 10 ml concentrated HNO_3 to 90 ml reagent water.

Reagent water. All references to water in this method refer to ASTM Type I grade water.

Matrix Modifier, dissolve 300 mg palladium (Pd) powder in conc. HNO_3 (1 ml of HNO_3, adding 0.1 ml of concentrated HCl if necessary). Dissolve 200 mg of $Mg(NO_3)_2$ in ASTM Type I water. Pour the two solutions together and dilute to 100 ml with ASTM Type I water.

> **NOTE**: It is recommended that the matrix modifier be analyzed separately in order to assess the contribution of the modifier to the absorbance of calibration and reagent blank solutions.

Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals (99.99 to 99.999% pure). All compounds must be dried for 1 h at 105°C, unless otherwise specified. It is recommended that stock solutions be stored in FEP bottles. Replace stock standards when succeeding dilutions for preparation of calibration standards can not be verified.

Typical stock solution preparation procedures follow for 1-L quantities, but for the purpose of pollution prevention, the analyst is encouraged to prepare smaller quantities when possible.

Silver solution, stock, 1 ml = 1000 μg Ag (1000 mg/L): Dissolve 1.575 g $AgNO_3$ in deionized distilled water. Add 10 ml of concentrated HNO_3 and make up to 1 liter.

Preparation of Calibration Standards - Fresh calibration standards (CAL Solution) should be prepared every two weeks, or as needed. Dilute each of the stock standard solutions to levels appropriate to the operating range of the instrument using the appropriate acid diluent (see note). The element concentrations in each CAL solution should be sufficiently high to produce good measurement precision and to accurately define the slope of the response curve. The instrument calibration should be initially verified using a quality control sample.

> **NOTE**: The appropriate acid diluent for the determination of dissolved elements in water and for the "direct analysis" of drinking water with turbidity < 1 NTU is 1% HNO_3. For total recoverable elements in waters, the appropriate acid diluent is 2% HNO_3 and 1% HCl, and the appropriate acid diluent is 2% HNO_3 and 1% HCl, and the appropriate acid diluent for total recoverable elements in solid samples is 2% HNO_3 and 2% HCl. The reason for these different diluents is to match the types of acids and the acid concentrations of the samples with the acid present in the standards and blanks.

Blanks - Four types of blanks are required for this method. A calibration blank is used to establish the analytical calibration curve, the laboratory reagent blank (LRB) is used to assess possible contamination from the sample preparation procedure and to assess spectral background, the laboratory fortified blank is used to assess routine laboratory performance, and a rinse blank is used to flush the instrument auto-sampler uptake system. All diluent acids should be made from concentrated acids and ASTM Type I water.

The calibration blank consists of the appropriate acid diluent (HCl/HNO_3) in ASTM Type I water. The calibration blank should be stored in a FEP bottle.

The laboratory reagent blank (LRB) must contain all the reagents in the same volumes as used in processing the samples. The LRB must be carried through the same entire preparation scheme as the samples including sample digestion when applicable.

The laboratory fortified blank (LFB) is prepared by fortifying an aliquot of the laboratory reagent blank with all metals to provide a final concentration which will produce an absorbance of approximately 0.1 for each metal. The LFB must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable.

The laboratory fortified blank (LFB) is prepared by fortifying an aliquot of the laboratory reagent blank with all metals to provide a final concentration which will produce an absorbance of approximately 0.1 for each metal. The LFB must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable.

The rinse blank is prepared as needed by adding 1.0 ml of conc. HNO_3 and 1.0 ml conc. HCl to 1 liter of ASTM Type I water and stored in a convenient manner.

Instrument Performance Check (IPC) Solution - The IPC solution is used to periodically verify instrument performance during analysis. It should be prepared in the same acid mixture as the calibration standards by combining method metals at appropriate concentrations to approximate the midpoint of the calibration curve. The IPC solution should be prepared from the same standard stock solutions used to prepare the calibration standards and stored in a FEP bottle. Agency programs may specify or request that additional instrument performance check solutions be prepared at specified concentrations in order to meet particular program needs.

Quality Control Sample (QCS) - For initial and periodic verification of calibration standards and instrument performance, analysis of a QCS is required. The QCS must be obtained from an outside source different from the standard stock solutions and prepared in the same acid mixture as the calibration standards. The concentration of the metals in the QCS solution should be such that the resulting solution will provide an absorbance reading of approximately 0.1. The QCS solution should be stored in a FEP bottle and analyzed as needed to meet data-quality needs. A fresh solution should be prepared quarterly or more frequently as needed.

VII. CALCULATIONS

Sample data should be reported in units of $\mu g/L$ for aqueous samples and mg/kg dry weight for solid samples. The instrument's calibrated software package calculates the silver concentration in $\mu g/L$ for each sample. The software package is incorporated into the instrumentation and results are displayed either digitally or printed to paper and saved to disk.

For dissolved aqueous metals report the data generated directly from the instrument with allowance for sample dilution. Do not report metal concentrations below the IDL.

For total recoverable aqueous metals, multiply solution metal concentrations by the dilution factor 0.5, when 100 ml aliquot is used to produce the 50 ml final solution, round the data to the tenths place and report the data in μg/L up to three significant figures. If a different aliquot volume other than 100 ml is used for sample preparation, adjust the dilution factor accordingly. Also, account for any additional dilution of the prepared sample solution needed to complete the determination of metals exceeding the upper limit of the calibration curve. Do not report data below the determined metal MDL concentration or below an adjusted detection limit reflecting smaller sample aliquots used in processing or additional dilutions required to complete the analysis.

For total recoverable metals in solid samples, round the solution metal concentrations (μg/L) to the tenths place. Report the data up to three significant figures as mg/kg dry-weight basis unless specified otherwise by the program or data user. Calculate the concentration using the equation below:

$$\text{Sample Conc. (mg/kg) dry-weight basis} = \frac{C \times V \times D}{W}$$

where: C = Concentration in extract (μg x 0.01/L)
V = Volume of extract (L, 100 ml = 0.1 L)
D = Dilution factor (undiluted = 1)
W = Weight of sample aliquot extracted (g x 0.001 = kg)

Do not report metal data below the estimated solids MDL or an adjusted MDL because of additional dilutions required to complete the analysis.

To report percent solids in solid samples calculate as follows:

$$\% \text{ solids (S)} = \frac{DW}{WW} \times 100$$

where: DW = Sample weight (g) dried at 60°C
WW =Sample weight (g) before drying

NOTE: If the data user, program or laboratory requires that the reported percent solids be determined by drying at 105°C, repeat the procedure using a separate portion (> 20 g) of the sample and dry to constant weight at 103-105°C.

The QC data obtained during the analyses provide an indication of the quality of the sample data and should be provided with the sample results.

VIII. PROCEDURE

Aqueous Sample Preparation - Dissolved Metals

For the determination of dissolved metals in ground and surface waters, pipet an aliquot (≥ 20 ml) of the filtered, acid preserved sample into a 50-ml polypropylene centrifuge tube. Add an appropriate volume of (1:1) nitric acid to adjust the acid concentration of the aliquot to approximate a 1% (v/v) nitric acid solution (e.g., add 0.4 ml (1:1) HNO_3 to a 20 ml aliquot of sample). Cap the tube and mix. The sample is now ready for analysis. Allowance for sample dilution should be made in the calculations.

NOTE: If a precipitant is formed during acidification, transport, or storage, the sample aliquot must be treated prior to analysis.

Aqueous Sample Preparation - Total Recoverable Metals

For the "direct analysis" of total recoverable metals in drinking water samples containing turbidity < 1 NTU, treat an unfiltered acid preserved sample aliquot using the sample preparation procedure while making allowance for sample dilution in the data calculation.

For the determination of total recoverable metals in aqueous samples (other than drinking water with < 1 NTU turbidity), use the microwave assisted digestion method procedures, see sections 1 through 10 of the SW-846 method 3510.

Allow any undissolved material to settle overnight, or centrifuge a portion of the prepa sample until clear. (If after centrifuging or standing overnight the sample contains suspended solids that would clog or affect the sample introduction system, a portion of the sample may be filtered for their removal prior to analysis. However, care should be exercised to avoid potential contamination from filtration.) The sample is now ready for analysis. Because the effects of various matrices on the salability of diluted samples cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.

Sample Analysis

Prior to daily calibration of the instrument inspect the graphite furnace, the sample uptake system and auto-sampler injector for any change in the system that would affect instrument performance. Clean the system and replace the graphite tube and/or platform when needed or on a daily basis.

Before beginning daily calibration the instrument system should be reconfigured to the selected optimized operating conditions for the "direct analysis" drinking water with turbidity < 1 NTU. Initiate data system and allow a period of not less than 15 min for instrument and hollow cathode lamp warm up. If an EDL is to be used, allow 30 min for warm up.

After the warm up period but before calibration, instrument stability must be demonstrated by analyzing a standard solution with a concentration 20 times the IDL a minimum of five ti

The resulting reactive standard deviation (RSD) of absorbance signals must be < 5%. If the RSD is > 5%, determine and correct the cause before calibrating the instrument.

For initial and daily operation calibrate the instrument according to the instrument manufacturer's recommended procedures using the calibration blank and calibration standards prepared at three or more concentrations within the usable linear dynamic range of the metal.

An auto sampler must be used to introduce all solutions into the graphite furnace. Once the standard, sample or QC solution plus the matrix modifier is injected, the furnace controller completes furnace cycles and clean out period as programmed. Metal signals must be integrated and collected as peak area measurements. Background absorbencies, background corrected metal signals, and determined metal concentrations on all solutions must be able to be displayed on a CRT for immediate review by the analyst and be available as hard copy for documentation to be kept on file. Flush the auto-sampler solution uptake system with the rinse blank between each solution injected.

After completion of the initial requirements of this method, samples should be analyzed in the same operational manner used in the calibration routine.

During the analysis of samples, the laboratory must comply with the required quality control. Only for the determination of dissolved metals or the "direct analysis" of drinking water with turbidity of < 1 NTU is the sample digestion step of the LRB, LFB, and LFM not required.

For every new or unusual matrix, when practical, it is highly recommended that an inductively coupled plasma atomic emission spectrometer be used to screen for high element concentration. Information gained from this may be used to prevent potential damage to the instrument and to better estimate which elements may require analysis by graphite furnace.

Determined sample metal concentrations that are 90% or more of the upper limit of calibration must either be diluted with acidified reagent water and reanalyzed with concern for memory effects, or determined by another approved test procedure that is less sensitive. Samples with a background absorbance > 1.0 must be appropriately diluted with acidified reagent water and reanalyzed.

When it is necessary to assess an operative matrix interference (e.g., signal reduction due to high dissolved solids), the test described is recommended.

Standard Additions - If the method of standard addition is required, the following procedure is recommended:

The standard addition technique involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the metal signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interference, which causes a baseline shift. The simplest version of this technique is the single-addition method. The procedure is as follows: Two identical aliquots

of the sample solution, each of the volume V_X, are taken. To the first (labeled A) is added a small volume V_S of a standard metal solution of concentration C_S. To the second (labeled B) is added the same volume V_S of the solvent. The analytical signals of A and B are measu and corrected for erroneous signals. The unknown sample concentration C_X is calculated:

$$C_x = \frac{S_B V_S C_S}{(S_A - S_B)V_X}$$

where, S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_S and C_S should be chosen so that S_A is roughly twice S_B on the average. It is best if V_S is made much less than V_X, and thus C_S is much greater than C_X, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results from this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.

2. The chemical form of the metal added must respond in the same manner as the metal in the sample.

3. The interference effect must be constant over the working range of concern.

4. The signal must be corrected for any additive interference.

IX. ALLOWABLE LIMITS.

The maximum silver concentration allowable in the discharge from NPDES outfall 001 at the sewage treatment plant is 0.010 mg/l

X. QC CHECKS.

One spiked blank and spiked sample will be run with every 20 sample determinations. The spike concentration shall consist of at least 1 time the average concentration found in a typical sample for each determined parameter. Code 4052 laboratory will obtain or prepare the standard solutions.

Duplicate analysis on one sample after every ten samples are analyzed shall be performed for each parameter if enough sample volume is available.

One reagent blank shall be analyzed each day an analysis is performed for each parameter.

Split samples shall be analyzed quarterly by a control laboratory.

Code 095 will obtain performance evaluation samples from a vendor and these will be analyzed by the Code 4052 laboratory every three months.

The Code 4052 laboratory will use Windowchem™ Software's ControlChart!™ software to generate quality control charts for the atomic absorption spectrophotometer. A separate control chart will be prepared for each concentration range represented in the outfall data. Duplicate sample range results will be charted to monitor the atomic absorption spectrophotometer's precision. Spiked blank and spiked sample percent recovery data will be charted to monitor its accuracy. Procedures for preparing and using control charts are in section 1, chapter 6 of this QA/QC manual.

XI. REFERENCES

Methods for Chemical Analysis of Water and Wastes, USEPA, EPA 600/4-79-020, Revised March 1983.

Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, USEPA, SW-846, Update II, September 1994.

Perkin Elmer, Flame AA, Analytical Methods for Atomic Absorption Spectrophotometry, Norwalk, Connecticut, Jan, 1982.

References:
EPA Method 249.1 AA, Direct Aspiration Technique
EPA Method 3015, Microwave Assisted Acid Digestion of Aqueous Samples and Extracts

Rev: Original
Effective Date: 8/1/97

NICKEL

I. SCOPE AND APPLICATION.

This method provides procedures for the determination of dissolved and total recoverable nickel in groundwater, storm runoff, drinking water, surface water, industrial and domestic waste water, and saline waters. This method may also be applicable to certain domestic and industrial wastes after filtration provided that no interfering substances are present.

The detection limit of this method is 0.04 milligram of nickel per liter and the range of analysis is 0.3 - 5 milligrams per liter.

II. SUMMARY OF METHOD.

In direst aspiration atomic absorption spectroscopy a sample is aspirated and atomized in a flame. A light beam from a hollow cathode lamp whose cathode is made of nickel is directed through the flame into a monochromator, and onto a detector that measures the amount of light absorbed. Absorption depends upon the presence of free unexcited ground state atoms in the flame. Since t wavelength of the light beam is characteristic of chromium, the light energy absorbed by the flame is a measure of the nickel concentration in the sample.

The method is limited to metals in solution. The microwave assisted acid digestion method is used to facilitate total metal determination in samples that contain suspended solids.

III. INTERFERENCES.

Several interference sources may cause inaccuracies in the determination of trace elements by direct aspiration atomic absorption. Chemical interferences are caused by a lack of absorption of atoms bound in molecular combinations in the flame. This can occur when the flame is not sufficiently hot to dissociate the molecule or when the when the dissociated atom is immediately oxidized to a compound that will not dissociate at the flame temperature. The presence of high levels of dissolved solids in the sample may result in interference from non-atomic absorbance such as light scattering. Ionization interferences may occur when the flame temperature is high enough to generate the removal of an electron from a neutral atom, giving a positive charged ion. Finally, spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the nickel absorption line.

Use of the microwave assisted digestion method can introduce interferences if high pressure develops in the digestion vessel causing venting. Venting can result in either a loss of metals or sample.

IV. APPARATUS.

Glassware -- Class A volumetric flasks and pipets as required. Procedures found to provide clean labware include washing with a detergent solution, rinsing with tap water, soaking for 4 hours in a mixture of dilute acids (10% HNO_3, 10% HCl, and 80% distilled water), rinsing with reagent water and storing clean. Ideally, ground glass surfaces should be avoided to eliminate a potential source of random contamination. When this is impractical, particular attention should given to all ground glass surfaces during cleaning. Chromic acid cleaning solutions must be avoided because chromium is an metal.

Cem Corporation, Microwave Digestion System, Model MDS-81D

Perkin Elmer Atomic Absorption Spectrophotometer Model 3300 or 5000

V. SAMPLE HANDLING AND PRESERVATION.

For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods Manual. All sample bottles and laboratory glassware should be throughly washed with detergent and tap water; rinsed with 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water and finally deionized distilled water in that order. Dissolved metal determination requires the sample be filtered through a 0.45 micron membrane before preserving the filtrate with nitric acid. Total metal determination the sample is preserved with nitric acid without filtering. The pH of the preserved samples should be <2. Before determining total metal concentrations the sample is digested using the microwave assisted acid digestion method.

VI. REAGENTS.

Deionized distilled water: Prepared by passing distilled water through a series of cation and anion exchange resins.

Nitric acid concentrated and (1:1): Dilute acid prepared by adding the concentrated acid to an equal volume of water.

Hydrochloric acid (1:1): Prepare a 1:1 solution of reagent grade hydrochloric acid and water.

Stock standard solutions and calibration standards: Commercially available stock standard solutions are diluted to make calibration standards to cover the concentration range desired. To make a stock solution dissolve 4.953 grams of analytical reagent grade nickel nitrate(CAS # 13475-00-7) in deionized distilled water. When the solution is complete, acidify with nitric acid and dilute to one liter with deionized distilled water. (1 ml = 1 mg Ni)

VII. CALCULATIONS

Calibration Curve. The instrument's calibrated software package calculates the nickel concentrati in milligrams/liter for each sample. The software package is incorporated into the instrumentation and results are displayed either digitally or printed to paper and saved to disk.

VIII. PROCEDURE

For the microwave assisted digestion method procedures see sections 1 through 10 of the SW-846 method 3510. For the analysis procedure and the calculation, see "direct aspiration" part 9.1 of the Atomic Absorption Methods Manual.

Notes:

1. The 352.4 nm wavelength is less susceptible to spectral interference than the 232.0 nm wavelength and may be used. The calibration curve is more linear at this wavelength: however, there is some loss of sensitivity .

2. For levels of nickel below 100 µg/l, either the special extraction procedure, given in part 9.2 of the Atomic Absorption Methods section or the furnace technique is recommended (USEPA 1983).

IX. ALLOWABLE LIMITS.

The NPDES effluent limit is 0.071 mg/l for nickel

X. QC CHECKS.

One spiked blank and spiked sample will be run with every 20 sample determinations. The spike concentration shall consist of at least 1 time the average concentration found in a typical sample for each determined parameter. Code 4052 laboratory will obtain or prepare standard solutions.

Duplicate analysis on one sample after every ten samples are analyzed shall be performed for each parameter if enough sample volume is available.

One reagent blank shall be analyzed each day an analysis is performed for each parameter.

Split samples shall be analyzed quarterly by a control laboratory.

Code 095 will obtain performance evaluation samples from a vendor and these will be analyzed by the Code 4052 laboratory every three months.

The Code 4052 laboratory will use Windowchem™ Software's ControlChart!™ software to generate quality control charts for the atomic absorption spectrophotometer. A separate control chart will be prepared for each concentration range represented in the outfall data. Duplicate sample range results will be charted to monitor the atomic absorption spectrophotometer's precision. Spiked blar

spiked sample percent recovery data will be charted to monitor its accuracy. Procedures for preparing and using control charts are in section 1, chapter 6 of this QA/QC manual.

XI. REFERENCES

Methods for Chemical Analysis of Water and Wastes, USEPA, EPA 600/4-79-020, Revised March 1983.

Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, USEPA, SW-846, Update II, September 1994.

Perkin Elmer, Flame AA, Analytical Methods for Atomic Absorption Spectrophotometry, Norwalk, Connecticut, Jan, 1982.

References:
EPA Method 239.2 AA, Graphite Furnace Technique
EPA Method 3015, Microwave Assisted Acid Digestion of Aqueous Samples and Extracts

Rev: Original
Effective Date: 8/1/97

LEAD

I. SCOPE AND APPLICATION.

This method provides procedures for the determination of dissolved and total recoverable elements by graphite furnace atomic absorption (GFAA) in ground water, surface water, drinking water, storm runoff, industrial and domestic wastewater. This method is also applicable to the determination of total recoverable elements in sediment, sludges, and soil.

For reference where this method is approved for use in compliance monitoring programs [e.g., Clean Water Act (NPDES) or Safe Drinking Water Act (SDWA)] consult both the appropriate sections of the Code of Federal Regulation (40 CFR Part 136 Table 1B for NPDES, and Part 141 & 141.23 for drinking water), and the latest Federal Register announcements.

Dissolved metals can be determined in aqueous samples after suitable filtration and acid preservation. The microwave assisted acid digestion method is used to facilitate total metal determination in samples that contain suspended solids.

With the exception of silver, where this method is approved for the determination of certain me and metalloid contaminants in drinking water, samples may be analyzed by direct injection into the furnace without acid digestion if the sample has been properly preserved with acid, has turbidity of < 1 NTU at the time of analysis, and is analyzed using the appropriate method matrix modifiers. This total recoverable determination procedure is referred to as "direct analysis". However, in the determination of some primary drinking water metal contaminants, such as arsenic and thallium concentration of the sample may be required prior to analysis in order to meet drinking water acceptance performance criteria.

For the determination of total recoverable metals in aqueous and solid samples a digestion/extraction is required prior to analysis when the elements are not in solution (e.g., soils, sludges, sediments and aqueous samples that may contain particulate and suspended solids). Aqueous samples containing suspended or particulate material ≥ 1% (w/v) should be extracted as a solid type sample. The microwave assisted acid digestion method is used to facilitate total metal determination in samples that contain solids.

Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples, fortified sample matrices and even fortified blanks if determined as a dissolved metal or by "direct analysis" where the sample has not been processed using the microwave assisted acid digestion method. For this reason it is recommended that samples be digested prior to the determination of silver. The microwave assisted acid digestion method is suitable for

determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, succeeding smaller volume, well mixed aliquots should be prepared until the analysis solution contains < 0.1 mg/L silver. The extraction of solid samples containing concentrations of silver > 50 mg/kg should be treated in a similar manner.

Method detection limits and instrument operating conditions for the applicable elements are intended as a guide and are typical of a system optimized for the element employing commercial instrumentation. However, actual method detection limits and linear working ranges will be dependent on the sample matrix, instrumentation and selected operating conditions.

The sensitivity and limited linear dynamic range (LDR) of GFAA often implies the need to dilute a sample prior to analysis. The actual magnitude of the dilution as well as the cleanliness of the labware used to perform the dilution can dramatically influence the quality of the analytical results. Therefore, sample types requiring large dilutions (>50:1) should be analyzed by an another approved test procedure which has a larger LDR or which is inherently less sensitive than GFAA.

II. SUMMARY OF METHOD.

An aliquot of a well mixed, homogeneous aqueous or solid sample is accurately weighed or measured for sample processing. For total recoverable analysis of a solid or an aqueous sample containing undissolved material, metals are first solubilized using the microwave assisted acid digestion method. After cooling, the sample is made up to volume, is mixed and centrifuged or allowed to settle overnight prior to analysis. For the determination of dissolved metals in a filtered aqueous sample aliquot, or for the "direct analysis" total recoverable determination of metals where sample turbidity is < 1 NTU, the sample is made ready for analysis by the appropriate addition of nitric acid, and then diluted to a predetermined volume and mixed before analysis.

The metals listed in this method are determined by stabilized temperature platform graphite furnace atomic absorption (STPGFAA). In STPGFAA, the sample and the matrix modifier are first pipetted onto the platform or a device which provides delayed atomization. The furnace chamber is then purged with a continuous flow of a premixed gas (95% argon - 5% hydrogen) and the sample is dried at a relatively low temperature (about 120°C) to avoid spattering. Once dried, the sample is treated in a char or ash step which is designed to minimize the interference effects caused by the contaminant sample matrix. After the char step the furnace is allowed to cool prior to atomization. The atomization cycle is characterized by rapid heating of the furnace to a temperature where the metal (metal) is atomized from the pyrolytic graphite surface into a stopped gas flow atmosphere of argon containing 5% hydrogen. (Only selenium is determined in an atmosphere of high purity argon.) The resulting atomic cloud absorbs the element specific atomic emission produced by a hollow cathode lamp (HCL) or an electrode-less discharge lamp (EDL). Following analysis the furnace is subjected to a clean out period of high temperature and continuous argon flow. Because the resulting absorbance usually has a nonspecific component associated with the actual metal absorbance, an instrumental background correction device is required to subtract from the total signal the component which is nonspecific to the metal. In the absence of interferences, the background corrected absorbance is directly related to the concentration of the metal. Interferences relating to

STPGFAA must be recognized and corrected. Suppressions or enhancements of instrument response cause by the sample matrix must be corrected by the method of standard addition.

III. INTERFERENCES.

Several interference sources may cause inaccuracies in the determination of trace elements by GFAA. These interferences can be classified into three major subdivisions, namely spectral, matrix, and memory.

Spectral interferences are caused by the resulting absorbance of light by a molecule or atom which is not the metal of interest or emission from black body radiation.

> Spectral interferences caused by an element only occur if there is a spectral overlap between the wavelength of the interfering element and the metal of interest. Fortunately, this type of interference is relatively uncommon in STPGFAA because of the narrow atomic line widths associated with STPFAA. In addition, the use of appropriate furnace temperature programs and high spectral purity lamps as light sources can minimize the possibility of this type of interference. However, molecular absorbencies can span several hundred nanometers producing broadband spectral interferences. This type of interference is far more common in STPGFAA. The use of matrix modifiers, selective volatilization, and background correctors are all attempts to eliminate unwanted nonspecific absorbance. The nonspecific component of the total absorbance can vary considerably from sample type to sample type. Therefore, the effectiveness of a particular background correction device may vary depending on the actual metal wavelength used as well as the nature and magnitude of the interference. The background correction device to be used with this method is not specified, however, it must provide an analytical condition that is not subject to the occurring inter-element spectral interferences of palladium on copper, iron on selenium, and aluminum on arsenic.
>
> Spectral interferences are also caused by the emissions from black body radiation produced during the atomization furnace cycle. This black body emission reaches the photomultiplier tube, producing erroneous results. The magnitude of this interference can be minimized by proper furnace tube alignment and monochromator design. In addition, atomization temperatures which adequately volatilize the metal of interest without producing unnecessary black body radiation can help reduce unwanted background emission during analysis.

Matrix interferences are caused by sample components which inhibit the formation of free atomic metal atoms during the atomization cycle.

> Matrix interferences can be of a chemical or physical nature. In this method the use of a delayed atomization device which provides stabilized temperatures is required. These devices provide an environment which is more conducive to the formation of free metal atoms and thereby minimize this type of interference. This type of interference can be detected by analyzing the sample plus a sample aliquot fortified with a known concentration of the metal. If the determined concentration of the metal addition is outside a designated range, a possible matrix effect should be suspected.

The use of nitric acid is preferred for GFAA analyses in order to minimize vapor state anionic chemical interferences, however, in this method hydrochloric acid is required to maintain stability in solution containing antimony and silver. When hydrochloric acid is used, the chloride ion vapor state interferences must be reduced using an appropriate matrix modifier. In this method a combination modifier of palladium, magnesium nitrate and a hydrogen (5%)-argon (95%) gas mixture is used for this purpose.

The palladium used in the modifier preparation may have elevated levels of Ag which will cause elevated blank absorbencies.

Memory interferences result from analyzing a sample containing a high concentration of an element (typically a high atomization temperature element) which cannot be removed quantitatively in one complete set of furnace steps. The metal which remains in the furnace can produce false positive signals on the subsequent sample(s). Therefore, the analyst should establish the metal concentration which can be injected into the furnace and adequately removed in one complete set of furnace cycles. If this concentration is exceeded, the sample should be diluted and a blank analyzed to assure the memory effect has been eliminated before reanalyzing the diluted sample.

Use of the microwave assisted digestion method can introduce interferences if high pressure develops in the digestion vessel causing venting. Venting can result in either a loss of metals or sample.

IV. APPARATUS.

Cem Corporation, Microwave Digestion System, Model MDS-81D

Perkin Elmer Graphite Furnace Atomic Absorbance Spectrophotometer Model 3300

The GFAA spectrometer must be capable of programmed heating of the graphite tube and the associated delayed atomization device. The instrument must be equipped with an adequate background correction device capable of removing undesirable non-specific absorbance over the spectral region of interest and provide an analytical condition not subject to the occurrence of inter-element spectral overlap interferences. The furnace device must be capable of utilizing an alternate gas supply during specified cycles of the analysis. The capability to record relatively fast (<1 s) transient signals and evaluate data on a peak area basis is preferred. In addition, a recirculating refrigeration bath is recommended for improved reproducibility of furnace temperatures.

Single element hollow cathode lamps or single element electrode-less discharge lamps along with the associated power supplies.

Argon gas supply (high-purity grade, 99.99%) for use during the atomization of selenium, for sheathing the furnace tube when in operation, and during furnace clean out.

Alternate gas mixture (hydrogen 5% - argon 95%) for use as a continuous gas flow environment during the dry and char furnace cycles.

Auto-sampler capable of adding matrix modifier solutions to the furnace, a single addition of metal, and completing methods of standard additions when required.

Analytical balance, with capability to measure to 0.1 mg, for use in weighing solids, for preparin standards, and for determining dissolved solids in digests or extracts.

A temperature adjustable hot plate capable of maintaining a temperature of 95°C.

(optional) A temperature adjustable block digester capable of maintaining a temperature of 95°C and equipped with 250-ml constricted digestion tubes.

(optional) A steel cabinet centrifuge with guard bowl, electric timer and brake.

A gravity convection drying oven with thermostatic control capable of maintaining 180°C ± 5°C.

(optional) An air displacement pipette capable of delivering volumes ranging from 100 to 2500 μL with an assortment of high quality disposable pipet tips.

Mortar and pestle, ceramic or nonmetallic material.

Polypropylene sieve, 5-mesh (4 mm opening).

Labware - All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives. Procedures found to provide clean labware include washing with a detergent solution, rinsing with tap water, soaking for 4 hours in a mixture of dilute acids (10% HNO_3, 10% HCl, and 80% distilled water), rinsing with reagent water and storing clean. Idea ground glass surfaces should be avoided to eliminate a potential source of random contamination. When this is impractical, particular attention should given to all ground glass surfaces during cleaning. Chromic acid cleaning solutions must be avoided because chromium is an metal.

Glassware - Volumetric flasks, graduated cylinders, funnels and centrifuge tubes (glass and/or metal-free plastic).

Assorted calibrated pipettes.

Conical Phillips beakers, 250-ml with 50-mm watch glasses.

Griffin beakers, 250-ml with 75-mm watch glasses and (optional) 75-mm ribbed watch glasses.

(optional) PTFE and/or quartz Griffin beakers, 250-ml with PTFE covers.

Evaporating dishes or high-form crucibles, porcelain, 100 ml capacity.

Narrow-mouth storage bottles, FEP (fluorinated ethylene propylene) with screw closure, 125-ml to 1-L capacities.

One piece stem FEP wash bottle with screw closure, 125-ml capacity.

V. SAMPLE HANDLING AND PRESERVATION.

Prior to the collection of an aqueous sample, consideration should be given to the type of data required, (i.e., dissolved or total recoverable), so that appropriate preservation and pretreatment steps can be taken. The pH of all aqueous samples must be tested immediately prior to dividing for processing or "direct analysis" to ensure the sample has been properly preserved. If properly acid preserved, the sample can be held up to 6 months before analysis.

For the determination of the dissolved elements, the sample must be filtered through a 0.45-μm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. (Glass or plastic filtering apparatus are recommended to avoid possible contamination.) Use a portion of the filtered sample to rinse the filter flask, discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1:1) nitric acid immediately following filtration to pH < 2.

For the determination of total recoverable elements in aqueous samples, samples are not filtered, but acidified with (1:1) nitric acid to pH < 2 (normally, 3 ml of (1:1) acid per liter of sample is sufficient for most ambient and drinking water samples). Preservation may be done at the time of collection, however, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination it is recommended that the samples be returned to the laboratory within two weeks of collection and acid preserved upon receipt in the laboratory. Following acidification, the sample should be mixed, held for sixteen hours, and then verified to be pH < 2 just prior withdrawing an aliquot for processing or "direct analysis". If for some reason such as high alkalinity the sample pH is verified to be > 2, more acid must be added and the sample held for sixteen hours until verified to be pH < 2.

> NOTE: When the nature of the sample is either unknown or is known to be hazardous, acidification should be done in a fume hood.

Solid samples usually require no preservation prior to analysis other than storage at 4°C. There is no established holding time limitation for solid samples.

For aqueous samples, a field blank should be prepared and analyzed as required by the data user. Use the same container and acid as used in sample collection.

VI. REAGENTS.

Reagents may contain elemental impurities which might affect analytical data. Only high-purity reagents that conform to the American Chemical Society specifications should be used whenever possible. If the purity of a reagent is in question, analyze for contamination. All acids used for this method must be of ultra high-purity grade or equivalent. Suitable acids are available from a number of manufacturers. Redistilled acids prepared by sub-boiling distillation are acceptable.

Hydrochloric acid, concentrated (sp.gr. 1.19) - HCl.

Hydrochloric acid (1:1) - Add 500 ml concentrated HCl to 400 ml reagent water and dilute to 1 L.

Hydrochloric acid (1:4) = Add 200 ml concentrated HCl to 400 ml reagent water and dilute to 1 L.

Nitric acid, concentrated (sp.gr. 1.41) - HNO_3.

Nitric acid (1:1) - Add 500 ml concentrated HNO_3 to 400 ml reagent water and dilute to 1 L.

Nitric acid (1:5) - Add to 50 ml concentrated HNO_3 to 250 ml reagent water.

Nitric acid (1:9) - Add 10 ml concentrated HNO_3 to 90 ml reagent water.

Reagent water. All references to water in this method refer to ASTM Type I grade water.

Ammonium hydroxide, concentrated (sp. gr. 0.902).

Tartaric acid, ACS reagent grade.

Matrix Modifier, dissolve 300 mg palladium (Pd) powder in conc. HNO_3 (1 ml of HNO_3, adding 0.1 ml of concentrated HCl if necessary). Dissolve 200 mg of $Mg(NO_3)_2$ in ASTM Type I water. Pour the two solutions together and dilute to 100 ml with ASTM Type I water.

NOTE: It is recommended that the matrix modifier be analyzed separately in order to ass. the contribution of the modifier to the absorbance of calibration and reagent blank solutions.

Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals (99.99 to 99.999% pure). All compounds must be dried for 1 h at 105°C, unless otherwise specified. It is recommended that stock solutions be stored in FEP bottles. Replace stock standards when succeeding dilutions for preparation of calibration standards can not be verified.

<u>CAUTION</u>: Many of these chemicals are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow for 1-L quantities, but for the purpose of pollution prevention, the analyst is encouraged to prepare smaller quantities when possible. Concentrations are calculated based upon the weight of the pure element or upon the weight of the compound multiplied by the fraction of the metal in the compound.

From pure element,

$$\text{Concentration} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

From pure compound,

$$\text{Concentration} = \frac{\text{weight (mg) X gravimetric factor}}{\text{volume (L)}}$$

where:
gravimetric factor = the weight fraction of the metal in the compound.

Silver solution, stock, 1 ml = 1000 μg Ag: Dissolve 1.000 g Ag metal, weighed accurately to at least four significant figures, in 80 ml (1:1) HNO_3 with heating to effect dissolution. Let solution cool and dilute with reagent water in a 1-L volumetric flask. Store solution in amber bottle or wrap bottle completely with aluminum foil to protect solution from light.

Preparation of Calibration Standards - Fresh calibration standards (CAL Solution) should be prepared every two weeks, or as needed. Dilute each of the stock standard solutions to levels appropriate to the operating range of the instrument using the appropriate acid diluent (see note). The element concentrations in each CAL solution should be sufficiently high to produce good measurement precision and to accurately define the slope of the response curve. The instrument calibration should be initially verified using a quality control sample.

NOTE: The appropriate acid diluent for the determination of dissolved elements in water and for the "direct analysis" of drinking water with turbidity < 1 NTU is 1% HNO_3. For total recoverable elements in waters, the appropriate acid diluent is 2% HNO_3 and 1% HCl, and the appropriate acid diluent is 2% HNO_3 and 1% HCl, and the appropriate acid diluent for total recoverable elements in solid samples is 2% HNO_3 and 2% HCl. The reason for these different diluents is to match the types of acids and the acid concentrations of the samples with the acid present in the standards and blanks.

Blanks - Four types of blanks are required for this method. A calibration blank is used to establish the analytical calibration curve, the laboratory reagent blank (LRB) is used to assess possible contamination from the sample preparation procedure and to assess spectral background, the laboratory fortified blank is used to assess routine laboratory performance, and a rinse blank is used to flush the instrument auto-sampler uptake system. All diluent acids should be made from concentrated acids and ASTM Type I water.

The calibration blank consists of the appropriate acid diluent (HCl/HNO_3) in ASTM Type I water. The calibration blank should be stored in a FEP bottle.

The laboratory reagent blank (LRB) must contain all the reagents in the same volumes as used in processing the samples. The LRB must be carried through the same entire preparation scheme as the samples including sample digestion when applicable.

The laboratory fortified blank (LFB) is prepared by fortifying an aliquot of the laboratory reagent blank with all metals to provide a final concentration which will produce an absorbance of approximately 0.1 for each metal. The LFB must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable.

The laboratory fortified blank (LFB) is prepared by fortifying an aliquot of the laboratory reagent blank with all metals to provide a final concentration which will produce an absorbance of approximately 0.1 for each metal. The LFB must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable.

The rinse blank is prepared as needed by adding 1.0 ml of conc. HNO_3 and 1.0 ml conc. HCl to 1 liter of ASTM Type I water and stored in a convenient manner.

Instrument Performance Check (IPC) Solution - The IPC solution is used to periodically verify instrument performance during analysis. It should be prepared in the same acid mixture as the calibration standards by combining method metals at appropriate concentrations to approximate the midpoint of the calibration curve. The IPC solution should be prepared from the same standard stock solutions used to prepare the calibration standards and stored in a FEP bottle. Agency programs may specify or request that additional instrument performance check solutions be prepared at specified concentrations in order to meet particular program needs.

Quality Control Sample (QCS) - For initial and periodic verification of calibration standards and instrument performance, analysis of a QCS is required. The QCS must be obtained from an outside source different from the standard stock solutions and prepared in the same acid mixture as the calibration standards. The concentration of the metals in the QCS solution should be such that the resulting solution will provide an absorbance reading of approximately 0.1. The QCS solution should be stored in a FEP bottle and analyzed as needed to meet data-quality needs. A fresh solution should be prepared quarterly or more frequently as needed.

VII. CALCULATIONS

Sample data should be reported in units of $\mu g/L$ for aqueous samples and mg/kg dry weight for solid samples. The instrument's calibrated software package calculates the lead concentration in $\mu g/L$ for each sample. The software package is incorporated into the instrumentation and results are displayed either digitally or printed to paper and saved to disk.

For dissolved aqueous metals report the data generated directly from the instrument with allowance for sample dilution. Do not report metal concentrations below the IDL.

For total recoverable aqueous metals, multiply solution metal concentrations by the dilution factor 0.5, when 100 ml aliquot is used to produce the 50 ml final solution, round the data to the tenths place and report the data in $\mu g/L$ up to three significant figures. If a different aliquot volume other than 100 ml is used for sample preparation, adjust the dilution factor accordingly. Also, account for any additional dilution of the prepared sample solution needed to complete the determination of metals exceeding the upper limit of the calibration curve. Do not report data below the determined metal MDL concentration or below an adjusted detection limit reflecting smaller sample aliquots used in processing or additional dilutions required to complete the analysis.

For total recoverable metals in solid samples, round the solution metal concentrations ($\mu g/L$) to the tenths place. Report the data up to three significant figures as mg/kg dry-weight basis unless

specified otherwise by the program or data user. Calculate the concentration using the equation below:

$$\text{Sample Conc. (mg/kg) dry-weight basis} = \frac{C \times V \times D}{W}$$

where: C = Concentration in extract (μg x 0.01/L)
V = Volume of extract (L, 100 ml = 0.1 L)
D = Dilution factor (undiluted = 1)
W = Weight of sample aliquot extracted (g x 0.001 = kg)

Do not report metal data below the estimated solids MDL or an adjusted MDL because of additional dilutions required to complete the analysis.

To report percent solids in solid samples calculate as follows:

$$\% \text{ solids (S)} = \frac{DW}{WW} \times 100$$

where: DW = Sample weight (g) dried at 60°C
WW =Sample weight (g) before drying

NOTE: If the data user, program or laboratory requires that the reported percent solids be determined by drying at 105°C, repeat the procedure using a separate portion (> 20 g) of the sample and dry to constant weight at 103-105°C.

The QC data obtained during the analyses provide an indication of the quality of the sample data and should be provided with the sample results.

VIII. PROCEDURE

Aqueous Sample Preparation - Dissolved Metals

For the determination of dissolved metals in ground and surface waters, pipet an aliquot (≥ 20 ml) of the filtered, acid preserved sample into a 50-ml polypropylene centrifuge tube. Add an appropriate volume of (1:1) nitric acid to adjust the acid concentration of the aliquot to approximate a 1% (v/v) nitric acid solution (e.g., add 0.4 ml (1:1) HNO_3 to a 20 ml aliquot of sample). Cap the tube and mix. The sample is now ready for analysis. Allowance for sample dilution should be made in the calculations.

NOTE: If a precipitant is formed during acidification, transport, or storage, the sample aliquot must be treated prior to analysis.

Aqueous Sample Preparation - Total Recoverable Metals

For the "direct analysis" of total recoverable metals in drinking water samples containing turbidity < 1 NTU, treat an unfiltered acid preserved sample aliquot using the sample preparation procedure while making allowance for sample dilution in the data calculation.

For the determination of total recoverable metals in aqueous samples (other than drinking water with < 1 NTU turbidity), use the microwave assisted digestion method procedures, see sections 1 through 10 of the SW-846 method 3510.

Allow any undissolved material to settle overnight, or centrifuge a portion of the prepared sample until clear. (If after centrifuging or standing overnight the sample contains suspended solids that would clog or affect the sample introduction system, a portion of the sample may be filtered for their removal prior to analysis. However, care should be exercised to avoid potential contamination from filtration.) The sample is now ready for analysis. Because the effects of various matrices on the salability of diluted samples cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.

Sample Analysis

Prior to daily calibration of the instrument inspect the graphite furnace, the sample uptake system and auto-sampler injector for any change in the system that would affect instrument performance. Clean the system and replace the graphite tube and/or platform when needed or on a daily basis.

Before beginning daily calibration the instrument system should be reconfigured to the selected optimized operating conditions for the "direct analysis" drinking water with turbidity < 1 NTU. Initiate data system and allow a period of not less than 15 min for instrument and hollow cathode lamp warm up. If an EDL is to be used, allow 30 min for warm up.

After the warm up period but before calibration, instrument stability must be demonstrated by analyzing a standard solution with a concentration 20 times the IDL a minimum of five times. The resulting reactive standard deviation (RSD) of absorbance signals must be < 5%. If the RSD is > 5%, determine and correct the cause before calibrating the instrument.

For initial and daily operation calibrate the instrument according to the instrument manufacturer's recommended procedures using the calibration blank and calibration standards prepared at three or more concentrations within the usable linear dynamic range of the metal.

An auto sampler must be used to introduce all solutions into the graphite furnace. Once the standard, sample or QC solution plus the matrix modifier is injected, the furnace controller completes furnace cycles and clean out period as programmed. Metal signals must be integrated and collected as peak area measurements. Background absorbencies, background corrected metal signals, and determined metal concentrations on all solutions must be able to be displayed on a CRT for immediate review by the analyst and be available as hard copy for

documentation to be kept on file. Flush the auto-sampler solution uptake system with the rinse blank between each solution injected.

After completion of the initial requirements of this method, samples should be analyzed in the same operational manner used in the calibration routine.

During the analysis of samples, the laboratory must comply with the required quality control. Only for the determination of dissolved metals or the "direct analysis" of drinking water with turbidity of < 1 NTU is the sample digestion step of the LRB, LFB, and LFM not required.

For every new or unusual matrix, when practical, it is highly recommended that an inductively coupled plasma atomic emission spectrometer be used to screen for high element concentration. Information gained from this may be used to prevent potential damage to the instrument and to better estimate which elements may require analysis by graphite furnace.

Determined sample metal concentrations that are 90% or more of the upper limit of calibration must either be diluted with acidified reagent water and reanalyzed with concern for memory effects, or determined by another approved test procedure that is less sensitive. Samples with a background absorbance > 1.0 must be appropriately diluted with acidified reagent water and reanalyzed.

When it is necessary to assess an operative matrix interference (e.g., signal reduction due to high dissolved solids), the test described is recommended.

Standard Additions - If the method of standard addition is required, the following procedure is recommended:

The standard addition technique involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the metal signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interference, which causes a baseline shift. The simplest version of this technique is the single-addition method. The procedure is as follows: Two identical aliquots of the sample solution, each of the volume V_X, are taken. To the first (labeled A) is added a small volume V_S of a standard metal solution of concentration C_S. To the second (labeled B) is added the same volume V_S of the solvent. The analytical signals of A and B are measured and corrected for erroneous signals. The unknown sample concentration C_X is calculated:

$$C_x = \frac{S_B V_S C_S}{(S_A - S_B)V_X}$$

where, S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_S and C_S should be chosen so that S_A is roughly twice S_B on the average. It is best if V_S is made much less than V_X, and thus C_S is much greater than C_X, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are

best made first and carried through the entire procedure. For the results from this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.

2. The chemical form of the metal added must respond in the same manner as the metal in the sample.

3. The interference effect must be constant over the working range of concern.

4. The signal must be corrected for any additive interference.

IX. ALLOWABLE LIMITS.

The NPDES effluent limit is 0.006 mg/l for lead.

X. QC CHECKS.

One spiked blank and spiked sample will be run with every 20 sample determinations. The spike concentration shall consist of at least 1 time the average concentration found in a typical sample for each determined parameter. Code 4052 laboratory will obtain or prepare standard solutions.

Duplicate analysis on one sample after every ten samples are analyzed shall be performed for each parameter if enough sample volume is available.

One reagent blank shall be analyzed each day an analysis is performed for each parameter.

Split samples shall be analyzed quarterly by a control laboratory.

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XI. REFERENCES

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Rev: Original
Effective Date: 8/1/97

COPPER

I. SCOPE AND APPLICATION.

This method provides procedures for the determination of dissolved and total recoverable elements by graphite furnace atomic absorption (GFAA) in ground water, surface water, drinking water, storm runoff, industrial and domestic wastewater. This method is also applicable to the determination of total recoverable elements in sediment, sludges, and soil.

For reference where this method is approved for use in compliance monitoring programs [e.g., Clean Water Act (NPDES) or Safe Drinking Water Act (SDWA)] consult both the appropriate sections of the Code of Federal Regulation (40 CFR Part 136 Table 1B for NPDES, and Part 141 & 141.23 for drinking water), and the latest Federal Register announcements.

Dissolved metals can be determined in aqueous samples after suitable filtration and acid preservation. The microwave assisted acid digestion method is used to facilitate total m determination in samples that contain suspended solids.

With the exception of silver, where this method is approved for the determination of certain metal and metalloid contaminants in drinking water, samples may be analyzed by direct injection into the furnace without acid digestion if the sample has been properly preserved with acid, has turbidity of < 1 NTU at the time of analysis, and is analyzed using the appropriate method matrix modifiers. This total recoverable determination procedure is referred to as "direct analysis". However, in the determination of some primary drinking water metal contaminants, such as arsenic and thallium concentration of the sample may be required prior to analysis in order to meet drinking water acceptance performance criteria.

For the determination of total recoverable metals in aqueous and solid samples a digestion/extraction is required prior to analysis when the elements are not in solution (e.g., soils, sludges, sediments and aqueous samples that may contain particulate and suspended solids). Aqueous samples containing suspended or particulate material ≥ 1% (w/v) should be extracted as a solid type sample. The microwave assisted acid digestion method is used to facilitate total metal determination in samples that contain solids.

Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples, fortified sample matrices and even fortified blanks if determined as a dissolved metal or by "direct analysis" where the sample has not been processed using the microwave assiste

digestion method. For this reason it is recommended that samples be digested prior to the determination of silver. The microwave assisted acid digestion method is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, succeeding smaller volume, well mixed aliquots should be prepared until the analysis solution contains < 0.1 mg/L silver. The extraction of solid samples containing concentrations of silver > 50 mg/kg should be treated in a similar manner.

Method detection limits and instrument operating conditions for the applicable elements are intended as a guide and are typical of a system optimized for the element employing commercial instrumentation. However, actual method detection limits and linear working ranges will be dependent on the sample matrix, instrumentation and selected operating conditions.

The sensitivity and limited linear dynamic range (LDR) of GFAA often implies the need to dilute a sample prior to analysis. The actual magnitude of the dilution as well as the cleanliness of the labware used to perform the dilution can dramatically influence the quality of the analytical results. Therefore, sample types requiring large dilutions (>50:1) should be analyzed by an another approved test procedure which has a larger LDR or which is inherently less sensitive than GFAA.

II. SUMMARY OF METHOD.

An aliquot of a well mixed, homogeneous aqueous or solid sample is accurately weighed or measured for sample processing. For total recoverable analysis of a solid or an aqueous sample containing undissolved material, metals are first solubilized using the microwave assisted acid digestion method. After cooling, the sample is made up to volume, is mixed and centrifuged or allowed to settle overnight prior to analysis. For the determination of dissolved metals in a filtered aqueous sample aliquot, or for the "direct analysis" total recoverable determination of metals where sample turbidity is < 1 NTU, the sample is made ready for analysis by the appropriate addition of nitric acid, and then diluted to a predetermined volume and mixed before analysis.

The metals listed in this method are determined by stabilized temperature platform graphite furnace atomic absorption (STPGFAA). In STPGFAA, the sample and the matrix modifier are first pipetted onto the platform or a device which provides delayed atomization. The furnace chamber is then purged with a continuous flow of a premixed gas (95% argon - 5% hydrogen) and the sample is dried at a relatively low temperature (about 120°C) to avoid spattering. Once dried, the sample is treated in a char or ash step which is designed to minimize the interference effects caused by the contaminant sample matrix. After the char step the furnace is allowed to cool prior to atomization. The atomization cycle is characterized by rapid heating of the furnace to a temperature where the metal (metal) is atomized from the pyrolytic graphite surface into a stopped gas flow atmosphere of argon containing 5% hydrogen. (Only selenium is determined in an atmosphere of high purity argon.) The resulting atomic cloud absorbs the element specific atomic emission produced by a hollow cathode lamp (HCL) or an electrode-less discharge lamp (EDL). Following analysis the furnace is subjected to a clean out period of high temperature and continuous argon flow. Because the resulting absorbance usually has a nonspecific component associated with the actual metal absorbance, an instrumental background correction device is required to subtract from the total signal the component which is nonspecific to the metal. In the absence of interferences, the background

corrected absorbance is directly related to the concentration of the metal. Interferences relating to STPGFAA must be recognized and corrected. Suppressions or enhancements of instrument response cause by the sample matrix must be corrected by the method of standard addition.

III. INTERFERENCES.

Several interference sources may cause inaccuracies in the determination of trace elements by GFAA. These interferences can be classified into three major subdivisions, namely spectral, matrix, and memory.

Spectral interferences are caused by the resulting absorbance of light by a molecule or atom which is not the metal of interest or emission from black body radiation.

Spectral interferences caused by an element only occur if there is a spectral overlap between the wavelength of the interfering element and the metal of interest. Fortunately, this type of interference is relatively uncommon in STPGFAA because of the narrow atomic line widths associated with STPFAA. In addition, the use of appropriate furnace temperature programs and high spectral purity lamps as light sources can minimize the possibility of this type of interference. However, molecular absorbencies can span several hundred nanometers producing broadband spectral interferences. This type of interference is far more common in STPGFAA. The use of matrix modifiers, selective volatilization, and background correctors are all attempts to eliminate unwanted nonspecific absorbance. The nonspecific component of the total absorbance can vary considerably from sample type to sample type. Therefore, the effectiveness of a particular background correction device may vary depending on the act metal wavelength used as well as the nature and magnitude of the interference. The background correction device to be used with this method is not specified, however, it must provide an analytical condition that is not subject to the occurring inter-element spectral interferences of palladium on copper, iron on selenium, and aluminum on arsenic.

Spectral interferences are also caused by the emissions from black body radiation produced during the atomization furnace cycle. This black body emission reaches the photomultiplier tube, producing erroneous results. The magnitude of this interference can be minimized by proper furnace tube alignment and monochromator design. In addition, atomization temperatures which adequately volatilize the metal of interest without producing unnecessary black body radiation can help reduce unwanted background emission during analysis.

Matrix interferences are caused by sample components which inhibit the formation of free atomic metal atoms during the atomization cycle.

Matrix interferences can be of a chemical or physical nature. In this method the use of a delayed atomization device which provides stabilized temperatures is required. These devices provide an environment which is more conducive to the formation of free metal atoms and thereby minimize this type of interference. This type of interference can be detected by analyzing the sample plus a sample aliquot fortified with a known concentration of the metal. If the determined concentration of the metal addition is outside a designated range, a possible matrix effect should be suspected.

The use of nitric acid is preferred for GFAA analyses in order to minimize vapor state anionic chemical interferences, however, in this method hydrochloric acid is required to maintain stability in solution containing antimony and silver. When hydrochloric acid is used, the chloride ion vapor state interferences must be reduced using an appropriate matrix modifier. In this method a combination modifier of palladium, magnesium nitrate and a hydrogen (5%)-argon (95%) gas mixture is used for this purpose.

The palladium used in the modifier preparation may have elevated levels of Ag which will cause elevated blank absorbencies.

Memory interferences result from analyzing a sample containing a high concentration of an element (typically a high atomization temperature element) which cannot be removed quantitatively in one complete set of furnace steps. The metal which remains in the furnace can produce false positive signals on the subsequent sample(s). Therefore, the analyst should establish the metal concentration which can be injected into the furnace and adequately removed in one complete set of furnace cycles. If this concentration is exceeded, the sample should be diluted and a blank analyzed to assure the memory effect has been eliminated before reanalyzing the diluted sample.

Use of the microwave assisted digestion method can introduce interferences if high pressure develops in the digestion vessel causing venting. Venting can result in either a loss of metals or sample.

IV. APPARATUS.

Cem Corporation, Microwave Digestion System, Model MDS-81D

Perkin Elmer Graphite Furnace Atomic Absorbance Spectrophotometer Model 3300

The GFAA spectrometer must be capable of programmed heating of the graphite tube and the associated delayed atomization device. The instrument must be equipped with an adequate background correction device capable of removing undesirable non-specific absorbance over the spectral region of interest and provide an analytical condition not subject to the occurrence of inter-element spectral overlap interferences. The furnace device must be capable of utilizing an alternate gas supply during specified cycles of the analysis. The capability to record relatively fast (<1 s) transient signals and evaluate data on a peak area basis is preferred. In addition, a recirculating refrigeration bath is recommended for improved reproducibility of furnace temperatures.

Single element hollow cathode lamps or single element electrode-less discharge lamps along with the associated power supplies.

Argon gas supply (high-purity grade, 99.99%) for use during the atomization of selenium, for sheathing the furnace tube when in operation, and during furnace clean out.

Alternate gas mixture (hydrogen 5% - argon 95%) for use as a continuous gas flow environment during the dry and char furnace cycles.

Auto-sampler capable of adding matrix modifier solutions to the furnace, a single addition of metal, and completing methods of standard additions when required.

Analytical balance, with capability to measure to 0.1 mg, for use in weighing solids, for preparing standards, and for determining dissolved solids in digests or extracts.

A temperature adjustable hot plate capable of maintaining a temperature of 95°C.

(optional) A temperature adjustable block digester capable of maintaining a temperature of 95°C and equipped with 250-ml constricted digestion tubes.

(optional) A steel cabinet centrifuge with guard bowl, electric timer and brake.

A gravity convection drying oven with thermostatic control capable of maintaining 180°C ± 5°C.

(optional) An air displacement pipette capable of delivering volumes ranging from 100 to 2500 μL with an assortment of high quality disposable pipet tips.

Mortar and pestle, ceramic or nonmetallic material.

Polypropylene sieve, 5-mesh (4 mm opening).

Labware - All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives. Procedures found to provide clean labware include washing with a detergent solution, rinsing with tap water, soaking for 4 hours in a mixture of dilute acids (10% HNO_3, 10% HCl, and 80% distilled water), rinsing with reagent water and storing clean. Ideally, ground glass surfaces should be avoided to eliminate a potential source of random contamination. When this is impractical, particular attention should given to all ground glass surfaces during cleaning. Chromic acid cleaning solutions must be avoided because chromium is an metal.

Glassware - Volumetric flasks, graduated cylinders, funnels and centrifuge tubes (glass and/or metal-free plastic).

Assorted calibrated pipettes.

Conical Phillips beakers, 250-ml with 50-mm watch glasses.

Griffin beakers, 250-ml with 75-mm watch glasses and (optional) 75-mm ribbed watch glasses.

(optional) PTFE and/or quartz Griffin beakers, 250-ml with PTFE covers.

Evaporating dishes or high-form crucibles, porcelain, 100 ml capacity.

Narrow-mouth storage bottles, FEP (fluorinated ethylene propylene) with screw closure, 125-ml to 1-L capacities.

One piece stem FEP wash bottle with screw closure, 125-ml capacity.

V. SAMPLE HANDLING AND PRESERVATION.

Prior to the collection of an aqueous sample, consideration should be given to the type of data required, (i.e., dissolved or total recoverable), so that appropriate preservation and pretreatment steps can be taken. The pH of all aqueous samples must be tested immediately prior to dividing for processing or "direct analysis" to ensure the sample has been properly preserved. If properly acid preserved, the sample can be held up to 6 months before analysis.

For the determination of the dissolved elements, the sample must be filtered through a 0.45-μm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. (Glass or plastic filtering apparatus are recommended to avoid possible contamination.) Use a portion of the filtered sample to rinse the filter flask, discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1:1) nitric acid immediately following filtration to pH < 2.

For the determination of total recoverable elements in aqueous samples, samples are not filtered, but acidified with (1:1) nitric acid to pH < 2 (normally, 3 ml of (1:1) acid per liter of sample is sufficient for most ambient and drinking water samples). Preservation may be done at the time of collection, however, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination it is recommended that the samples be returned to the laboratory within two weeks of collection and acid preserved upon receipt in the laboratory. Following acidification, the sample should be mixed, held for sixteen hours, and then verified to be pH < 2 just prior withdrawing an aliquot for processing or "direct analysis". If for some reason such as high alkalinity the sample pH is verified to be > 2, more acid must be added and the sample held for sixteen hours until verified to be pH < 2.

> **NOTE:** When the nature of the sample is either unknown or is known to be hazardous, acidification should be done in a fume hood.

Solid samples usually require no preservation prior to analysis other than storage at 4°C. There is no established holding time limitation for solid samples.

For aqueous samples, a field blank should be prepared and analyzed as required by the data user. Use the same container and acid as used in sample collection.

VI. REAGENTS.

Reagents may contain elemental impurities which might affect analytical data. Only high-purity reagents that conform to the American Chemical Society specifications should be used whenever possible. If the purity of a reagent is in question, analyze for contamination. All acids used for this method must be of ultra high-purity grade or equivalent. Suitable acids are available from a number of manufacturers. Redistilled acids prepared by sub-boiling distillation are acceptable.

Hydrochloric acid, concentrated (sp.gr. 1.19) - HCl.

Hydrochloric acid (1:1) - Add 500 ml concentrated HCl to 400 ml reagent water and dilute to 1 L.

Hydrochloric acid (1:4) = Add 200 ml concentrated HCl to 400 ml reagent water and dilute to 1 L.

Nitric acid, concentrated (sp.gr. 1.41) - HNO_3.

Nitric acid (1:1) - Add 500 ml concentrated HNO_3 to 400 ml reagent water and dilute to 1 L.

Nitric acid (1:5) - Add to 50 ml concentrated HNO_3 to 250 ml reagent water.

Nitric acid (1:9) - Add 10 ml concentrated HNO_3 to 90 ml reagent water.

Reagent water. All references to water in this method refer to ASTM Type I grade water.

Ammonium hydroxide, concentrated (sp. gr. 0.902).

Tartaric acid, ACS reagent grade.

Matrix Modifier, dissolve 300 mg palladium (Pd) powder in concentrated HNO_3 (1 ml of HNO_3, adding 0.1 ml of concentrated HCl if necessary). Dissolve 200 mg of $Mg(NO_3)_2$ in ASTM Type I water. Pour the two solutions together and dilute to 100 ml with ASTM Type I water.

NOTE: It is recommended that the matrix modifier be analyzed separately in order to asses the contribution of the modifier to the absorbance of calibration and reagent blank solutions.

Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals (99.99 to 99.999% pure). All compounds must be dried for 1 h at 105°C, unless otherwise specified. It is recommended that stock solutions be stored in FEP bottles. Replace stock standards when succeeding dilutions for preparation of calibration standards can not be verified.

CAUTION: Many of these chemicals are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow for 1-L quantities, but for the purpose of pollution prevention, the analyst is encouraged to prepare smaller quantities when possible. Concentrations are calculated based upon the weight of the pure element or upon the weight of the compound multiplied by the fraction of the metal in the compound.

From pure element,

$$\text{Concentration} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

From pure compound,

$$\text{Concentration} = \frac{\text{weight (mg) X gravimetric factor}}{\text{volume (L)}}$$

where:
gravimetric factor = the weight fraction of the metal in the compound.

Silver solution, stock, 1 ml = 1000 μg Ag: Dissolve 1.000 g Ag metal, weighed accurately to at least four significant figures, in 80 ml (1:1) HNO_3 with heating to effect dissolution. Let solution cool and dilute with reagent water in a 1-L volumetric flask. Store solution in amber bottle or wrap bottle completely with aluminum foil to protect solution from light.

Preparation of Calibration Standards - Fresh calibration standards (CAL Solution) should be prepared every two weeks, or as needed. Dilute each of the stock standard solutions to levels appropriate to the operating range of the instrument using the appropriate acid diluent (see note). The element concentrations in each CAL solution should be sufficiently high to produce good measurement precision and to accurately define the slope of the response curve. The instrument calibration should be initially verified using a quality control sample.

NOTE: The appropriate acid diluent for the determination of dissolved elements in water and for the "direct analysis" of drinking water with turbidity < 1 NTU is 1% HNO_3. For total recoverable elements in waters, the appropriate acid diluent is 2% HNO_3 and 1% HCl, and the appropriate acid diluent is 2% HNO_3 and 1% HCl, and the appropriate acid diluent for total recoverable elements in solid samples is 2% HNO_3 and 2% HCl. The reason for these different diluents is to match the types of acids and the acid concentrations of the samples with the acid present in the standards and blanks.

Blanks - Four types of blanks are required for this method. A calibration blank is used to establish the analytical calibration curve, the laboratory reagent blank (LRB) is used to assess possible contamination from the sample preparation procedure and to assess spectral background, the laboratory fortified blank is used to assess routine laboratory performance, and a rinse blank is used to flush the instrument auto-sampler uptake system. All diluent acids should be made from concentrated acids and ASTM Type I water.

The calibration blank consists of the appropriate acid diluent (HCl/HNO_3) in ASTM Type I water. The calibration blank should be stored in a FEP bottle.

The laboratory reagent blank (LRB) must contain all the reagents in the same volumes as used in processing the samples. The LRB must be carried through the same entire preparation scheme as the samples including sample digestion when applicable.

The laboratory fortified blank (LFB) is prepared by fortifying an aliquot of the laboratory reagent blank with all metals to provide a final concentration which will produce an absorbance of approximately 0.1 for each metal. The LFB must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable.

The laboratory fortified blank (LFB) is prepared by fortifying an aliquot of the laboratory reagent blank with all metals to provide a final concentration which will produce an absorbance of approximately 0.1 for each metal. The LFB must be carried through the sam- entire preparation scheme as the samples including sample digestion, when applicable.

The rinse blank is prepared as needed by adding 1.0 ml of concentrated HNO_3 and 1.0 ml concentrated HCl to 1 liter of ASTM Type I water and stored in a convenient manner.

Instrument Performance Check (IPC) Solution - The IPC solution is used to periodically verify instrument performance during analysis. It should be prepared in the same acid mixture as the calibration standards by combining method metals at appropriate concentrations to approximate the midpoint of the calibration curve. The IPC solution should be prepared from the same standard stock solutions used to prepare the calibration standards and stored in a FEP bottle. Agency programs may specify or request that additional instrument performance check solutions be prepared at specified concentrations in order to meet particular program needs.

Quality Control Sample (QCS) - For initial and periodic verification of calibration standards and instrument performance, analysis of a QCS is required. The QCS must be obtained from an outside source different from the standard stock solutions and prepared in the same acid mixture as the calibration standards. The concentration of the metals in the QCS solution should be such that the resulting solution will provide an absorbance reading of approximately 0.1. The QCS solution should be stored in a FEP bottle and analyzed as needed to meet data-quality needs. A fresh solution should be prepared quarterly or more frequently as needed.

VII. CALCULATIONS

Sample data should be reported in units of μg/L for aqueous samples and mg/kg dry weight for solid samples. The instrument's calibrated software package calculates the copper concentration in μg/L for each sample. The software package is incorporated into the instrumentation and results are displayed either digitally or printed to paper and saved to disk.

For dissolved aqueous metals report the data generated directly from the instrument with allowance for sample dilution. Do not report metal concentrations below the IDL.

For total recoverable aqueous metals, multiply solution metal concentrations by the dilution factor 0.5, when 100 ml aliquot is used to produce the 50 ml final solution, round the data to the tenths place and report the data in μg/L up to three significant figures. If a different aliquot volume other than 100 ml is used for sample preparation, adjust the dilution factor accordingly. Also, account for any additional dilution of the prepared sample solution needed to complete the determination of metals exceeding the upper limit of the calibration curve. Do not report data below the determined metal MDL concentration or below an adjusted detection limit reflecting smaller sample aliquots used in processing or additional dilutions required to complete the analysis.

For total recoverable metals in solid samples, round the solution metal concentrations (μg/L) to the tenths place. Report the data up to three significant figures as mg/kg dry-weight basis unless

specified otherwise by the program or data user. Calculate the concentration using the equation below:

$$\text{Sample Conc. (mg/kg) dry-weight basis} = \frac{C \times V \times D}{W}$$

where: C = Concentration in extract (μg x 0.01/L)
V = Volume of extract (L, 100 ml = 0.1 L)
D = Dilution factor (undiluted = 1)
W = Weight of sample aliquot extracted (g x 0.001 = kg)

Do not report metal data below the estimated solids MDL or an adjusted MDL because of additional dilutions required to complete the analysis.

To report percent solids in solid samples calculate as follows:

$$\% \text{ solids (S)} = \frac{DW}{WW} \times 100$$

where: DW = Sample weight (g) dried at 60°C
WW =Sample weight (g) before drying

NOTE: If the data user, program or laboratory requires that the reported percent solids be determined by drying at 105°C, repeat the procedure using a separate portion (> 20 g) of the sample and dry to constant weight at 103-105°C.

The QC data obtained during the analyses provide an indication of the quality of the sample data and should be provided with the sample results.

VIII. PROCEDURE

Aqueous Sample Preparation - Dissolved Metals

For the determination of dissolved metals in ground and surface waters, pipet an aliquot (≥ 20 ml) of the filtered, acid preserved sample into a 50-ml polypropylene centrifuge tube. Add an appropriate volume of (1:1) nitric acid to adjust the acid concentration of the aliquot to approximate a 1% (v/v) nitric acid solution (e.g., add 0.4 ml (1:1) HNO_3 to a 20 ml aliquot of sample). Cap the tube and mix. The sample is now ready for analysis. Allowance for sample dilution should be made in the calculations.

NOTE: If a precipitant is formed during acidification, transport, or storage, the sample aliquot must be treated prior to analysis.

Aqueous Sample Preparation - Total Recoverable Metals

For the "direct analysis" of total recoverable metals in drinking water samples containi. turbidity < 1 NTU, treat an unfiltered acid preserved sample aliquot using the sample preparation procedure while making allowance for sample dilution in the data calculation.

For the determination of total recoverable metals in aqueous samples (other than drinking water with < 1 NTU turbidity), use the microwave assisted digestion method procedures, see sections 1 through 10 of the SW-846 method 3510.

Allow any undissolved material to settle overnight, or centrifuge a portion of the prepared sample until clear. (If after centrifuging or standing overnight the sample contains suspended solids that would clog or affect the sample introduction system, a portion of the sample may be filtered for their removal prior to analysis. However, care should be exercised to avoid potential contamination from filtration.) The sample is now ready for analysis. Because the effects of various matrices on the salability of diluted samples cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.

Sample Analysis

Prior to daily calibration of the instrument inspect the graphite furnace, the sample uptake system and auto-sampler injector for any change in the system that would affect instrument performance. Clean the system and replace the graphite tube and/or platform when needed or on a daily basis.

Before beginning daily calibration the instrument system should be reconfigured to the selected optimized operating conditions for the "direct analysis" drinking water with turbidity < 1 NTU. Initiate data system and allow a period of not less than 15 min for instrument and hollow cathode lamp warm up. If an EDL is to be used, allow 30 min for warm up.

After the warm up period but before calibration, instrument stability must be demonstrated by analyzing a standard solution with a concentration 20 times the IDL a minimum of five times. The resulting reactive standard deviation (RSD) of absorbance signals must be < 5%. If the RSD is > 5%, determine and correct the cause before calibrating the instrument.

For initial and daily operation calibrate the instrument according to the instrument manufacturer's recommended procedures using the calibration blank and calibration standards prepared at three or more concentrations within the usable linear dynamic range of the metal.

An auto sampler must be used to introduce all solutions into the graphite furnace. Once the standard, sample or QC solution plus the matrix modifier is injected, the furnace controller completes furnace cycles and clean out period as programmed. Metal signals must be integrated and collected as peak area measurements. Background absorbencies, background corrected metal signals, and determined metal concentrations on all solutions must be able to be displayed on a CRT for immediate review by the analyst and be available as hard copy for

documentation to be kept on file. Flush the auto-sampler solution uptake system with the rinse blank between each solution injected.

After completion of the initial requirements of this method, samples should be analyzed in the same operational manner used in the calibration routine.

During the analysis of samples, the laboratory must comply with the required quality control. Only for the determination of dissolved metals or the "direct analysis" of drinking water with turbidity of < 1 NTU is the sample digestion step of the LRB, LFB, and LFM not required.

For every new or unusual matrix, when practical, it is highly recommended that an inductively coupled plasma atomic emission spectrometer be used to screen for high element concentration. Information gained from this may be used to prevent potential damage to the instrument and to better estimate which elements may require analysis by graphite furnace.

Determined sample metal concentrations that are 90% or more of the upper limit of calibration must either be diluted with acidified reagent water and reanalyzed with concern for memory effects, or determined by another approved test procedure that is less sensitive. Samples with a background absorbance > 1.0 must be appropriately diluted with acidified reagent water and reanalyzed.

When it is necessary to assess an operative matrix interference (e.g., signal reduction due to high dissolved solids), the test described is recommended.

Standard Additions - If the method of standard addition is required, the following procedure is recommended:

The standard addition technique involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the metal signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interference, which causes a baseline shift. The simplest version of this technique is the single-addition method. The procedure is as follows: Two identical aliquots of the sample solution, each of the volume V_X, are taken. To the first (labeled A) is added a small volume V_S of a standard metal solution of concentration C_S. To the second (labeled B) is added the same volume V_S of the solvent. The analytical signals of A and B are measured and corrected for erroneous signals. The unknown sample concentration C_X is calculated:

$$C_x = \frac{S_B V_S C_S}{(S_A - S_B)V_X}$$

where, S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_S and C_S should be chosen so that S_A is roughly twice S_B on the average. It is best if V_S is made much less than V_X, and thus C_S is much greater than C_X, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are

best made first and carried through the entire procedure. For the results from this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.

2. The chemical form of the metal added must respond in the same manner as the metal in the sample.

3. The interference effect must be constant over the working range of concern.

4. The signal must be corrected for any additive interference.

IX. ALLOWABLE LIMITS.

The NPDES effluent limit is 0.006 mg/l for lead.

X. QC CHECKS.

One spiked blank and spiked sample will be run with every 20 sample determinations. The spike concentration shall consist of at least 1 time the average concentration found in a typical sample for each determined parameter. Code 4052 laboratory will obtain or prepare a standard solution.

Duplicate analysis on one sample after every ten samples are analyzed shall be performed for each parameter if enough sample volume is available.

One reagent blank shall be analyzed each day an analysis is performed for each parameter.

Split samples shall be analyzed quarterly by a control laboratory.

Code 095 will obtain performance evaluation samples from a vendor and these will be analyzed by the Code 4052 laboratory every three months.

The Code 4052 laboratory will use Windowchem™ Software's ControlChart!™ software to generate quality control charts for the atomic absorption spectrophotometer. A separate control chart will be prepared for each concentration range represented in the outfall data. Duplicate sample range results will be charted to monitor the atomic absorption spectrophotometer's precision. Spiked blank and spiked sample percent recovery data will be charted to monitor its accuracy. Procedures for preparing and using control charts are in section 1, chapter 6 of this QA/QC manual.

XI. REFERENCES

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Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, USEPA, SW-846, Update II, September 1994.

Perkin Elmer, Flame AA, Analytical Methods for Atomic Absorption Spectrophotometry, Norwalk, Connecticut, Jan, 1982.

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Rev: Original
Effective Date: 8/1/97

CADMIUM

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This method provides procedures for the determination of dissolved and total recoverable elements by graphite furnace atomic absorption (GFAA) in ground water, surface water, drinking water, storm runoff, industrial and domestic wastewater. This method is also applicable to the determination of total recoverable elements in sediment, sludges, and soil.

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For the determination of total recoverable metals in aqueous and solid samples a digestion/extraction is required prior to analysis when the elements are not in solution (e.g., soils, sludges, sediments and aqueous samples that may contain particulate and suspended solids). Aqueous samples containing suspended or particulate material ≥ 1% (w/v) should be extracted as a solid type sample. The microwave assisted acid digestion method is used to facilitate total metal determination in samples that contain solids.

Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples, fortified sample matrices and even fortified blanks if determined as a dissolved metal or by "direct analysis" where the sample has not been processed using the microwave assisted

digestion method. For this reason it is recommended that samples be digested prior to the determination of silver. The microwave assisted acid digestion method is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, succeeding smaller volume, well mixed aliquots should be prepared until the analysis solution contains < 0.1 mg/L silver. The extraction of solid samples containing concentrations of silver > 50 mg/kg should be treated in a similar manner.

Method detection limits and instrument operating conditions for the applicable elements are intended as a guide and are typical of a system optimized for the element employing commercial instrumentation. However, actual method detection limits and linear working ranges will be dependent on the sample matrix, instrumentation and selected operating conditions.

The sensitivity and limited linear dynamic range (LDR) of GFAA often implies the need to dilute a sample prior to analysis. The actual magnitude of the dilution as well as the cleanliness of the labware used to perform the dilution can dramatically influence the quality of the analytical results. Therefore, sample types requiring large dilutions (>50:1) should be analyzed by an another approved test procedure which has a larger LDR or which is inherently less sensitive than GFAA.

II. SUMMARY OF METHOD.

An aliquot of a well mixed, homogeneous aqueous or solid sample is accurately weighed or measured for sample processing. For total recoverable analysis of a solid or an aqueous sample containing undissolved material, metals are first solubilized using the microwave assisted acid digestion method. After cooling, the sample is made up to volume, is mixed and centrifuged or allowed to settle overnight prior to analysis. For the determination of dissolved metals in a filtered aqueous sample aliquot, or for the "direct analysis" total recoverable determination of metals where sample turbidity is < 1 NTU, the sample is made ready for analysis by the appropriate addition of nitric acid, and then diluted to a predetermined volume and mixed before analysis.

The metals listed in this method are determined by stabilized temperature platform graphite furnace atomic absorption (STPGFAA). In STPGFAA, the sample and the matrix modifier are first pipetted onto the platform or a device which provides delayed atomization. The furnace chamber is then purged with a continuous flow of a premixed gas (95% argon - 5% hydrogen) and the sample is dried at a relatively low temperature (about 120°C) to avoid spattering. Once dried, the sample is treated in a char or ash step which is designed to minimize the interference effects caused by the contaminant sample matrix. After the char step the furnace is allowed to cool prior to atomization. The atomization cycle is characterized by rapid heating of the furnace to a temperature where the metal (metal) is atomized from the pyrolytic graphite surface into a stopped gas flow atmosphere of argon containing 5% hydrogen. (Only selenium is determined in an atmosphere of high purity argon.) The resulting atomic cloud absorbs the element specific atomic emission produced by a hollow cathode lamp (HCL) or an electrode-less discharge lamp (EDL). Following analysis the furnace is subjected to a clean out period of high temperature and continuous argon flow. Because the resulting absorbance usually has a nonspecific component associated with the actual metal absorbance, an instrumental background correction device is required to subtract from the total signal the component which is nonspecific to the metal. In the absence of interferences, the background

corrected absorbance is directly related to the concentration of the metal. Interferences relating to STPGFAA must be recognized and corrected. Suppressions or enhancements of instrument response cause by the sample matrix must be corrected by the method of standard addition.

III. INTERFERENCES.

Several interference sources may cause inaccuracies in the determination of trace elements by GFAA. These interferences can be classified into three major subdivisions, namely spectral, matrix, and memory.

Spectral interferences are caused by the resulting absorbance of light by a molecule or atom which is not the metal of interest or emission from black body radiation.

Spectral interferences caused by an element only occur if there is a spectral overlap between the wavelength of the interfering element and the metal of interest. Fortunately, this type of interference is relatively uncommon in STPGFAA because of the narrow atomic line widths associated with STPFAA. In addition, the use of appropriate furnace temperature programs and high spectral purity lamps as light sources can minimize the possibility of this type of interference. However, molecular absorbencies can span several hundred nanometers producing broadband spectral interferences. This type of interference is far more common in STPGFAA. The use of matrix modifiers, selective volatilization, and background correctors are all attempts to eliminate unwanted nonspecific absorbance. The nonspecific component of the total absorbance can vary considerably from sample type to sample type. Therefore, the effectiveness of a particular background correction device may vary depending on the actual metal wavelength used as well as the nature and magnitude of the interference. [illegible] background correction device to be used with this method is not specified, however, it [illegible] provide an analytical condition that is not subject to the occurring inter-element spectral interferences of palladium on copper, iron on selenium, and aluminum on arsenic.

Spectral interferences are also caused by the emissions from black body radiation produced during the atomization furnace cycle. This black body emission reaches the photomultiplier tube, producing erroneous results. The magnitude of this interference can be minimized by proper furnace tube alignment and monochromator design. In addition, atomization temperatures which adequately volatilize the metal of interest without producing unnecessary black body radiation can help reduce unwanted background emission during analysis.

Matrix interferences are caused by sample components which inhibit the formation of free atomic metal atoms during the atomization cycle.

Matrix interferences can be of a chemical or physical nature. In this method the use of a delayed atomization device which provides stabilized temperatures is required. These devices provide an environment which is more conducive to the formation of free metal atoms and thereby minimize this type of interference. This type of interference can be detected by analyzing the sample plus a sample aliquot fortified with a known concentration of the metal. If the determined concentration of the metal addition is outside a designated range, a possible matrix effect should be suspected.

The use of nitric acid is preferred for GFAA analyses in order to minimize vapor state anionic chemical interferences, however, in this method hydrochloric acid is required to maintain stability in solution containing antimony and silver. When hydrochloric acid is used, the chloride ion vapor state interferences must be reduced using an appropriate matrix modifier. In this method a combination modifier of palladium, magnesium nitrate and a hydrogen (5%)-argon (95%) gas mixture is used for this purpose.

The palladium used in the modifier preparation may have elevated levels of Ag which will cause elevated blank absorbencies.

Memory interferences result from analyzing a sample containing a high concentration of an element (typically a high atomization temperature element) which cannot be removed quantitatively in one complete set of furnace steps. The metal which remains in the furnace can produce false positive signals on the subsequent sample(s). Therefore, the analyst should establish the metal concentration which can be injected into the furnace and adequately removed in one complete set of furnace cycles. If this concentration is exceeded, the sample should be diluted and a blank analyzed to assure the memory effect has been eliminated before reanalyzing the diluted sample.

Use of the microwave assisted digestion method can introduce interferences if high pressure develops in the digestion vessel causing venting. Venting can result in either a loss of metals or sample.

IV. APPARATUS.

Cem Corporation, Microwave Digestion System, Model MDS-81D

Perkin Elmer Graphite Furnace Atomic Absorbance Spectrophotometer Model 3300

The GFAA spectrometer must be capable of programmed heating of the graphite tube and the associated delayed atomization device. The instrument must be equipped with an adequate background correction device capable of removing undesirable non-specific absorbance over the spectral region of interest and provide an analytical condition not subject to the occurrence of inter-element spectral overlap interferences. The furnace device must be capable of utilizing an alternate gas supply during specified cycles of the analysis. The capability to record relatively fast (<1 s) transient signals and evaluate data on a peak area basis is preferred. In addition, a recirculating refrigeration bath is recommended for improved reproducibility of furnace temperatures.

Single element hollow cathode lamps or single element electrode-less discharge lamps along with the associated power supplies.

Argon gas supply (high-purity grade, 99.99%) for use during the atomization of selenium, for sheathing the furnace tube when in operation, and during furnace clean out.

Alternate gas mixture (hydrogen 5% - argon 95%) for use as a continuous gas flow environment during the dry and char furnace cycles.

Auto-sampler capable of adding matrix modifier solutions to the furnace, a single addition of metal, and completing methods of standard additions when required.

Analytical balance, with capability to measure to 0.1 mg, for use in weighing solids, for preparing standards, and for determining dissolved solids in digests or extracts.

A temperature adjustable hot plate capable of maintaining a temperature of 95°C.

(optional) A temperature adjustable block digester capable of maintaining a temperature of 95°C and equipped with 250-ml constricted digestion tubes.

(optional) A steel cabinet centrifuge with guard bowl, electric timer and brake.

A gravity convection drying oven with thermostatic control capable of maintaining 180°C ± 5°C.

(optional) An air displacement pipette capable of delivering volumes ranging from 100 to 2500 μL with an assortment of high quality disposable pipet tips.

Mortar and pestle, ceramic or nonmetallic material.

Polypropylene sieve, 5-mesh (4 mm opening).

Labware - All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives. Procedures found to provide clean labware include washing with a detergent solution, rinsing with tap water, soaking for 4 hours in a mixture of dilute acids (10% HNO_3, 10% HCl, and 80% distilled water), rinsing with reagent water and storing clean. Ideally, ground glass surfaces should be avoided to eliminate a potential source of random contamination. When this is impractical, particular attention should given to all ground glass surfaces during cleaning. Chromic acid cleaning solutions must be avoided because chromium is an metal.

Glassware - Volumetric flasks, graduated cylinders, funnels and centrifuge tubes (glass and/or metal-free plastic).

Assorted calibrated pipettes.

Conical Phillips beakers, 250-ml with 50-mm watch glasses.

Griffin beakers, 250-ml with 75-mm watch glasses and (optional) 75-mm ribbed watch glasses.

(optional) PTFE and/or quartz Griffin beakers, 250-ml with PTFE covers.

Evaporating dishes or high-form crucibles, porcelain, 100 ml capacity.

Narrow-mouth storage bottles, FEP (fluorinated ethylene propylene) with screw closure, 125-ml to 1-L capacities.

One piece stem FEP wash bottle with screw closure, 125-ml capacity.

V. SAMPLE HANDLING AND PRESERVATION.

Prior to the collection of an aqueous sample, consideration should be given to the type of data required, (i.e., dissolved or total recoverable), so that appropriate preservation and pretreatment steps can be taken. The pH of all aqueous samples must be tested immediately prior to dividing for processing or "direct analysis" to ensure the sample has been properly preserved. If properly acid preserved, the sample can be held up to 6 months before analysis.

For the determination of the dissolved elements, the sample must be filtered through a 0.45-μm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. (Glass or plastic filtering apparatus are recommended to avoid possible contamination.) Use a portion of the filtered sample to rinse the filter flask, discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1:1) nitric acid immediately following filtration to pH < 2.

For the determination of total recoverable elements in aqueous samples, samples are not filtered, but acidified with (1:1) nitric acid to pH < 2 (normally, 3 ml of (1:1) acid per liter of sample is sufficient for most ambient and drinking water samples). Preservation may be done at the time of collection, however, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination it is recommended that the samples be returned to the laboratory within two weeks of collection and acid preserved upon receipt in the laboratory. Following acidification, the sample should be mixed, held for sixteen hours, and then verified to be pH < 2 just prior withdrawing an aliquot for processing or "direct analysis". If for some reason such as high alkalinity the sample pH is verified to be > 2, more acid must be added and the sample held for sixteen hours until verified to be pH < 2.

NOTE: When the nature of the sample is either unknown or is known to be hazardous, acidification should be done in a fume hood.

Solid samples usually require no preservation prior to analysis other than storage at 4°C. There is no established holding time limitation for solid samples.

For aqueous samples, a field blank should be prepared and analyzed as required by the data user. Use the same container and acid as used in sample collection.

VI. REAGENTS.

Reagents may contain elemental impurities which might affect analytical data. Only high-purity reagents that conform to the American Chemical Society specifications should be used whenever possible. If the purity of a reagent is in question, analyze for contamination. All acids used for this method must be of ultra high-purity grade or equivalent. Suitable acids are available from a number of manufacturers. Redistilled acids prepared by sub-boiling distillation are acceptable.

Hydrochloric acid, concentrated (sp.gr. 1.19) - HCl.

Hydrochloric acid (1:1) - Add 500 ml concentrated HCl to 400 ml reagent water and dilute to 1 L.

Hydrochloric acid (1:4) = Add 200 ml concentrated HCl to 400 ml reagent water and dilute to 1 L.

Nitric acid, concentrated (sp.gr. 1.41) - HNO_3.

Nitric acid (1:1) - Add 500 ml concentrated HNO_3 to 400 ml reagent water and dilute to 1 L.

Nitric acid (1:5) - Add to 50 ml concentrated HNO_3 to 250 ml reagent water.

Nitric acid (1:9) - Add 10 ml concentrated HNO_3 to 90 ml reagent water.

Reagent water. All references to water in this method refer to ASTM Type I grade water.

Ammonium hydroxide, concentrated (sp. gr. 0.902).

Tartaric acid, ACS reagent grade.

Matrix Modifier, dissolve 300 mg palladium (Pd) powder in concentrated HNO_3 (1 ml of HNO_3, adding 0.1 ml of concentrated HCl if necessary). Dissolve 200 mg of $Mg(NO_3)_2$ in ASTM Type I water. Pour the two solutions together and dilute to 100 ml with ASTM Type I water.

NOTE: It is recommended that the matrix modifier be analyzed separately in order to assess the contribution of the modifier to the absorbance of calibration and reagent blank solutions.

Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals (99.99 to 99.999% pure). All compounds must be dried for 1 h at 105°C, unless otherwise specified. It is recommended that stock solutions be stored in FEP bottles. Replace stock standards when succeeding dilutions for preparation of calibration standards can not be verified.

CAUTION: Many of these chemicals are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow for 1-L quantities, but for the purpose of pollution prevention, the analyst is encouraged to prepare smaller quantities when possible. Concentrations are calculated based upon the weight of the pure element or upon the weight of the compound multiplied by the fraction of the metal in the compound.

From pure element,

$$\text{Concentration} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

From pure compound,

$$\text{Concentration} = \frac{\text{weight (mg) X gravimetric factor}}{\text{volume (L)}}$$

where:
gravimetric factor = the weight fraction of the metal in the compound.

Silver solution, stock, 1 ml = 1000 μg Ag: Dissolve 1.000 g Ag metal, weighed accurately to at least four significant figures, in 80 ml (1:1) HNO_3 with heating to effect dissolution. Let solution cool and dilute with reagent water in a 1-L volumetric flask. Store solution in amber bottle or wrap bottle completely with aluminum foil to protect solution from light.

Preparation of Calibration Standards - Fresh calibration standards (CAL Solution) should be prepared every two weeks, or as needed. Dilute each of the stock standard solutions to levels appropriate to the operating range of the instrument using the appropriate acid diluent (see note). The element concentrations in each CAL solution should be sufficiently high to produce good measurement precision and to accurately define the slope of the response curve. The instrument calibration should be initially verified using a quality control sample.

NOTE: The appropriate acid diluent for the determination of dissolved elements in water and for the "direct analysis" of drinking water with turbidity < 1 NTU is 1% HNO_3. For total recoverable elements in waters, the appropriate acid diluent is 2% HNO_3 and 1% HCl, and the appropriate acid diluent is 2% HNO_3 and 1% HCl, and the appropriate acid diluent for total recoverable elements in solid samples is 2% HNO_3 and 2% HCl. The reason for these different diluents is to match the types of acids and the acid concentrations of the samples with the acid present in the standards and blanks.

Blanks - Four types of blanks are required for this method. A calibration blank is used to establish the analytical calibration curve, the laboratory reagent blank (LRB) is used to assess possible contamination from the sample preparation procedure and to assess spectral background, the laboratory fortified blank is used to assess routine laboratory performance, and a rinse blank is used to flush the instrument auto-sampler uptake system. All diluent acids should be made from concentrated acids and ASTM Type I water.

The calibration blank consists of the appropriate acid diluent (HCl/HNO_3) in ASTM Type I water. The calibration blank should be stored in a FEP bottle.

The laboratory reagent blank (LRB) must contain all the reagents in the same volumes as used in processing the samples. The LRB must be carried through the same entire preparation scheme as the samples including sample digestion when applicable.

The laboratory fortified blank (LFB) is prepared by fortifying an aliquot of the laboratory reagent blank with all metals to provide a final concentration which will produce an absorbance of approximately 0.1 for each metal. The LFB must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable.

The laboratory fortified blank (LFB) is prepared by fortifying an aliquot of the laboratory reagent blank with all metals to provide a final concentration which will produce an absorbance of approximately 0.1 for each metal. The LFB must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable.

The rinse blank is prepared as needed by adding 1.0 ml of concentrated HNO_3 and 1.0 ml concentrated HCl to 1 liter of ASTM Type I water and stored in a convenient manner.

Instrument Performance Check (IPC) Solution - The IPC solution is used to periodically verify instrument performance during analysis. It should be prepared in the same acid mixture as the calibration standards by combining method metals at appropriate concentrations to approximate the midpoint of the calibration curve. The IPC solution should be prepared from the same standard stock solutions used to prepare the calibration standards and stored in a FEP bottle. Agency programs may specify or request that additional instrument performance check solutions be prepared at specified concentrations in order to meet particular program needs.

Quality Control Sample (QCS) - For initial and periodic verification of calibration standards and instrument performance, analysis of a QCS is required. The QCS must be obtained from an outside source different from the standard stock solutions and prepared in the same acid mixture as the calibration standards. The concentration of the metals in the QCS solution should be such that the resulting solution will provide an absorbance reading of approximately 0.1. The QCS solution should be stored in a FEP bottle and analyzed as needed to meet data-quality needs. A fresh solution should be prepared quarterly or more frequently as needed.

VII. CALCULATIONS

Sample data should be reported in units of μg/L for aqueous samples and mg/kg dry weight for solid samples. The instrument's calibrated software package calculates the cadmium concentration in μg/L for each sample. The software package is incorporated into the instrumentation and results are displayed either digitally or printed to paper and saved to disk.

For dissolved aqueous metals report the data generated directly from the instrument with allowance for sample dilution. Do not report metal concentrations below the IDL.

For total recoverable aqueous metals, multiply solution metal concentrations by the dilution factor 0.5, when 100 ml aliquot is used to produce the 50 ml final solution, round the data to the tenths place and report the data in μg/L up to three significant figures. If a different aliquot volume other than 100 ml is used for sample preparation, adjust the dilution factor accordingly. Also, account for any additional dilution of the prepared sample solution needed to complete the determination of metals exceeding the upper limit of the calibration curve. Do not report data below the determined metal MDL concentration or below an adjusted detection limit reflecting smaller sample aliquots used in processing or additional dilutions required to complete the analysis.

For total recoverable metals in solid samples, round the solution metal concentrations (μg/L) to the tenths place. Report the data up to three significant figures as mg/kg dry-weight basis unless

specified otherwise by the program or data user. Calculate the concentration using the equation below:

$$\text{Sample Conc. (mg/kg) dry-weight basis} = \frac{C \times V \times D}{W}$$

where: C = Concentration in extract (μg x 0.01/L)
V = Volume of extract (L, 100 ml = 0.1 L)
D = Dilution factor (undiluted = 1)
W = Weight of sample aliquot extracted (g x 0.001 = kg)

Do not report metal data below the estimated solids MDL or an adjusted MDL because of additional dilutions required to complete the analysis.

To report percent solids in solid samples calculate as follows:

$$\% \text{ solids (S)} = \frac{DW}{WW} \times 100$$

where: DW = Sample weight (g) dried at 60°C
WW =Sample weight (g) before drying

NOTE: If the data user, program or laboratory requires that the reported percent solids be determined by drying at 105°C, repeat the procedure using a separate portion (> 20 g) of the sample and dry to constant weight at 103-105°C.

The QC data obtained during the analyses provide an indication of the quality of the sample data and should be provided with the sample results.

VIII. PROCEDURE

Aqueous Sample Preparation - Dissolved Metals

For the determination of dissolved metals in ground and surface waters, pipet an aliquot (≥ 20 ml) of the filtered, acid preserved sample into a 50-ml polypropylene centrifuge tube. Add an appropriate volume of (1:1) nitric acid to adjust the acid concentration of the aliquot to approximate a 1% (v/v) nitric acid solution (e.g., add 0.4 ml (1:1) HNO_3 to a 20 ml aliquot of sample). Cap the tube and mix. The sample is now ready for analysis. Allowance for sample dilution should be made in the calculations.

NOTE: If a precipitant is formed during acidification, transport, or storage, the sample aliquot must be treated prior to analysis.

Aqueous Sample Preparation - Total Recoverable Metals

For the "direct analysis" of total recoverable metals in drinking water samples containi. turbidity < 1 NTU, treat an unfiltered acid preserved sample aliquot using the sample preparation procedure while making allowance for sample dilution in the data calculation.

For the determination of total recoverable metals in aqueous samples (other than drinking water with < 1 NTU turbidity), use the microwave assisted digestion method procedures, see sections 1 through 10 of the SW-846 method 3510.

Allow any undissolved material to settle overnight, or centrifuge a portion of the prepared sample until clear. (If after centrifuging or standing overnight the sample contains suspended solids that would clog or affect the sample introduction system, a portion of the sample may be filtered for their removal prior to analysis. However, care should be exercised to avoid potential contamination from filtration.) The sample is now ready for analysis. Because the effects of various matrices on the salability of diluted samples cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.

Sample Analysis

Prior to daily calibration of the instrument inspect the graphite furnace, the sample uptake system and auto-sampler injector for any change in the system that would affect instrument performance. Clean the system and replace the graphite tube and/or platform when needed or on a daily basis.

Before beginning daily calibration the instrument system should be reconfigured to the selected optimized operating conditions for the "direct analysis" drinking water with turbidity < 1 NTU. Initiate data system and allow a period of not less than 15 min for instrument and hollow cathode lamp warm up. If an EDL is to be used, allow 30 min for warm up.

After the warm up period but before calibration, instrument stability must be demonstrated by analyzing a standard solution with a concentration 20 times the IDL a minimum of five times. The resulting reactive standard deviation (RSD) of absorbance signals must be < 5%. If the RSD is > 5%, determine and correct the cause before calibrating the instrument.

For initial and daily operation calibrate the instrument according to the instrument manufacturer's recommended procedures using the calibration blank and calibration standards prepared at three or more concentrations within the usable linear dynamic range of the metal.

An auto sampler must be used to introduce all solutions into the graphite furnace. Once the standard, sample or QC solution plus the matrix modifier is injected, the furnace controller completes furnace cycles and clean out period as programmed. Metal signals must be integrated and collected as peak area measurements. Background absorbencies, background corrected metal signals, and determined metal concentrations on all solutions must be able to be displayed on a CRT for immediate review by the analyst and be available as hard copy for

documentation to be kept on file. Flush the auto-sampler solution uptake system with the rinse blank between each solution injected.

After completion of the initial requirements of this method, samples should be analyzed in the same operational manner used in the calibration routine.

During the analysis of samples, the laboratory must comply with the required quality control. Only for the determination of dissolved metals or the "direct analysis" of drinking water with turbidity of < 1 NTU is the sample digestion step of the LRB, LFB, and LFM not required.

For every new or unusual matrix, when practical, it is highly recommended that an inductively coupled plasma atomic emission spectrometer be used to screen for high element concentration. Information gained from this may be used to prevent potential damage to the instrument and to better estimate which elements may require analysis by graphite furnace.

Determined sample metal concentrations that are 90% or more of the upper limit of calibration must either be diluted with acidified reagent water and reanalyzed with concern for memory effects, or determined by another approved test procedure that is less sensitive. Samples with a background absorbance > 1.0 must be appropriately diluted with acidified reagent water and reanalyzed.

When it is necessary to assess an operative matrix interference (e.g., signal reduction due to high dissolved solids), the test described is recommended.

Standard Additions - If the method of standard addition is required, the following procedure is recommended:

The standard addition technique involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the metal signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interference, which causes a baseline shift. The simplest version of this technique is the single-addition method. The procedure is as follows: Two identical aliquots of the sample solution, each of the volume V_X, are taken. To the first (labeled A) is added a small volume V_S of a standard metal solution of concentration C_S. To the second (labeled B) is added the same volume V_S of the solvent. The analytical signals of A and B are measured and corrected for erroneous signals. The unknown sample concentration C_X is calculated:

$$C_x = \frac{S_B V_S C_S}{(S_A - S_B) V_X}$$

where, S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_S and C_S should be chosen so that S_A is roughly twice S_B on the average. It is best if V_S is made much less than V_X, and thus C_S is much greater than C_X, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are

best made first and carried through the entire procedure. For the results from this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.

2. The chemical form of the metal added must respond in the same manner as the metal in the sample.

3. The interference effect must be constant over the working range of concern.

4. The signal must be corrected for any additive interference.

IX. ALLOWABLE LIMITS.

The NPDES effluent limit is 0.006 mg/l for lead.

X. QC CHECKS.

One spiked blank and spiked sample will be run with every 20 sample determinations. The spike concentration shall consist of at least 1 time the average concentration found in a typical sample for each determined parameter. Code 4052 laboratory will obtain or prepare a standard solution.

Duplicate analysis on one sample after every ten samples are analyzed shall be performed for each parameter if enough sample volume is available.

One reagent blank shall be analyzed each day an analysis is performed for each parameter.

Split samples shall be analyzed quarterly by a control laboratory.

Code 095 will obtain performance evaluation samples from a vendor and these will be analyzed by the Code 4052 laboratory every three months.

The Code 4052 laboratory will use Windowchem™ Software's ControlChart!™ software to generate quality control charts for the atomic absorption spectrophotometer. A separate control chart will be prepared for each concentration range represented in the outfall data. Duplicate sample range results will be charted to monitor the atomic absorption spectrophotometer's precision. Spiked blank and spiked sample percent recovery data will be charted to monitor its accuracy. Procedures for preparing and using control charts are in section 1, chapter 6 of this QA/QC manual.

XI. REFERENCES

Methods for Chemical Analysis of Water and Wastes, USEPA, EPA 600/4-79-020, Revised March 1983.

Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, USEPA, SW-846, Update II, September 1994.

Perkin Elmer, Flame AA, Analytical Methods for Atomic Absorption Spectrophotometry, Norwalk, Connecticut, Jan, 1982.

References: EPA Method 245.1 Manual Colorimetry	Rev: Original Effective Date: 8/1/97

MERCURY

I. SCOPE AND APPLICATION.

This procedure measures total mercury (organic & inorganic) in drinking, surface, ground, sea, brackish, industrial and domestic wastewater.

The range of the method is 0.1 to 10 µg Hg/L. This range was extended from the methods normal range by modifying the method. A 200 milliliter sample volume is used to reach the lower detection limit.

II. SUMMARY OF METHOD.

A 200-ml portion of a water sample is transferred to a BOD bottle (or an equivalent flask fitted with a ground glass stopper). It is digested in diluted potassium permanganate-potassium per sulfate solutions and oxidized for 2 h at 95-C. Mercury in the digested water sample is reduced w stannous chloride to elemental mercury and measured by the conventional cold vapor aton.. absorption technique.

III. INTERFERENCES.

Interferences have been reported for waters containing sulfide, chloride, copper and tellurium. Organic compounds which have broad band UV absorbance (around 253.7 nm) are confirmed interferences. The concentration levels for interfering compounds are difficult to define. This suggests that quality control procedures must be strictly followed.

Volatile materials which absorb at 253.7 nm will cause a positive interference. In order to remove any interfering volatile materials, the dead air space in the BOD bottle should be purged before addition of stannous chloride solution.

IV. APPARATUS.

ABSORPTION CELL - Standard spectrophotometer cells 10-cm long, having quartz windows may be used. Suitable cells may be constructed from plexiglass tubing, 1-in. O.D. by 4 ½-in. long. The ends are ground perpendicular to the longitudinal axis and quartz windows (1-in. diameter by 1/16-in. thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but 1/4-in. O.D.) are attached approximately ½-in. from each end. The cell is strapped to a burner for support and aligned in the light beam to give the maximum transmittance.

AERATION TUBING - Inert mercury-free tubing is used for passage of mercury vapor from the sample bottle to the absorption cell. In some systems, mercury vapor is recycled. Straight glass tubing terminating in a coarse porous glass aspirator is used for purging mercury released from the water sample in the BOD bottle.

AIR PUMP - Any pump (pressure or vacuum system) capable of passing air 1 L/min is used. Regulated compressed air can be used in an open one-pass system.

PERKIN ELMER ATOMIC ABSORPTION SPECTROPHOTOMETER MODEL 3300- Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for mercury measurement using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

BIOCHEMICAL OXYGEN DEMAND (BOD) BOTTLE

DRINKING TUBE - Tube (6 in. X 3/4-in. OD) containing 20 g of magnesium perchlorate. The filled tube is inserted (in-line) between the BOD bottle and the absorption tube. In place of the magnesium perchlorate drying tube, a small reading lamp is positioned to radiate heat (about 10-C above ambient, on the absorption cell. Heat from the lamp prevents water condensation in the cell.

FLOWMETER - Capable of measuring an air flow of 1 L/min.

MERCURY HOLLOW CATHODE LAMP - Single element hollow cathode lamp or electrode-less discharge lamp and associated power supply.

RECORDER - Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

WATER BATH - The water bath should have a covered top and capacity to sustain a water depth of 2-in. to 3-in. at 95-C +/- 1-C. The dimensions of the water bath should be large enough to accommodate BOD bottles containing CAL, LFB, LFM, LRB, QCS and water samples with the lid on.

GLASSWARE - Class A volumetric flasks and pipets as required.

V. SAMPLE HANDLING AND PRESERVATION.

Because of the extreme sensitivity of the analytical procedure and the presence of mercury in a laboratory environment, care must be taken to avoid extraneous contamination. Sampling devices, sample containers and plastic items should be determined to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contamination from airborne mercury vapor. Procedures found to provide clean labware include washing with a detergent solution, rinsing with tap water, soaking for 4 hours in a mixture of dilute acids (10% $HN0_3$, 10% HC1, and 80% distilled water), rinsing with reagent water and storing clean. Ideally, ground glass surfaces should be avoided to eliminate a potential source of random contamination. When this is

impractical, particular attention should given to all ground glass surfaces during cleaning. Chromic acid cleaning solutions must be avoided because chromium is an metal.

The water sample should be preserved with HNO_3 to pH <= 2.

VI. REAGENTS.

Reagents may contain elemental impurities which bias analytical results. All reagents should be assayed by the chemical manufacturer for mercury and meet ACS specifications. It is recommended that the laboratory analyst assay all reagents for mercury.

Hydroxylamine Hydrochloride (NH20H#HC1), (CAS# 5470-11-1) may be used in place of hydroxylamine sulfate; assayed mercury level of compound is not to exceed 0.05 ppm.

Hydroxylamine Sulfate [(NH20H)2*H2S04], (CASRN 10039-54-0); assayed mercury level of compound is not to exceed 0.05 ppm.

Mercuric Chloride (HgC12), (CASRN 7487-94-7).

Nitric Acid (HN03), concentrated (sp.gr. 1.41), (CASRN 7697-37-2); assayed mercury level is not to exceed 1 ppb.

Potassium Permanganate (KMn04), (CASRN 7722-C4-7); assayed mercury level is not to exceed 0.05 ppm.

Potassium Per sulfate (K2S208), (CASRN 7727-21-1); assayed mercury level is not to exceed 0.05 ppm.

Reagent water, ASTM type 115.

Sodium Chloride (NaC1), (CASRN 7647-14-5); assayed mercury level is not to exceed 0.05 ppm.

Stannous Chloride (SnC12*2H20), (CASRN 1--25-69-1); assayed mercury level is not to exceed 0.05 ppm.

Stannous Sulfate, (SnS04), (CASRN 7488-55-3); assayed mercury level is not to exceed 0.05 ppm.

Sulfuric Acid (H2S04), concentrated (sp. gr. 1.84), (CASRN 7664-93-9); assayed mercury level is not to exceed 1 ppb.

MERCURY CALIBRATION STANDARD - To each volumetric flask used for serial dilutions, acidify with (p.1 to 0.2% by volume) $HN0_3$. Using mercury stock standard, make serial dilutions to obtain a concentration of 0.1 µg Hg/ml. This standard should be prepared just before analyses.

MERCURY STOCK STANDARD - Dissolve in a 100-ml volumetric flask 0.1354 g HgC1 with 75 ml of reagent water. Add 10 ml of concentrated $HN0_3$ and dilute to mark. Concentration is 1.0 mg Hg/ml.

POTASSIUM PERMANGANATE SOLUTION - Dissolve 5 g of $KMn0_4$ in 100 ml of reagent water.

POTASSIUM PERSULFATE SOLUTION - Dissolve 5 g of $K_2S_20_8$ in 100 ml of reagent water.

SODIUM CHLORIDE-HYDROXYLAMINE SULFATE SOLUTION - Dissolve 12 g of NaC1 and 12 g of $(_{NH20H})_2*H_2S0_4$ or 12 g of $NH_20H*HC1$ regent water to 100 ml.

STANNOUS CHLORIDE SOLUTION - Add 25 g of $SnCl_2*2H_20$ or 25 g of $SnS0_4$ to 250 ml of 0.5 N H_2S0_4. This mixture is a suspension and should be stirred continuously during use.

SULFURIC ACID, 0.5 N - Slowly add 14.0 ml of concentrated H_2S0_4 dilute to 1 L with reagent water.

VII. CALCULATIONS

Measure the peak height of the unknown from the chart and read the mercury value from the standard curve. The standard calibration curve is calculated plotting the known concentration standards on a lotus spread sheet.

Calculate the mercury concentration in the sample by the formula:

mg Hg/L = (µg Hg in aliquot) (1000/ml of aliquot)

Report mercury concentrations as follows: Below 0.2 µg/L, < 0.2 µg/L; between 1 and 10 µg/L, one decimal; above 10 µg/L, whole numbers.

VIII. PROCEDURE

Transfer 200 ml of the water sample [or an aliquot diluted with reagent water to 100 ml] into a BOD bottle.

Add 5 ml of H_2S0_4 and 2.5 ml of $HN0_3$ to the sample.

To each bottle add 50 ml reagent water and 15 ml $KMn0_4$ solution. For sewage or industry waste waters, additional $KMn0_4$ may be required. Shake and add additional portions of $KMn0_4$ solution, if necessary, until the purple color persist for at least 15 min. Add 8 ml of $K_2S_20_8$ solution to each bottle. Mix thoroughly, cap and cover the top of the BOD bottle with aluminum foil or other appropriate cover. Heat for 2 h in a water bath at 95-C.

Turn on the spectrophotometer and circulating pump. Adjust the pump rate to 1 L/min. Allow the spectrophotometer and pump to stabilize.

Cool the BOD bottles to room temperature and dilute in the following manner:

To each BOD bottle containing the instrument calibration LFB and LRB, add 50 ml of reagent water.

To each BOD bottle containing a water sample, QCS or LFM, add 55 ml of reagent water.

To each BOD bottle, add 6 ml of $NaCl\text{-}(NH_2OH)_2{*}H_2SO_4$ solution to reduce the excess permanganate.

Treating each bottle individually:

Placing the aspirator inside the BOD bottle and above the liquid, purge the head space (20 to 30 sec) to remove possible gaseous interference.

Add 5 ml of $SnCl_2$ solution and immediately attach the bottle to the aeration apparatus.

The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 sec. As soon as the recorder pen levels off, approximately 1 min, open the bypass value (or optionally remove aspirator from the BOD bottle if it is vented under the hood) and continue aeration until the absorbance returns to its minimum value.

Close the by-pass value, remove the aspirator from the BOD bottle and continue aeration. Repeat until all BOD bottles have been aerated and recorded.

IX. ALLOWABLE LIMITS.

The daily maximum concentration for the NPDES outfall 001 at the sewage treatment plant is 0.0001 mg/L.

X. QC CHECKS.

One spiked blank and spiked sample will be run with every 20 sample determinations. The spike concentration shall consist of at least 1 time the average concentration found in a typical sample for each determined parameter. Code 4052 laboratory will obtain or prepare a standard solution.

Duplicate analysis on one sample after every ten samples are analyzed shall be performed for each parameter if enough sample volume is available.

One reagent blank shall be analyzed each day an analysis is performed for each parameter.

Split samples shall be analyzed quarterly by a control laboratory.

Code 095 will obtain performance evaluation samples from a vendor and these will be analyzed by the Code 4052 laboratory every three months.

References:
EPA Method 8330

Rev: Original
Effective Date: 8/1/97

NITROAROMATICS AND NITRAMINES

I. SCOPE AND APPLICATION.

Method 8330 is intended for the trace analysis of explosives residues by high performance liquid chromatography using a UV detector. This method is used to determine the concentration of the following compounds in a water, soil, or sediment matrix:

COMPOUND:	Abbreviation	CAS No. (a)
Octahydro-1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetrazocine	HMX	2691-41-0
Hexahydro-1, 3, 5-trinitro-1, 3, 5-triazine	RDX	121-82-4
1, 3, 5-Trinitrobenzene	1, 3, 5-TNB	99-35-4
1, 3-Dinitrobenzene	1, 3-DNB	99-65-0
Methyl-2, 4, 6-trinitophenylnitramine	Tetryl	479-45-8
Nitrobenzene	NB	98-95-3
2, 4, 6-Trinitrotoluene	2, 4, 6-TNT	118-96-7
4-Amino-2, 6-dinitrotoluene	4-Am-DNT	1946-51-0
2-Amino-4, 6-Dinitrotoluene	2-Am-DNT	355-72-78-2
2, 4-Dinitrotoluene	2, 4-DNT	121-14-2
2, 6-Dinitrotoluene	2, 6-DNT	606-20-2
2-Nitrotoluene	2-NT	88-72-2
3-Nitrotoluene	3-NT	99-08-1
4-Nitrotoluene	4-NT	99-99-0

(a) Chemical Abstracts Service registry number.

II. SUMMARY OF METHOD.

Method 8330 provides high performance liquid chromatographic (HPLC) conditions for the detection of ppb levels of certain explosives residues in water, soil and sediment matrix. Prior to use of this method, appropriate sample preparation techniques must be used.

The Code 4052 laboratory will use Windowchem™ Software's ControlChart!™ software to generate quality control charts for the atomic absorption spectrophotometer. A separate control chart will be prepared for each concentration range represented in the outfall data. Duplicate sample range results will be charted to monitor the atomic absorption spectrophotometer's precision. Spiked blank and spiked sample percent recovery data will be charted to monitor its accuracy. Procedures for preparing and using control charts are in section 1, chapter 6 of this QA/QC manual.

XI. REFERENCES

Methods for Chemical Analysis of Water and Wastes, USEPA, EPA 600/4-79-020, Revised March 1983.

Perkin Elmer, Flame AA, Analytical Methods for Atomic Absorption Spectrophotometry, Norwalk, Connecticut, Jan, 1982.

High-level Direct Injection Method: Aqueous samples of higher concentration can be diluted 1/1 (v/v) with methanol or acetonitrile, filtered, separated on a C-18 reverse phase column, determine at 254 nm, and confirmed on a CN reverse phase column. If HMX is an important target compound, methanol is preferred.

III. INTERFERENCES.

Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts or elevated baselines, causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interferences.

2, 4-DNT and 2, 6-DNT elute at similar retention times (retention time difference of 0.2 minutes). a large concentration of one isomer may mask the response of the other isomer. If it is not apparent that both isomers are present (or are not detected), an isomeric mixture should be reported.

Tetryl decomposes rapidly in methanol/water solutions, as well as with heat. All aqueous samples expected to contain tetryl should be diluted with acetonitrile prior to filtration and acidified to pH <3. All samples expected to contain tetryl should not be exposed to temperatures above room temperature.

Degradation products of tetryl appear as a shoulder on the 2,4,6-TNT peak. Peak heights rather than peak areas should be used when tetryl is present in concentrations that are significant relative to the concentration of 2,4,6-TNT.

IV. APPARATUS.

HPLC System

HPLC - equipped with a pump capable of achieving 4000 psi, a 100 ul loop injector and a 254 nm UV detector (Perkin Elmer Series 3, or equivalent).
Recommended Columns:

Primary column: C-18 Reverse phase HPLC column, 25 cm x 4.6 mm (5 um), (Supelco LC-18, or equivalent).

Secondary column: CN Reverse phase HPLC column, 25 cm x 4.6 mm (5 um), (Supelco LC-CN, or equivalent).

Strip chart recorder.

Digital integrator (optional).

Auto-sampler (optional).

Other equipment:

Temperature controlled ultrasonic bath.

Vortex mixer.

Balance +/- 0.001 g.

Magnetic stirrer with stirring pellets.

Water bath - Heated, with concentric ring cover, capable of temperature control (+/- 5-C). The bath should be used in a hood.

Oven - Forced air, without heating.

V. SAMPLE HANDLING AND PRESERVATION.

Follow conventional sampling and sample handling procedures as specified for semivolatile organics.

Samples and sample extracts must be stored in the dark at 4-C. Holding times are the same as for semivolatile organics.

VI. REAGENTS.

Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of American Chemical Society, where such specifications are available. Other gases may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination.

Acetonitrile, CH_3CN - HPLC grade.
Methanol, CH_3OH - HPLC grade.
Calcium chloride, $CaCl_2$ - Reagent grade. Prepare an aqueous solution of 5 g/L.
Sodium chloride, NaCl, shipped in glass bottles - reagent grade.

Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

Stock standard Solutions

Dry each solid compound standard to constant weight in a vacuum desiccator in the dark. Place about 0.100 g (weighed to 0.0001 g) of a single compound into a 100 ml volumetric flask and dilute to volume with acetonitrile. Invert flask several times until dissolved. Store in refrigerator at 4-C in the dark. Calculate the concentration of the stock solution from the actual weight used (nominal concentration = 1,000 mg/L). Stock solutions may be used for up to one year.

Mobile Phase: 50/50 (v/v) methanol/organic-free reagent water.

Flow Rate: 1.5 ml/min

Injection volume: 100-uL

UV Detector: 254 nm

IX. ALLOWABLE LIMITS.

NO INFORMATION AVAILABLE.

X. QC CHECKS.

One spiked blank and spiked sample will be run with every 20 sample determinations. The spike concentration shall consist of at least 1 time the average concentration found in a typical sample for each determined parameter. Code 4052 laboratory will obtain or prepare a standard solution.

Duplicate analysis on one sample after every ten samples are analyzed shall be performed for each parameter if enough sample volume is available.

One reagent blank shall be analyzed each day, an analysis is performed for each parameter.

Split samples shall be analyzed quarterly by a control laboratory.

The Code 4052 laboratory will use Windowchem™ Software's ControlChart!™ software to generate quality control charts for the ion liquid chromatograph . A separate control chart will be prepared for each concentration range represented in the outfall data. Duplicate sample range results will be charted to monitor the ion liquid chromatograph's precision. Spiked blank and spiked sample percent recovery data will be charted to monitor its accuracy. Procedures for preparing and using control charts are in section 1, chapter 6 of this QA/QC manual.

XI. REFERENCES

Methods for Chemical Analysis of Water and Wastes, USEPA, EPA 600/4-79-020, Revised March 1983.

Perkin Elmer, Flame AA, Analytical Methods for Atomic Absorption Spectrophotometry, Norwalk, Connecticut, Jan, 1982.

NOTE: The HMX, RDX, Tetryl, and 2, 4, 6-TNT are explosives and the neat material should be handled carefully. HMX, RDX, and Tetryl reference materials are shipped under water. Drying at ambient temperature requires several days. DO NOT DRY AT HEATED TEMPERATURES!

Intermediate Standards Solutions

If both 2, 4-DNT and 2, 6-DNT are to be determined, prepare two separate intermediate stock solutions containing (1) HMX< RDX< 1, 3, 5-TNB, 1, 3-DNB, NB, 2, 4, 6-TNT, and 2, 4-DNT and 2) Tetryl, 2, 6-DNT, 2-NT, 3-NT, and 4-NT. Intermediate stock standard solutions should be prepared at 1,000 µg/L, in acetonitrile when analyzing soil samples, and in methanol when analyzing aqueous samples.

Dilute the two concentrated intermediate stock solutions, with the appropriate solvent, to prepare intermediate standard solutions that cover the range of 2.5 - 1,000 µg/L. These solutions should be refrigerated on preparation, and may be used for 30 days.

Working Standards

Calibration standards at a minimum of five concentration levels should be prepared through dilution of the intermediate standards solutions by 50% (v/v) with 5 g/L calcium chloride solution. These solutions must be refrigerated and stored in the dark, and prepared fresh on the day of calibration.

Surrogate Spiking Solution

The analyst should monitor the performance of the extraction and analytical system as well as the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard and reagent water blank with one or two surrogates (e.g., compounds not expected to be present in the sample).

Matrix Spiking Solutions

Prepare matrix spiking solutions in methanol such that the concentration in the sample is five times the Estimated Quantitation Limit. All target compounds should be included.

HPLC Mobile Phase

To prepare 1 liter of mobile phase, add 500 ml of methanol to 500 ml of organic-free reagent water.

VII. CALCULATIONS

Calculate sample concentrations by obtaining a response factor by dividing the standard concentration by the standard peak area. Multiply the sample peak areas, that have the same

retention times as the explosive standard peaks, by the response factor to obtain the sample concentration.

VIII. PROCEDURE

Sample Preparation

Aqueous Samples - High Level Method

Sample filtration: Place a 5 ml aliquot of each water sample in a scintillation vial, add 5 ml of acetonitrile, shake thoroughly, and filter through a 0.45-µm Teflon filter using a disposable syringe. Discard the first 3 ml of filtrate, and retain the remainder in a Teflon-capped vial for Rp-HPLC analysis. HMX quantitation can be improved with the use of methanol rather than acetonitrile for dilution before filtration.

Soil and Sediment Samples

Sample homogenization: Dry soil samples in air at room temperature or colder to a constant weight, being careful not to expose the samples to direct sunlight. Grind and homogenize the dried sample thoroughly in an acetonitrile rinsed mortar to pass a 30 mesh sieve.

NOTE: Soil samples should be screened by Method 8515 prior to grinding in a mortar and pestle.

Sample extraction

Place a 2.0 g sub-sample of each soil sample in a 15 ml glass vial. Add 10.0 ml of acetonitrile, cap with Teflon-lined cap, vortex swirl for one minute, and place in a cooled ultrasonic bath for 18 hours.

After sonication, allow sample to settle for 30 minutes. Remove 5.0 ml of supernatant, and combine with 5.0 ml of calcium chloride solution in a 20 ml vial. Shake, and let stand for 15 minutes.

Place supernate in a disposable syringe and filter through a 0.45-µm Teflon filter. Discard first 3 ml and retain remainder in a Teflon-capped vial for RP-HPLC analysis.

Chromatographic Conditions (Recommended)

Primary Column: C-18 reverse phase HPLC column, 25 cm X 4.6-nm, 5 um, (Supelco LC-18 or equivalent).

Secondary Column: CN reverse phase HPLC column, 25-cm X 4.6-nm, 5 um, (Supelco LC-CN or equivalent).

SECTION III

III-1 Quality Assurance Policy Statement

The Explosive Sciences Branch, Laboratory, Building 2707, is committed to continuous quality improvement through identifying and managing variation within each analytical process. This improvement is achieved by implementing required quality control procedures such as analyzing matrix blanks, sample matrices spiked with known analyte concentrations and duplicate analysis of discrete samples. Quality Control reference standards submitted by the customer are also analyzed. Corrective Action Forms are maintained and submitted to appropriate authorities. Control charts of duplicates and percent recovery of reference standards and spiked samples are maintained by the laboratory. Through teamwork and accountability, the Explosive Sciences Branch laboratory strives to meet and exceed regulatory expectations, so that legislative compliance is second nature. It is essential that this statement be promulgated throughout the organization.

III-2 Ethics Policy on Waste, Fraud and Abuse

Per DoD Directive 7050.1, Crane shall encourage personnel to register complaints and grievances through appropriate management and grievance channels, and submit suggestions for management improvements through the proper DoD Incentive Awards Program. There shall be no requirement for any individual who makes complaints or provides information to the Inspector General or DoD Defense Hotline representatives to discuss such complaints or information with the individual's supervisor or the head of the activity. Crane shall encourage the reporting of suspected fraud and mismanagement to the Defense Hotline either through the toll-free 800-424-9098 commercial, FTS 202-693-5080, or AUTOVON 223-5080 telephone system or by mail to the Defense Hotline, The Pentagon, Washington, D.C. 20301-1900.

III-3 Quality Assurance, Administrative Management and Personnel Qualifications

The direct and ultimate responsibility for assuring data quality at the Explosive Sciences Branch laboratory rests with the Explosive Sciences Branch Manager. In delegating QA responsibilities/authorities, the Explosive Sciences Branch Manager divides her delegated work to her subordinate line managers (see Figure III-3-1). The Explosive Sciences Branch laboratory QA officer provides technical support and reviews and approves QA products. The laboratory analyst will provide the first level of data review in the laboratory, however, the Explosive Sciences Branch Manager will also provide quality assurance/control of all data gathered or reported for NPDES compliance testing. It may also be reviewed by the Code 095 QA officer if so requested by the Explosive Sciences Branch Manager. If a problem arises and is not addressed by the Explosive Sciences Branch Manager, the laboratory analyst may seek an alternative channel of resolution through the Code 095 QA Officer.

Explosive Sciences Branch Laboratory
Organizational Chart and
Personnel Qualifications

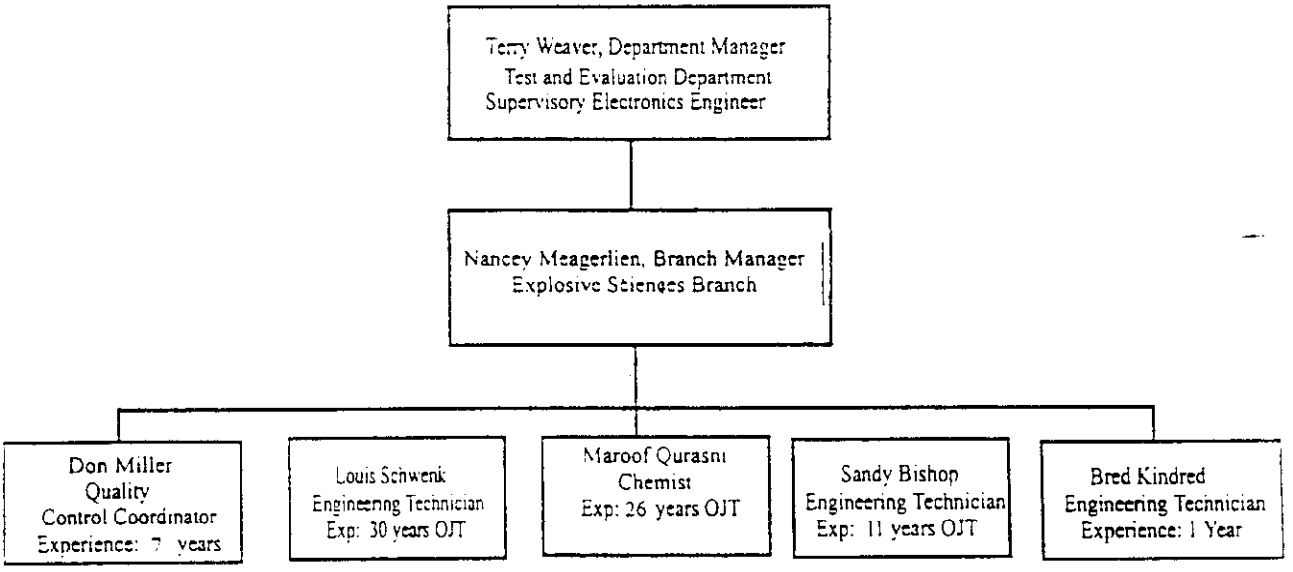

Figure III-3-1. Explosive Sciences Branch Laboratory Organization Chart

III-4 Facility Description, Capital Equipment and Supplies

The Explosive Sciences Branch laboratory is a 11,250 square foot state-of-the-art facility which conducts explosives analysis, metallurgical determinations, ultrasonic metallurgical analysis for faults, environmental multi-media analysis and TCLP hazardous waste determination testing. Explosive Sciences Branch equipment includes gas chromatography-mass spectrometry (GC/MS), high performance liquid chromatography (HPLC), gel permeation liquid chromatography (GPLC), graphite furnace atomic absorption spectrometry and a scanning electron microscope (SEM) with a qualitative elemental analyzer. The Explosive Sciences Branch laboratory has a large capital equipment inventory
(see Figure III-4-1).

Figure III-4-1
EXPLOSIVE SCIENCES BRANCH CAPITAL EQUIPMENT LIST

Instrument Description	Purchased	Manufacturer	Model
MICROWAVE DIGESTION SYS.	1987	CEM CORPORATION	MDS-81D
INFRARED SPECTROMETER	1985	BIORAD	QUALI-MATIC
INFRARED SPECTROMETER	1986	BIORAD	FTS-60
INFRARED SPECTROMETER	1981	PERKIN-ELMER	CO683
ELECTRONIC BALANCE	1981	OHAUS	1500D
EXTRACTOR	1981	MILLIPORE CORP	YS 31
FILTRATION SYSTEM	1981	MILLIPORE CORP	0M0100
GAS CHROMATOGRAPH / MASS SPECTROMETER	1993	HEWLETT PACKARD	5890-II
INFRARED DATA SYSTEM	1981	PERKIN ELMER	683
AUTO SAMPLE INJECTOR	1988	SHUMADZU	SIL-9A
COMPUTING INTEGRATOR	1983	SPECTRA PHYSIC	4270
X RAY ENERGY SPECTROMETER	1983	TRACOR NORTHERN	126 14
SCANNING ELECTRON MICROSCOPE	1996	AMRAY	3200S-ECO
SCANNING ELECTRON MICROSCOPE	1983	AMRAY	1600
SPECTROPHOTOMETER	1979	PERKIN ELMER	552
BALANCE	1970	METTLER	B5C1000
CHROMATOGRAPHY PUMP SYS	1971	WATERS	C903
CHROMATOGRAPH GAS	1993	HEWLETT PACKARD	5890
GAS CHROMATOGRAPH	1976	GOW MAC INSTRUMENTS	69 750

GAS CHROMATOGRAPH / MASS SPECTROMETER	1977 - modernized in 1997	FINNIGAN	4500
GAS CHROMATOGRAPH / MASS SPECTROMETER	1989	FINNIGAN	TSQ-70
ANALYTICAL BALANCE	1980	PERKIN ELMER	AD-2Z
MERCURY ANALYZER SYSTEM	1984	PERKIN ELMER	MAS 50A
BALANCE	1984	METTLER	AE160
ANALYTICAL BALANCE	1985	METTLER	PE1600
ANALYTICAL BALANCE	1985	METTLER	PE1600
ATOMIC ABSORPTION SPECTROMETER	1985	PERKIN ELMER	5000
ATOMIC ABSORPTION SPECTROMETER	1994	PERKIN ELMER	300
BALANCE	1985	METTLER	AE160
BALANCE	1985	METTLER	AE160
BALANCE	1985	METTLER	AE160
GAS CHROMATOGRAPH	1985	TRACOR INSTRUMENTS	540
GAS CHROMATOGRAPH	1985	TRACOR INSTRUMENTS	540
CHROMATOGRAPHY INTEGRATOR	1985	SPECTRA PHYSIC	4270
CHROMATOGRAPHY INTEGRATOR	1985	SPECTRA PHYSIC	4270
ORGANIC VAPOR ANALYZER	1986	THERMO ELECTRON	590
ION/LIQUID CHROMATOGRAPH	1986	WATERS MILLIPOR	430
ION/LIQUID CHROMATOGRAPH	1986	WATERS MILLIPOR	490
BALANCE	1986	OHAUS	GALAXY 160

III-5 NPDES Compliance Sampling, Handling and Chain of Custody

III-5.1 NPDES Compliance Sampling

To comply with the requirements of the NPDES program and Crane's NPDES permit (number IN0021539), employees at the Crane waste water treatment plant collect water samples and deliver them to the Explosive Sciences Branch laboratory for analysis. The Explosive Sciences Branch laboratory analyzes for ammonia, cyanide, oil & grease, hexavalent chromium, nitrate, explosives and metals. (see Table III-5-1) The other parameters are analyzed by a contract laboratory.

Table III-5-1
NPDES EFFLUENT LIMITATION AND MONITORING REQUIREMENTS

DISCHARGE LIMITATIONS[1]						
Effluent Characteristic	lbs/day		Other Limitations		Monitoring Requirement	
	Monthly Average	Daily Maximum	Monthly Average	Daily Maximum	Measurement Frequency	Sample Type
Flow (MGD)	--	--	--	--	5 X Weekly	24 hr comp.
$CBOD_5$	30.54	45.81	10 mg/l	15 mg/l	2 X Weekly	24 hr comp.
TSS	30.54	45.81	10 mg/l	15 mg/l	2 X Weekly	24 hr comp.
Ammonia (as NH_3-N)						
Summer[2]	4.58	9.16	1.5 mg/l	3.0 mg/l	2 X Weekly	24 hr comp.
Winter[3]	9.16	18.33	3.0 mg/l	6.0 mg/l	2 X Weekly	24 hr comp.
Dissolved Oxygen						
Summer[2]	--	--	6.0 min.	Daily Avg.	2 X Weekly	3 grabs/24 hr[4]
Winter[3]	--	--	5.0 min.	Daily Avg.	2 X Weekly	3 grabs/24 hr[4]
Cadmium[5]	0.006	0.009	0.002 mg/l	0.003 mg/l	Monthly	24 hr comp.
Hex. Chromium[7]	0.024	0.055	0.008 mg/l	0.018 mg/l	Monthly	24 hr comp.
Chromium[5,7]	0.776	1.802	0.254 mg/l	0.590 mg/l	Monthly	24 hr comp.
Copper[5]	0.046	0.061	0.015 mg/l	0.020 mg/l	Monthly	24 hr comp.
Total Cyanide	0.015	0.027	0.005 mg/l	0.009 mg/l	Weekly	24 hr comp.
Lead[5,7]	0.018	0.037	0.006 mg/l	0.012mg/l	Monthly	24 hr comp.
Mercury[5,7]	Report	0.0003	Report	0.0001 mg/l	Monthly	24 hr comp.
Nickel[5,7]	0.217	0.501	0.071 mg/l	0.164 mg/l	Monthly	24 hr comp.
Zinc[5,7]	0.403	0.941	0.132 mg/l	0.308 mg/l	Monthly	24 hr comp.
Silver[5,7]	Report	0.040	Report	0.010 mg/l	Monthly	24 hr comp.
Residual chlorine[6]						
After disinfection	--	--	between 0.5 and 1.0 mg/l	between 0.5 and 1.0 mg/l	5 X Weekly	Grab
After dechlorination	--	--	--	0.05 mg/l	5 X Weekly	Grab

1 See PART I.E. - SCHEDULE OF COMPLIANCE for effectiveness of interim and final limitations.
2 Summer limitations apply from May 1 to November 30 of each year.
3 Winter limitations apply from December 1 to April 30 of each year.
4 The reported daily average concentration of dissolved oxygen in the effluent shall be the arithmetic mean determined by summation of the three daily grab sample results and dividing this sum by three. These samples are to be collected over equal time intervals during the period of operator attendance.
5 At this time an approved analytical method for acid-soluble metal is not available. The permittee shall measure and report noted limitations as total recoverable metal until such a test method is approved for acid-soluble metal.
6 The effluent shall be disinfected on a continuous basis April 1 through October 31, annually. Practice of chlorination for any reason November 1 through March 31 will require monitoring and reporting and result in the maximum effluent limitation after dechlorination applying at such time.
7 If, after 12 months of sampling for these pollutants, the permittee is able to demonstrate that any of them are not present in detectable quantities, they may request modification of this permit to delete effluent limitations and monitoring requirements for such pollutants.

III-5.2 Handling

The Explosive Sciences Branch laboratory staff does not collect the NPDES samples, therefore no field sample handling procedures are specified. They do, however, handle the sample bottles prior to analysis. Laboratory technicians wear latex disposable gloves while preparing and analyzing hazardous samples.

III-5.3 Chain of Custody

Proper sample tracking is accomplished with a chain of custody form. The chain of custody form is used to record a sample's identity and provide a record showing custody from sampling to delivery. The chain of custody shall accompany samples at all times. The following information shall be supplied on a completed the chain of custody from:

- project name and number
- signature of samplers
- sampling station number or sample number, date and time of collection, grab or composite sampling designation, and a brief description of the type of sample (matrix) and sampling location
- signatures of individuals involved in sample transfer (i.e., relinquishing and accepting samples). Individuals receiving the samples shall sign, date, and note the time that they received the samples on the form

As soon as samples are received by the Explosive Sciences Branch laboratory, the sample is entered into the sample log book. The original chain of custody form is signed and a copy is returned to the courier. The Explosive Sciences Branch laboratory files the original chain of custody form.

III-6 Preventive Maintenance

The Explosive Sciences Branch laboratory relies on mechanical equipment to perform sample analysis. With such great reliance on this equipment, it is imperative that all equipment be kept in excellent operating condition. All capital equipment is routinely maintenanced at the Explosive Sciences Branch laboratory to ensure it runs efficiently when needed. An ample supply of probes, reagents, water filters columns, and filter disks are kept on hand and are replaced on a regular basis. Following is a list of supplies used for the various analytical methods:

PARAMETER: Hexavalent Chromium

1. Inventory and reorder if necessary, every three months, of all required reagents and supplies for EPA method 218.4.

2. Nitric acid rinse of dedicated glassware once every three months to eliminate trace chromium contamination.

PARAMETER: Oil and Grease

1. Inventory and reorder if necessary, every three months, of all required reagents and supplies for EPA method 1664 that uses the Solid Phase Extraction technique.

   Critical Solid Phase Extraction technique requirements:

   a. Extraction disks
   b. Hexane, HPLC grade
   c. Methanol, HPLC grade

PARAMETER: Nitrate-Nitrogen

1. Inventory and reorder if necessary, every three months, of all required reagents and supplies for EPA method 300 that uses the Ion Chromatography (IC) technique.

   Critical IC technique requirements:

   a. HPLC pump repair kits
   b. 0.2 micron filter cartridges
   c. HPLC grade acetonitrile
   e. HPLC grade butanol
   f. Autosampler injector needles
   g. Autosampler sample vials

PARAMETER: Ammonia-Nitrogen

1. Inventory and reorder if necessary, every three months, of all required reagents and supplies for EPA method 350.3 that using the Specific Ion Electrode (SIE) technique.

   Critical SIE technique requirements:

   a. Specific Ion Electrode membranes
   b. Reagent grade ammonium chloride
   c. 50 percent sodium hydroxide solution

2. The membrane of the ammonia specific ion electrode will be changed every month.

PARAMETER: Total Cyanide

1. Inventory and reorder if necessary, every three months, of all required reagents and supplies for EPA method 335.2 that uses the Titrimetric, Spectrophotometric technique.

   Critical EPA method 335.2 requirements:

   a. Silver nitrate 0.0192 N standard solution, not older then expiration date
   b. Chloramine T
   c. Barbituric acid (fresh)

2. The Perkin-Elmer Model 552 Spectrophotometer shall be calibrated with a didymium glass calibration filter every three months. Maintenance on the spectrophotometer will performed by the vender repair person when a performance issue is observed.

PARAMETER: Metals (Cd, Cr, Cu, Pb, Ni, Ag, Zn, Hg)

1. Inventory and reorder if necessary, every three months, of all required reagents and supplies for EPA metals methods that use the Atomic Absorption (AA) graphite furnace, direct aspiration (flame), and cold vapor techniques.

   Critical EPA metals method requirements:

   a. AA graphite furnace tubes
   b. Up to date AA metals standard solutions
   c. Maintenance on the AA spectrophotometers will performed by the vendor repair person when a performance issue is observed.

III-7 Corrective Action

A corrective action program able to handle performance failures at any point in data generation is an indispensable tool for quality assurance and quality control management. A laboratory technician or data user can use a corrective action report form to notify the laboratory quality manager of an issue (Figure III-7-1). The employee can expect a response to the corrective action report. It is important that the response documents the actions taken and the response time.

Each corrective action report form is numbered for tracking and archiving purposes. The name of the requesting individual and organization, as well as the individual receiving the request, are recorded. If a review was done then the reviewer's name is also recorded. In general, if a data user corrective action report form is not initiated by the Code 095 QA representative, then the QA representative should review and approve the form. The corrective action report form will become a part of the administrative files. The following information will also be on the report:

1. Where did the out-of-control incident occur (laboratory name, address, telephone number section name)?

CORRECTIVE ACTION REPORT FORM	NO._____
TO: (ORGANIZATION) RECEIVED BY:	Date:
PREPARED BY: REVIEWED BY:	Date:
ACTIVITY:	LOCATION:
Where did out-of-control incident occur (laboratory name, address, telephone number, code)?	
When - did the incident occur? - was it corrected?	
What - was the name of the analysis? - was the problem with the test/control/instrument? - was the nature of the correction action? - will be done to prevent the reoccurrence of the problem?	
Why - did the incident happen (if a scientific explanation is available)?	
RESPONSE-SIGNATURE:	TITLE, CODE:
APPROVAL SIGNATURE:	TITLE, CODE:

CORRECTIVE ACTION REPORT FORM COMMENTS:

1. The corrective action report form will be filled out, reviewed and forwarded to the Public Works Department, Code 09, when ever an incident occurs involving analyses that are out of control of the Quality Control Chart limits. Also, whenever a incident/problem occurs with an analytical instrument that needs corrective action the same procedure will be followed.

Figure III-7-1 Corrective Action Report

2. When - did the incident occur?
   - was it corrected?

3. Who - discovered the out-of-control incident?
   - verified the incident?
   - corrected the problem?

4. What - was the name of the test?
   - was the disposition of the test or control and/or instrument?
   - was the nature of the corrective action?
   - will be done to prevent the reoccurrence of the problem?

5. Why - did the incident happen (if scientific explanation is available)?

Discovery and elimination of an issue's root cause is the goal of the corrective action program. The immediate actions taken to relieve the issue are recorded. Of equal (or greater) importance to continual laboratory performance improvement is documenting action taken to prevent a recurrence. If an issue is severe the laboratory quality control coordinator shall be contacted immediately.

Tracking corrective actions report forms and responses is important to discovery of repeating issues and discovering underlying problems. Corrective action report forms will be examined for tre and repeating issues, and their responses tracked by the Explosive Sciences Branch quality cont. coordinator.

III-8 Laboratory Evaluation and Audits

Performance evaluation (PE) audits are necessary to ensure data quality and should be routinely conducted. PE audit results are used to evaluate laboratory technician, instrumentation, and analytical system performance. PE samples contain a known set of target analytes. The laboratory analyzes the samples using its specified methods and submits results back to the PE audit program administrator. The laboratory's results are compared to results from all the laboratories participating in the program. The Explosive Sciences Branch laboratory will participate in a PE audit at a frequency to be determined.

III-9 Quality Assurance Reports to Management

Corrective action report forms will be given to the Explosive Sciences Branch Manager immediately if the action corrected a result that was a NPDES permit violation. Copies of all corrective action report forms will be submitted to the Explosive Sciences Branch Manager monthly by the fifth of the following month. Another copy of the corrective action report form should be provided to the Code 095 QA representative. The QA representative can include corrective action reports with the Indiana Department of Environmental Management monthly operation report.

It is recommended that this Explosive Sciences Branch laboratory QA/QC Manual be reviewed and updated annually by the Code 095 QA representative. This review should be accompanied by a quality systems and standard operating procedures reviews.

III-10 Lab Documentation and Forms

The following are copies of data collection and report forms used in the Explosive Sciences Branch laboratory. Each form is dated and when updated, the revised form will supersede the older forms. These forms may be reproduced for use by Explosive Sciences Branch laboratory analysts.

III-11 Sub-Contracting of Services

A portion of Crane's requirements for metal and total cyanide analysis is sub-contracted to Synergic Laboratories. Duplicate samples for these parameters are analyzed by ATC Laboratory, Synergic and the Explosive Sciences Branch laboratory. Sub-contracted laboratories will be involved in a PE audit program for the parameters they are required to test at a frequency to be determined.

III-12 Standard Operating Procedures

Standard Operating Procedures (SOPs) are available for all routinely used sampling or analytical laboratory methods. The Explosive Sciences Branch laboratory must maintain a log of all SOPs in use and must maintain a file of all revisions of SOPs used in the past. Appendix A is a current list of all SOPs with revision number and date.

III-13 Laboratory Personnel Training Record

The Explosive Sciences Branch laboratory maintains training records and documents procedures for each analyst in all methods that each analyst is conducting. The Explosive Sciences Branch laboratory only allows analysts who have completed training to conduct analytical methods independently. An analyst in training is directly supervised by an analyst who has completed training.

References

EPA *Guidance on Preparation of Laboratory Quality Plans*, EPA 910/9-92-032 Region 10, Seattle, WA (1992).

Naval Surface Warfare Center Standard Operating Procedures for Sewage Treatment Plant, Howard Needles Tammen & Bergendoff Architects Engineers Planners, Indianapolis, IN (1994).

NPDES TOTAL CYANIDE SAMPLES CUSTODY INFORMATION

NO.	SAMPLE IDENTIFICATION	COLLECTION DATE	COLLECTION TIME
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11			
12			

Collector sample preservation _____
Laboratory sample preservation _____
Storage of samples at laboratory _____

HANDLING/ANALYSIS OF TOTAL CYANIDE SAMPLES

ANALYST'S NAME _____

DATE OF ANALYSIS _____

Removal time of sample(s) from refrigerator: _____
Procedure identification: EPA 335.2
Instrumentation used for analysis: P&E 552
Initiation time of analysis: _____
Sample temperature at analysis start time: _____
Conductivity of distilled water used in analysis: _____
Purity level of solvent used in analysis: _____
Cyanide Stock std. serial number: _____
Cyanide Stock std. make up date: _____
Lot number cyanide stock standard used: _____

NOTE: A BLANK ENTRY MEANS NOT APPLICABLE

CALIBRATION STANDARDS CYANIDE ANALYSIS DATA

STOCK CYANIDE STANDARDIZATION TITRATION WITH 0.0192 NORMAL $AgNO_3$

BLANK TITRATION	#1 TITRATION	#2 TITRATION	#3 TITRATION
_____	_____	_____	_____
_____ ML	_____ ML	_____ ML	_____ ML

MG/L (PPM) CYANIDE = (ML TITER - ML BLANK) X 1000/ML STOCK SOL.=__MG/L

ML STOCK NEEDED = 1000/__ PPM CN X _x_/100. x = __ML

DILUTE __ML STOCK STD. TO 1000 ML MAKES A 100 MG/L CN^- INTERMEDIATE STD.

DILUTE INTERMEDIATE STD. 1:10 TO MAKE A 10 MICROGRAM/ML CN^- WORKING STD.
NOTE: **MAKE CALIBRATION STDS. BY PIPETTING APPROPRIATE AMOUNT OF WORKING STD (10 MICROGRAMS CN^-/ML) INTO 250 ML VOLUMETRIC FLASKS.**

CALIBRATION STANDARDS	ABSORBANCE @ 578 NM	ANALYSIS DATE	ANALYST'S INITIALS
BLANK	_____	_____	_____
__ MICROGRAMS CYANIDE	_____		
__ "	_____		
__ "	_____		
__ "	_____		
__	_____		

SAMPLE DATA OBTAINED PERFORMING EPA METHOD 335.2 COLORMETRIC PROCEDURE

SAMPLE IDENTIFICATION	ABSORBANCE @ 578NM	DILUTION FACTOR	MG/L TOTAL CYANIDE

SAMPLE DATA OBTAINED PERFORMING EPA METHOD 335.2 TITRATION PROCEDURE

SAMPLE IDENT.	ML 0.0192 NORMAL $AgNO_3$	BLANK TITER	MG/L CYANIDE

MODIFICATION/MAINTENANCE/REPAIR OF INSTRUMENTATION OR EQUIPMENT:

_____
_____
_____

UNDERSTOOD BY ME_____ DATE_____

NPDES OIL AND GREASE SAMPLES CUSTODY INFORMATION

NO.	SAMPLE IDENTIFICATION	COLLECTION DATE	COLLECTION TIME
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11			
12			

HANDLING/ANALYSIS OF OIL AND GREASE SAMPLES

ANALYST'S NAME _____

DATE OF ANALYSIS _____

Removal time of sample(s) from refrigerator: _____
Procedure identification: EPA 1664
Instrumentation used for analysis: _____
Initiation time of analysis: _____
Sample temperature at analysis start time: _____
Conductivity of distilled water used in analysis: _____
Purity level of solvent used in analysis: _____
Serial number of stock oil and grease standard: _____
Lot number of laboratory stock hexadecane used: _____
Lot number of laboratory stock stearic acid used: _____

NOTE: A BLANK ENTRY MEANS NOT APPLICABLE

Revision: Original
Effective Date:August 1, 1997

STANDARD/SAMPLE OIL AND GREASE ANALYSIS DATA

ANALYTICAL BALANCE		ANALYSIS DATE	ANALYST'S INITIALS
MODEL	_____		
CALIBRATION #	_____		
EXPIRATION DATE	_____	_____	_____

SAMPLE IDENT.	ML SAMPLE	GROSS WT., FLASK	TARE WT., FLASK	CONCENTRATION OIL & GREASE, MG/L

MODIFICATION/MAINTENANCE/REPAIR OF INSTRUMENTATION OR EQUIPMENT:

_____

_____

_____

UNDERSTOOD BY ME_____ DATE_____

NPDES NITRATE SAMPLES CUSTODY INFORMATION

NO.	SAMPLE IDENTIFICATION	COLLECTION DATE	COLLECTION TIME
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11			
12			

Collector sample preservation _____
Laboratory sample preservation _____
Storage of samples at laboratory _____

HANDLING/ANALYSIS OF NITRATE SAMPLES

ANALYST'S NAME _____

DATE OF ANALYSIS _____

Removal time of sample(s) from refrigerator: _____
Procedure identification: EPA 300
Instrumentation used for analysis: _____
Initiation time of analysis _____
Sample temperature at analysis start time: _____
Conductivity of distilled water used in analysis: _____
Purity level of solvent used in analysis: _____
Stock nitrate std. serial number: _____
Stock nitrate std. make up date: _____
Lot number of laboratory stock nitrate std. used: _____

NOTE: A BLANK ENTRY MEANS NOT APPLICABLE

Revision: Original
Effective Date: August 1, 1997

NO_3-N CALIBRATION STANDARDS DATA

	CALIBRATION STD 2.5 mg/l	CALIBRATION STD. 5.0 MG/L	CALIBRATION STD. 10.0 MG/L
PEAK AREA =			

SAMPLE ANALYSIS DATA

SAMPLE IDENT.	DATE	ANALYST'S INITIALS	NO_3-N PEAK AREA	DILUT. FACTOR	NO_3-N, MG/L

MODIFICATION/MAINTENANCE/REPAIR OF INSTRUMENTATION OR EQUIPMENT:

_____

_____

_____

UNDERSTOOD BY ME_____ DATE_____

NPDES HEXAVALENT CHROMIUM SAMPLES CUSTODY INFORMATION

NO.	SAMPLE IDENTIFICATION	COLLECTION DATE	COLLECTION TIME
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11			
12			

Collector sample preservation _____
Laboratory sample preservation _____
Storage of samples at laboratory _____

HANDLING/ANALYSIS OF HEXAVALENT CHROMIUM SAMPLES

ANALYST'S NAME _____

DATE OF ANALYSIS _____

Removal time of sample(s) from refrigerator: _____
Procedure identification: EPA 218.4
Instrumentation used for analysis: _____
Initiation time of analysis: _____
Sample temperature at analysis start time: _____
Conductivity of distilled water used in analysis: _____
Purity level of solvent used in analysis: _____
Stock std. serial number: _____
Stock std. make up date: _____
Serial number of AA lamp used: _____
Lot number of AA stock standard used: _____

NOTE: A BLANK ENTRY MEANS NOT APPLICABLE

Revision: Original
Effective Date: August 1, 1997

STANDARD HEXAVALENT CHROMIUM ANALYSIS DATA

CALIBRATION STANDARDS	ABSORBANCE	ANALYSIS DATE	ANALYST'S INITIALS
BLANK	_____	_____	_____
0.25 MICROGRAM/Cr^{+6}	_____		
0.5 "	_____		
1.0 "	_____		
2.5 "	_____		

SAMPLE HEXAVALENT CHROMIUM ANALYSIS DATA

SAMPLE IDENTIFICATION	ABSORBANCE	MICROGRAM/Cr^{+6}	DILUT. FACTOR	MG/L Cr^{+6}

MODIFICATION/MAINTENANCE/REPAIR OF INSTRUMENTATION OR EQUIPMENT:

_____

_____

_____

UNDERSTOOD BY ME_____ DATE_____

NPDES AMMONIA-NITROGEN SAMPLES CUSTODY INFORMATION

NO.	SAMPLE IDENTIFICATION	COLLECTION DATE	COLLECTION TIME
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11			
12			

Collector sample preservation _____
Laboratory sample Preservation _____
Storage of samples at laboratory _____

HANDLING/ANALYSIS OF NH_3-N SAMPLES

ANALYST'S NAME _____

DATE OF ANALYSIS _____

Removal time of sample(s) from refrigerator: _____
Procedure identification: EPA 350.3
Instrumentation used for analysis: _____
Initiation time of analysis _____
Sample temperature at analysis start time: _____
Conductivity of distilled water used in analysis: _____
Purity level of solvent used in analysis: _____
NH_3-N Stock std. serial number: _____
NH_3-N Stock std. make up date: _____
Lot number of laboratory stock NH_3-N std. used: _____

NOTE: A BLANK ENTRY MEANS NOT APPLICABLE

NH_3-N CALIBRATION STANDARDS DATA

CALIBRATION STANDARDS	MILLIVOLTS	ANALYSIS DATE	ANALYSTS INITIALS
BLANK	_____	_____	_____
0.03 MG/L NH_3-N	_____		
0.1 MG/L NH_3-N	_____		
1.0 "	_____		
10.0 "	_____		
100.0 "	_____		

NH_3-N SAMPLE ANALYSIS DATA

SAMPLE IDENT	MILLIVOLTS	DILUTION FACTOR	CONCENTRATION NH_3-N MG/L
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____

MODIFICATION/MAINTENANCE/REPAIR OF INSTRUMENTATION OR EQUIPMENT:

_____

_____

_____

UNDERSTOOD BY ME_____ DATE_____

SECTION FOUR

COMPLIANCE SAMPLING (NPDES)

Laboratory Quality Assurance/ Quality Control Manual

Prepared for:
Environmental Protection Department
Code 4052

THIS SECTION DOES NOT APPLY TO PROJECT

It is recommended that the QA/QC Manual be reviewed and updated at least annually by the Crane Quality Assurance Officer at Code 095. This should be accompanied by a quality system review of the laboratory's quality system and its standard operating procedures.

Section Four

Compliance Sampling
(NPDES)
Laboratory Quality Assurance/Quality Control Manual

for

Naval Surface Warfare Center Crane

300 Highway 361

Crane, Indiana 47522-5001

(812) 854-5500

August 1, 1997

Approvals:

Name: Jim Hunsicker Date:_____
Title: Environmental Protection Dept. Manager
Signature: _____

Name: Jim Market Date:_____
Title: QC Coordinator
Signature: _____

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SECTION IV

IV-1 Compliance Sampling (NPDES)

National Pollution Discharge Elimination System (NPDES) permit number IN 0021539 requires twelve sites to be monitored for various parameters by Naval Surface Warfare Center (NSWC), Crane. As a form of quality control, a number of other sites are frequently monitored for metals, cyanide, ammonia, and explosives. Due to the vast amount of sampling that is required, NSWC, Crane has contracted a large portion of the laboratory analyses to a private laboratory. Douglass Environmental from Indianapolis uses Synergic Analysis from Wyoming, Michigan and ATC from Indianapolis, Indiana for analytical testing purposes. Samples that must be analyzed within 24 hours are sent to the laboratory at Code 40.

Two permitted locations, Buildings 3049 and 3064, are operated by the Water Treatment Branch. These sites are under the supervision of Gary Bradfield, Code 09725.

Water Treatment Branch
Building 3064 Outfall 101 Chemical Treatment (electroplating waste water)
Building 3049 Outfall 001 (sewage treatment plant)

The treatment operators from the water treatment branch collect and preserve samples pertaining to their own operations. It is the responsibility of the Environmental Protection Department personnel to provide sample pick-up and shipment to the appropriate laboratories.

IV-2 Responsibilities and Quality Objectives

Personnel from the Environmental Protection Department are also responsible for flow monitoring, pH measurements, and sample collection for the remaining permitted outfalls. Environmental Protection Department personnel are also called upon to collect, preserve, and ship samples from a number of other sites that are of an environmental concern.

It is important to note that the contract laboratories provide NSWC Crane with new sample bottles, preservative included in bottles, and ice packs. These sampling necessities are shipped to the laboratory at building 3260 where they are kept until needed. The sample collector in turn will provide the treatment plant operators with the preserved sample bottles upon request.

The Table IV-2-1, on the following page, summarizes the matrices and outfalls to be sampled as well as the sample frequency. The table also illustrates the source of the required analyses.

The data quality objectives for field sampling are to demonstrate the ability to collect, preserve, and to ship samples to the laboratory without introducing contamination by the sampler's technique, the sample containers, the sampling apparatus, or other means of contamination of the sample prior to or during the shipment of the sample to the laboratory.

Table IV-2-1
Analyses For NPDES Sampling

Outfall Location	Parameter	Frequency of Analysis	Source - Present
001 Sewage Treatment Plate (STP)	Flow	Daily	STP Operators
	pH	5 × week	STP Operators
	$CBOD_5$	2 × week	STP Operators
	TSS	2 × week	STP Operators
	DO	2 × week	STP Operators
	NH_3-(N)	2 × week	Code 40
	Residual CL_2	5 × week	STP Operators
	Hex. Chrome	1 × month	Code 40
	Other Metals	1 × month	Synergic
	% Total Solids	variable (season)	STP Operators
	Total Cyanide	1 × week	Code 40
002, 003, 004, 008 - Demo. Rng. Sedimentation Ponds	Flow	2 × month	Code 095 -Env.
	pH	2 × month	Code 095 -Env.
	TSS	2 × month	STP Operators
	Settle able Solids	2 × month	STP Operators
009 - Scrapyard Oil/Water Separator	Flow	2 × month	Code 095 -Env.
	pH	2 × month	Code 095 -Env.
	TSS	2 × month	STP Operators
	Settle able Solids	2 × month	STP Operators
	Oil and Grease	2 × month	Code 40
Building 3064 Pre-Treatment Plant	Flow	Daily	STP Operators
	pH	Daily	STP Operators
	Oil and Grease	2 × month	Code 40
	Cadmium	1 × week	Synergic
	Total Cyanide	2 × week	Code 40
	Zinc	2 × month	Synergic
	Hex. Chrome	2 × month	Code 40
107 - Rockeye	Flow	2 × month	Code 095 -Env.
	pH	N/A	Code 095 -Env.
	Oil and Grease	2 × month	Code 40
	Nitrates	1 × month	Code 40
	Total Explosives	1 × month	Synergic
	NH_3-(N)	1 × month	Code 40
301 - Building 3110	Flow	2 × month	Code 095 -Env.
	pH	N/A	Code 095 -Env.
	Oil and Grease	2 × month	Code 40
	Nitrates	1 × month	Code 40
	Total Explosives	1 × month	Synergic
	NH_3-(N)	1 × month	Code 40
501 - Building 2521	Flow	1 × week	Code 095 -Env.
	pH	2 × month	Code 095 -Env.
	Oil and Grease	2 × month	Code 40

IV-3 Project Organization

This manual outlines procedures used for field sampling and collection methods and shall be incorporated as standard operating procedures. Figure IV-3-1 shows the organization's structure. Figure IV-3-2 shows sample collection procedures.

James Hunsicker is the Environmental Protection Department's Manager. It is his responsibility to provide legally defensible sampling procedures for NSWC, Crane. The department employs James Andis. James Andis has worked for the Environmental Protection Department for fifteen years as a Hazardous Waste Handler. Mr. Andis is the field sample collector and shipper.

Garth Greenwell has worked for the Environmental Protection Department for three years as a Hazardous Waste Handler and can adequately fill in for James Andis if necessary.

ENVIRONMENTAL PROTECTION DEPARTMENT SAMPLING STRUCTRUE

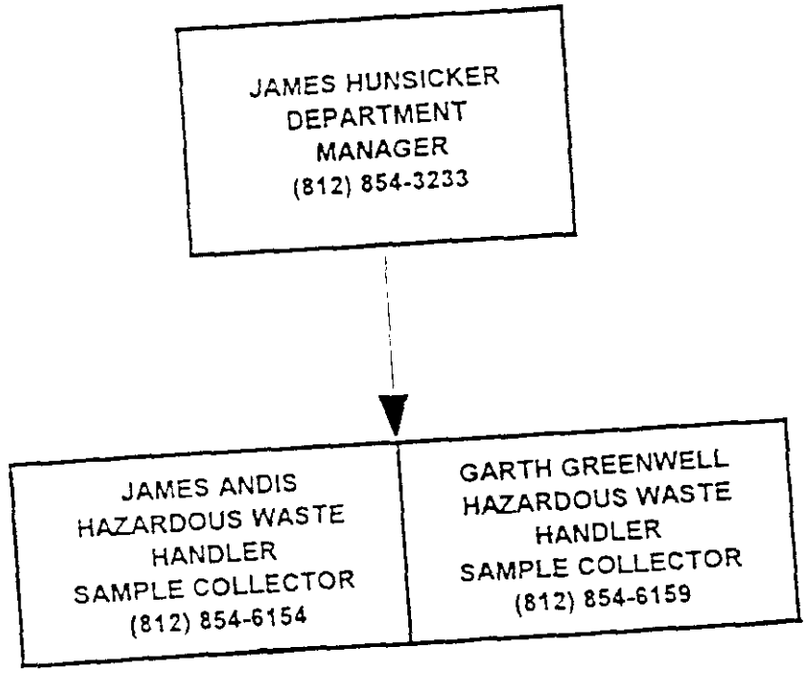


FIGURE IV-3-1

SAMPLE COLLECTION FOR NPDES OUTFALLS AND SPECIAL SAMPLING

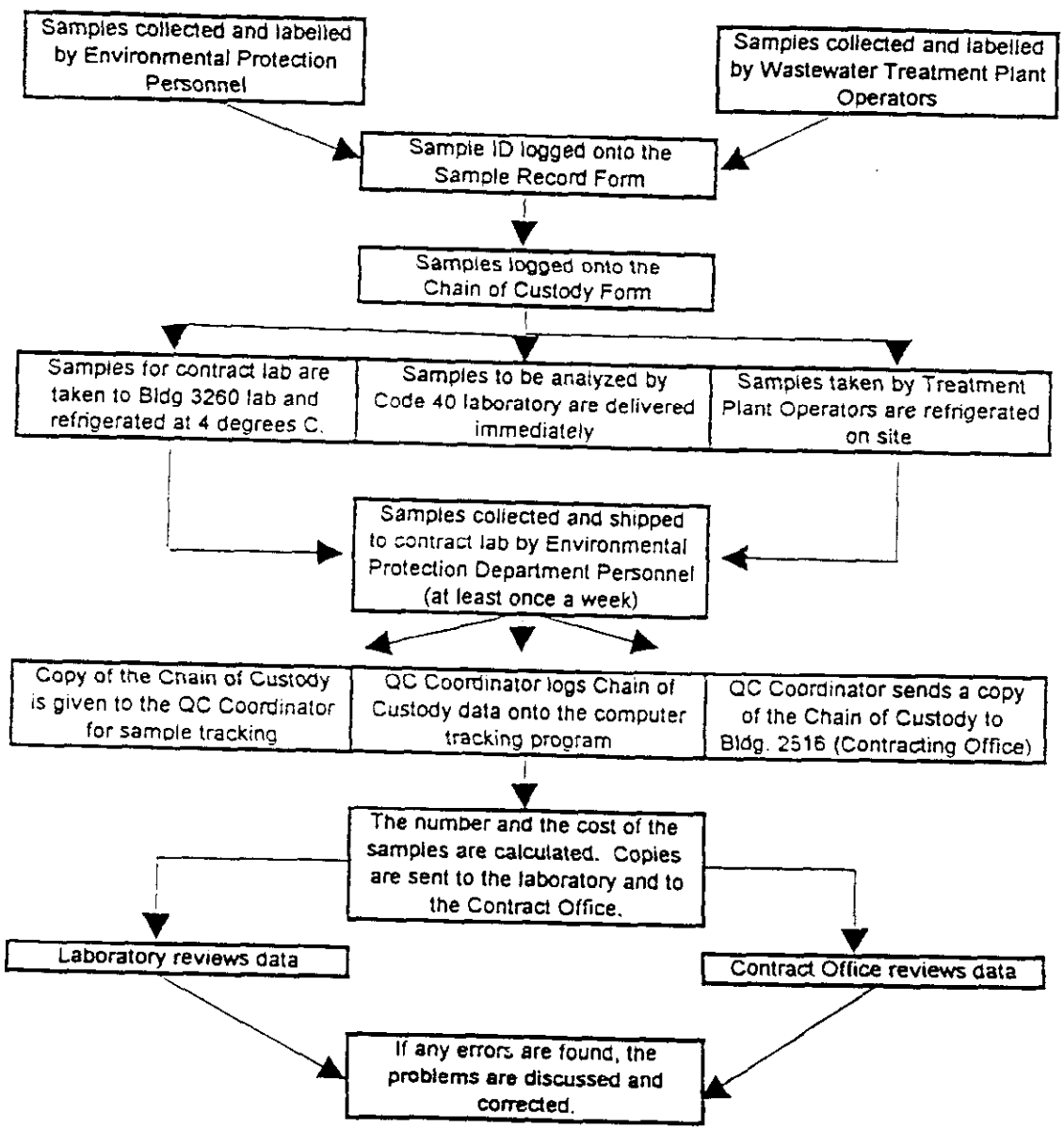


FIGURE IV-3-2

IV-4 Sample Pick-up Procedure - Outfalls 001-101-401

The Sewage Treatment Plant (STP) operators have previously collected and preserved the samples and placed them in a sample refrigerator at 4° Celsius. The sample shipper drives to the facility to collect the samples and he prepares them for shipment.

The sample shipper arrives at the site with a cooler containing frozen ice packs. The shipper should don non-talc latex gloves when handling the sample bottles. When the sample shipper has accounted for all of the samples, the sample custodian at the treatment facility will sign the chain of custody form and relinquish the samples to the shipper. At this time the sample shipper becomes the custodian of the collected samples.

Once the samples have been picked up by the Environmental Protection Department personnel, they are taken to the laboratory at Building 3260 and prepared for shipment. Shipment of samples will be discussed on page 31.

IV-5 Sample Site Selection - General Instructions

There are a few basic rules and precautions that are applicable to the collection of waste water samples. The following procedures are those outlined in Standard Methods for the Examination of Wastewater.

- Samples that are collected should be taken where the water is well mixed.
- Handle a sample in such a way that it does not deteriorate or become contaminated before it reaches the laboratory.
- Sample carefully to insure that analytical results represent the actual sample composition.
- Before filling, rinse the sample bottle out two or three times with the water being collected.
- For samples that will be shipped, it is recommended that an air space of about 1% of the container capacity be left to allow for thermal expansion.
- If preservatives are needed for composite samples, they should be added to the sample container initially (if collecting for one matrix) so that all portions of the composite are preserved.

The Environmental Protection Department adopts the guidelines prescribed by the U.S. Environmental Protection Agency (EPA) memorandum on the Interpretation and Implementation of Aquatic Life Metals Criteria.

- Separate sets of sampling containers, labware, and sampling apparatus should be dedicated for different types of samples, (e.g., manhole samples, effluent samples, etc.).

- All labware, sample containers, and sampling apparatus must be cleaned before reuse. Figure IV-6-1 is a list of sampling equipment.

- Field samples must be collected in such a manner that eliminates the potential for contamination from the sampling area.

- Probes and thermometers must not be put in samples that are to be analyzed for metals. If pH or temperature is measured, it must be done on a separate aliquot.

- Sample preservatives must be laboratory grade reagents or ultra pure. Figure IV-6-2 shows volume, preservative, container, and holding time for Crane's NPDES parameters

- Samples must be stored in the dark at 4 ^{0} C.

IV-6 Heavy Metals

Special precautions are taken when collecting samples for heavy metal analyses. Care must be taken to prevent cross-contamination during sampling. The following precautions could be used when collecting the required NPDES samples or other samples in the collection system.

- Wear new disposable (non-talc) latex gloves each time samples are taken at different locations. Gloves are to be applied prior to the collection of the samples.

- Sample containers can be placed in plastic bags immediately after collection, preservation, and labeling.

To avoid cross-contamination, precautions can be taken to minimize handling of the samples after they have been collected. Sample bottles can be kept in plastic bags and stored in the sample cooler. Other heavy metal samples from various other sample sites should not be placed in the same plastic sample bag.

SAMPLE COLLECTION
FIELD SAMPLING KIT

AUTOMATIC SAMPLER
BUCKET
C/O/C/FORMS
COOLER (ICE PACKS)
CUBITAINERS
FIELD LOG BOOK
GLOVES
K-WIPES
LABELS
pH BUFFERS
pH METER
POCKET KNIFE
PRESERVATIVES
ROPE
SAFETY GLASSES
SAMPLE BAILERS
SAMPLE BOTTLES
SAMPLE RECORD FORMS
STOP WATCH
THERMOMETER
PLASTIC BAGS

FIGURE IV-6-1

NSWC, CRANE
SAMPLING AND PRESERVATION TABLE

The "Methods for Chemical Analyses of Water and Wastes " (USEPA) guide is used by the Environmental Protection Department personnel when collecting, preserving, and storing samples. NSWC, Crane used laboratory guide or ultra pure quality acid for the preservation of heavy metals.

PARAMETER IDENTIFICATION	VOLUME REQUIRED	PRESERVATIVE USED	CONTAINER USED	HOLDING TIME
Ammonia as Nitrogen	250 ml	H_2SO_4 <2 pH	Plastic	28 days
Cadmium	250 ml	HNO_3 <2 pH	Plastic	6 months
Chromium	250 ml	HNO_3 <2 pH	Plastic	6 months
Copper	250 ml	HNO_3 <2 pH	Plastic	6 months
Cyanide	250 ml	*NaOH>12pH	Plastic	14 days
Explosives	1000 ml	None Required	Glass	N/A
Hex Chrome	250 ml	None Required	Plastic	Analyze Immediately
Lead	250 ml	HNO_3 <2 pH	Plastic	6 months
Mercury	250 ml	HNO_3 <2 pH	Plastic	6 months
Nickel	250 ml	HNO_3 <2 pH	Plastic	6 months
Nitrates	250 ml	None Required	Plastic	48 hours
Nitrites	250 ml	None Required	Plastic	28 days
Oil and Grease	1000 ml	H_2SO_4 <2 pH	Glass (Teflon lined lid)	28 days
PCB	1000 ml	None Required	Glass (Teflon lined lid)	7 days
pH	25 ml (min.)	HNO_3 <2 pH	Plastic or Glass	Analyze Immediately
Phosphorous	250 ml	H_2SO_4 <2 pH	Plastic	28 days
Silver	250 ml	HNO_3 <2 pH	Plastic	6 months
Settle able Solids	500 ml	None Required	Plastic	2 days
TKN	500 ml	H_2SO_4 <2 pH	Plastic	48 hrs
TSS	500	None Required	Plastic	7 days
Zinc	250 ml	HNO_3 <2 pH	Plastic	6 months

*It may be necessary to use ascorbic acid when preserving the sample if chlorine is suspected to be present in the sample.

FIGURE IV-6-2

IV-7 pH Measurement

pH measurement in the field is done with a Model 612 Cole-Parmer digital pH meter. The meter is portable and is equipped with a Model 5840-00 pH wand. The pH measurement is done at the sample site and calibrated in the field according to the manufacturer's recommendations.

IV-7.1 Calibration Procedure

Use a screwdriver to set the temperature, standardize and slope control. There is a small screwdriver inset at the top of the wand. Since the pH measurements from the sedimentation pond outfalls vary between 6.5 and 7.2, pH buffers 7 and 4 are used for calibration.

1. Insert the pH electrode into the pH meter.

2. Rinse the electrode in distilled water and then immerse it in pH buffer 7 solution.

3. Using a separate thermometer, measure the buffer temperature, and set the temperature control to the pH buffer 7 temperature. Allow a few seconds for the electrode reading to stabilize.

4. Adjust the standardize control of the meter to read the buffer value at the temperature set in step 3. See table IV-7.1-1 for the correct buffer pH value.

5. Remove the pH electrode from the buffer 7, rinse with distilled water, and then immerse in buffer 4. Allow a few seconds for the pH electrode reading to stabilize.

6. Adjust the slope control for the meter to show the value of buffer 4, corresponding to the temperature of the pH buffer 7 used in step 3. Refer to the temperature table to determine the correct buffer pH value.

7. Rinse the electrode with distilled water.

8. The pH meter is now calibrated and ready for measurements.

TABLE IV-7.1-1
TEMPERATURE TABLE
pH

Buffers

C	10.01	7.00	4.01
0	10.32	7.11	4.000
10	10.18	7.06	4.00
20	10.06	7.01	4.00
25	10.01	7.00	4.01
30	9.97	6.98	4.02
40	9.89	6.97	4.03
50	9.8	6.97	4.06
60	9.78	6.98	4.10

IV-8 Sedimentation Pond Sampling Procedure
Outfalls 002-003-004-008

Figures IV-8-1 through IV-8-4 show the sediment pond sampling points.

IV-8.1 Sampling Requirements

Total Suspended Solids
Settle able Solids
Flow
pH

Flow - is monitored at the end of the discharge pipe and measured by the bucket and stop watch method.

pH - the pH measurement is taken in the field and recorded by the sampler. The pH meter is calibrated on site as recommended by the manufacturer.

IV-8.2 Total Suspended Solids and Settle able Solids

These samples are collected simultaneously and placed in a new one gallon cubitainer. The cubitainer is pre-rinsed with the sample water before filling. The sample is collected by holding the cubitainer at the base with the mouth pointed toward the discharge pipe. A label is filled out and attached to the sample container and an "In House" chain of custody is prepared.

These samples are placed in a cooler with ice packs or crushed ice and are ready for delivery to the sewage treatment plant laboratory. Ice is never filled to the level that it could contaminate the sample when melted.

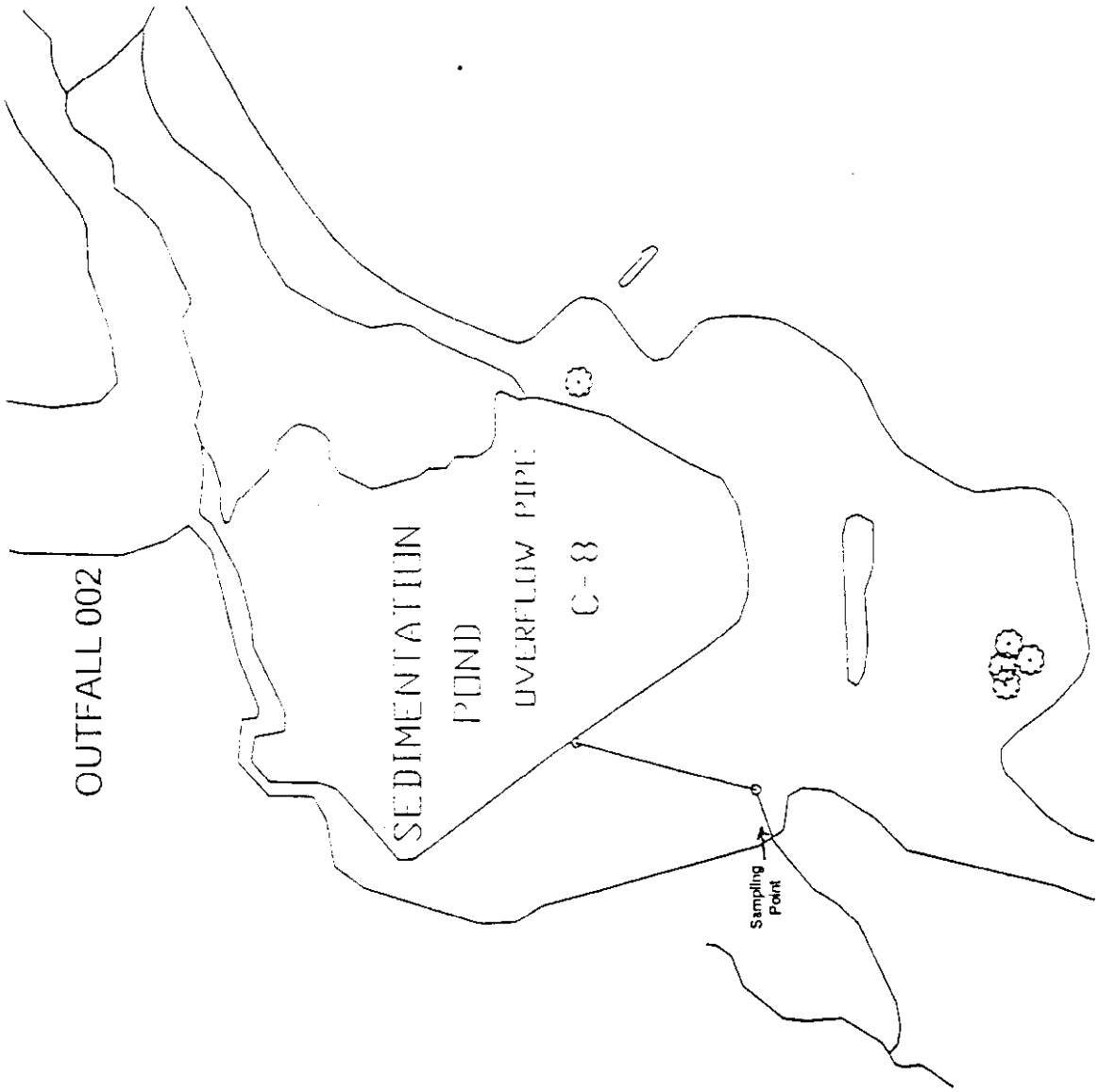

OUTFALL 002
SEDIMENTATION
POND
OVERFLOW PIPE
C-8
Sampling
Point

FIGURE IV-8-1

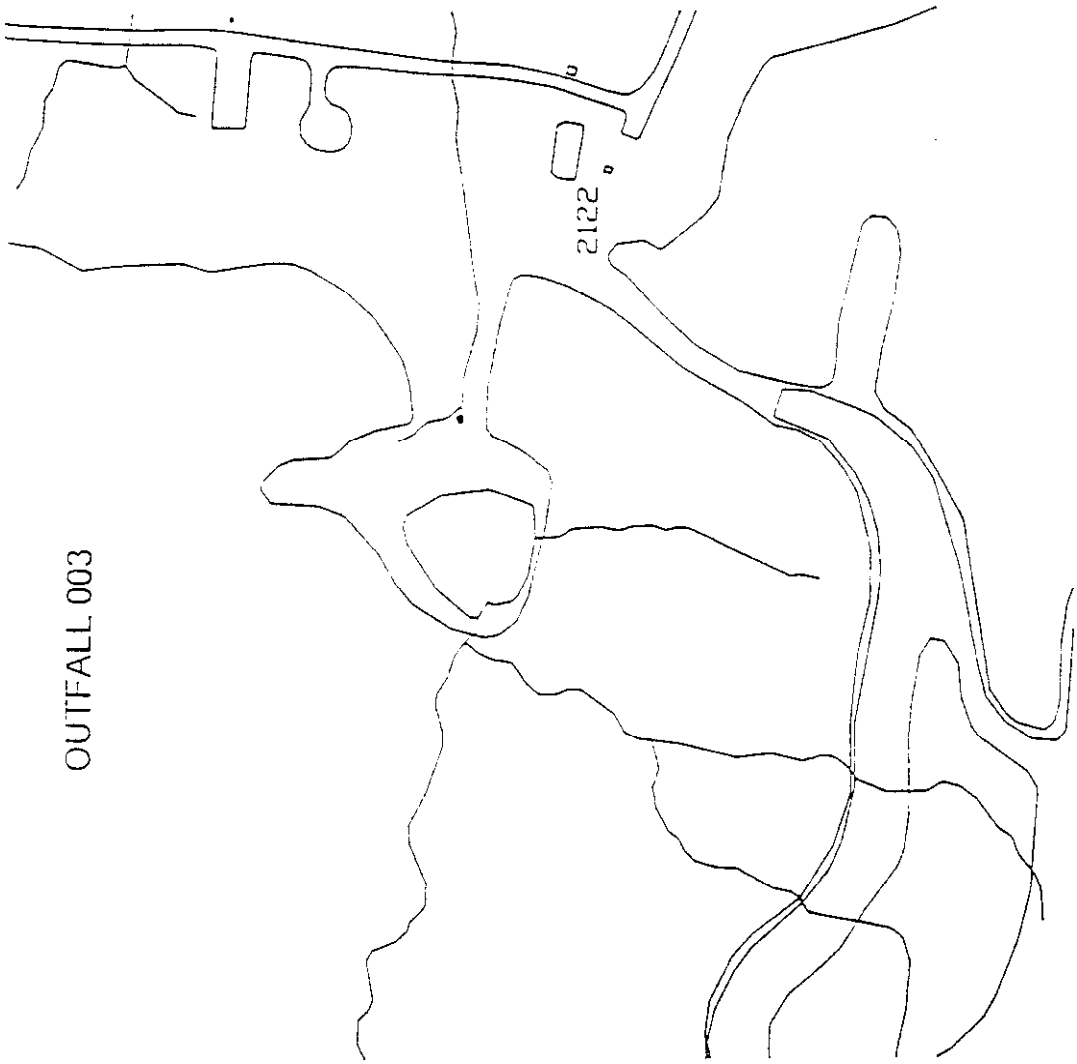


FIGURE IV-8-2

FIGURE IV-8-3

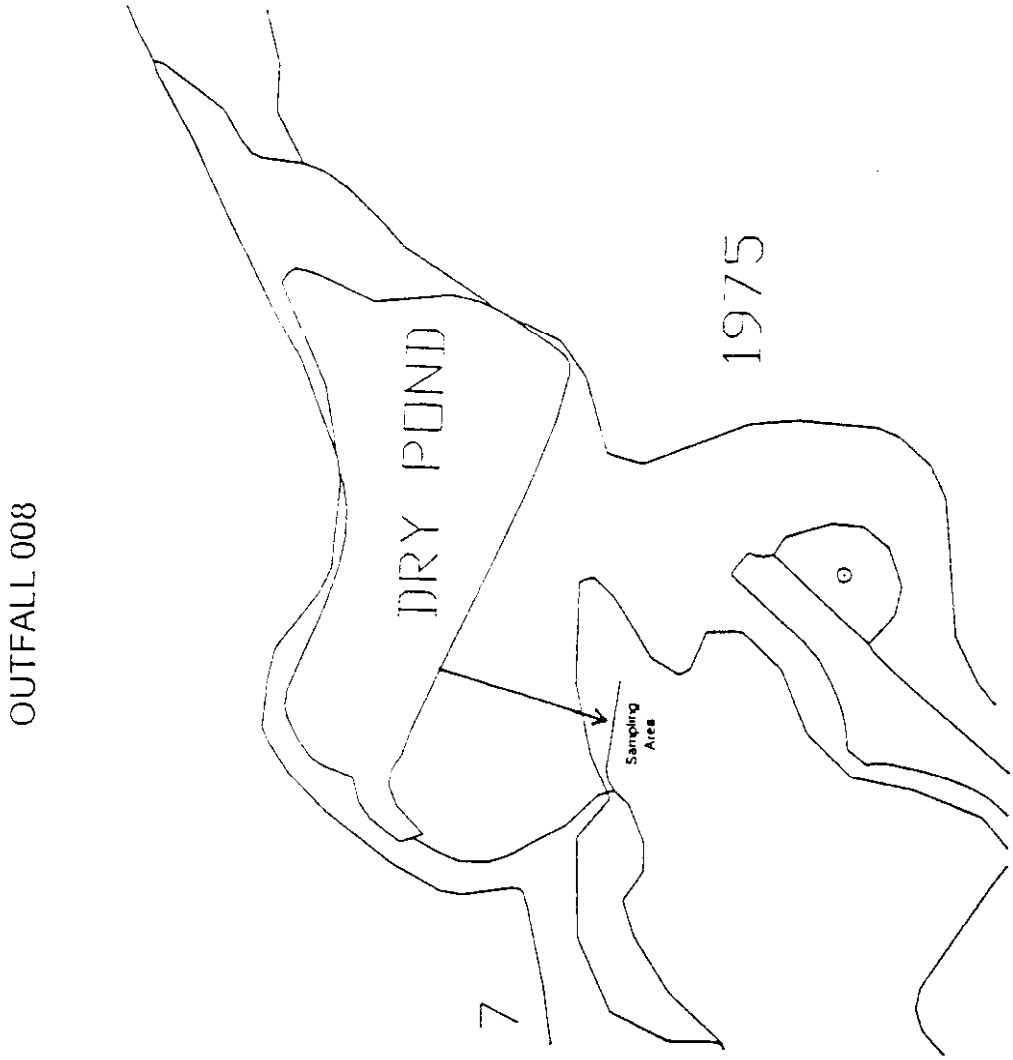


FIGURE IV-8-4

IV-9 Outfall 107

IV-9.1 Sampling Requirements

Ammonia as Nitrogen
Explosives
Flow
Nitrates
Oil and Grease

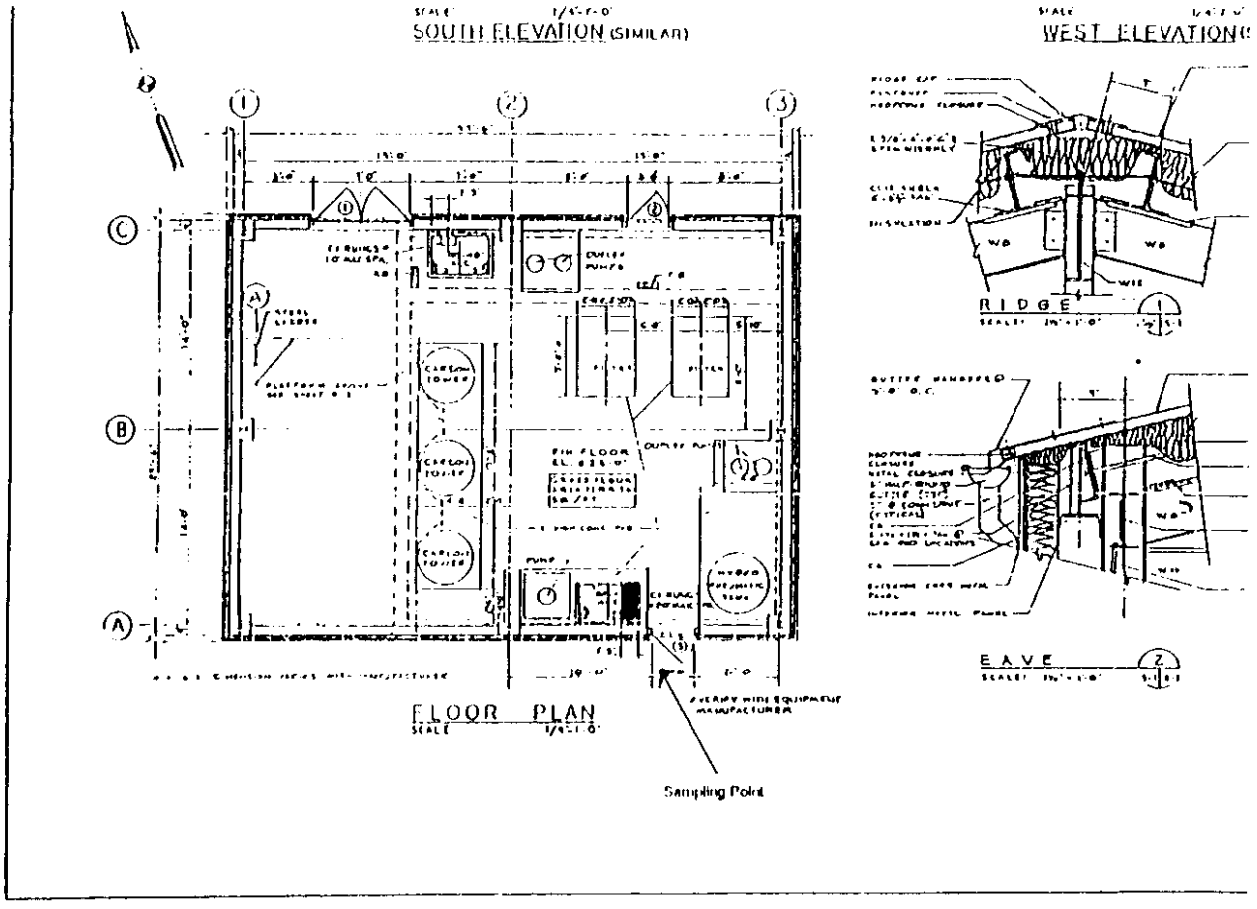
Outfall 107 pertains to Building 3044 waste water treatment system. Figure IV-9-1 is a layout of Building 3044. The treatment facility is owned and operated by CAAA. The Environmental Protection Department provides sample collection services for this operation. The treated waste water is held in a collection tank prior to discharge. When it is necessary to discharge the treated water, Building 3044 personnel contact the Environmental Protection Department sample collector. The sample collector drives to the sample site with the field sampling kit.

The sampler collects two samples to be analyzed for total explosives and one sample to be analyzed for nitrates. One explosive sample and the nitrate sample are labeled and sent to Code 40 laboratory with a chain of custody form. Explosive samples that are analyzed by the Code 40 laboratory are used as a reference to determine if the water in the collection pit can be discharged. The second explosive sample is held for shipment to the contract laboratory for analyses. If the results from the Code 40 laboratory indicate that the water meets the limits of the NPDES Permit, it is discharged from the collection pit and the second explosive sample is submitted to the contract laboratory to obtain analyses or compliance reporting. If the Code 40 laboratory results indicate that the waste water is not suitable for discharge into the sanitary sewer, the water will be recycled through the treatment system and the process is repeated; the second explosives sample will be discarded back into the collection tank.

IV-9.2 107 Sampling Procedures

Flow - The flow is recorded by the operators of the treatment facility and sent to the Environmental Protection Department by mail. The flow is determined by the volume of water being held in the holding tank. Since the tank capacity is a known volume, flow equals tank capacity.

Sampling - The sampler collects the waste water sample with a clean Teflon sample bailer. The water is poured into the cubitainer and the cubitainer is rinsed out. Since two sets of samples are taken the sampler ensures that the container is well mixed prior to splitting the samples. The samples are mixed by shaking and swirling the sample container. Sample bottles are then filled with water from the cubitainer and appropriately preserved and labeled.



BUILDING 3044

FIGURE IV-9-1

IV-9.3 Parameters

Ammonia as Nitrogen - The well mixed water from the sample container is poured into a new plastic 250 ml sample bottle. The sample container is rinsed with the waste water sample and then refilled. The sample is preserved with reagent grade sulfuric acid. A sample label is filled out and attached to the sample bottle.

Nitrates - The new 250 ml plastic sample bottle is pre-rinsed with the waste water sample and then refilled. Nitrate samples do not require preservation. Sample labels are filled out and attached to the sample bottle.

Oil and Grease - Oil and grease can adhere to the sample collection apparatus. It is important to try to use the sample container to collect the oil and grease sample. The sample bottle should be rinsed with the water sample and then refilled. After filling the sample container, the sample is preserved with reagent grade sulfuric acid and appropriately labeled.

After the samples have been collected and preserved, the sampler prepares the chain of custody and updates the field log book. Samples that are to be taken to Code 40 laboratory are delivered immediately. Samples that are to be shipped to the contract laboratory are taken to Building 3260 and stored in the sample refrigerator. Samples are usually shipped to the contract lab once each week.

IV-10 Outfall 301

IV-10.1 Sampling Requirements

Ammonia as Nitrogen
Explosives
Flow
Nitrates
Oil and Grease

Outfall 301 pertains to Building 3110 waste water treatment system. The treatment facility is owned and operated by CAAA. The Environmental Protection Department provides sample collection services for this operation. The treated waste water is held in a collection tank prior to discharge. When it is necessary to discharge the treated water, Building 3110 personnel contact the Environmental Protection Department sample collector. The sample collector drives to the sample site with the field sampling kit.

The sampler collects two samples to be analyzed for total explosives and one sample to be analyzed for nitrates. One explosive sample and the nitrate sample are labeled and sent to Code 40 laboratory with a chain of custody form. The second explosive sample is held for shipment to the contract laboratory. Explosive samples that are analyzed by the Code 40 laboratory are used as a reference to determine if the water in the collection pit can be discharged. If the results from the Code 40 laboratory indicate that the water meets the limits of the NPDES Permit, it is discharged from the collection pit and the second explosive sample is sent to the contract

laboratory to obtain analyses for compliance reporting. If the Code 40 laboratory results indicate that the waste water is not suitable for discharge into the sanitary sewer, the water will be recycled through the treatment system and the process is repeated; the second sample will be discarded into the collection tank.

IV-10.2 301 Sampling Procedures

Flow - The flow is recorded by the operators of the treatment facility and sent to the Environmental Protection Department by mail. The flow is determined by the volume of water being held in the holding tank. Since the tank capacity is a known volume, flow equals tank capacity.

Sampling - The sampler collects the waste water sample with a clean Teflon sample bailer. The water is poured into the cubitainer and the cubitainer is rinsed out. Since two sets of samples are taken the sampler ensures that the container is well mixed prior to splitting the samples. The samples are mixed by shaking and swirling the sample container. Sample bottles are then filled with water from the cubitainer and appropriately preserved and labeled.

IV-10.3 Parameters

Ammonia as Nitrogen - The well mixed water from the sample container is poured into a new plastic 250 ml sample bottle. The sample container is rinsed with the waste water sample and then refilled. The sample is preserved with reagent grade sulfuric acid. A sample label is filled out and attached to the sample bottle.

Nitrates - The new 250 ml plastic sample bottle is pre-rinsed with the waste water sample and then refilled. Nitrate samples do not require preservation. Sample labels are filled out and attached to the sample bottle.

Oil and Grease - Oil and grease can adhere to the sample collection apparatus. It is important to try to use the sample container to collect the oil and grease sample. The sample bottle should be rinsed with the water sample and then refilled. After filling the sample container, the sample is preserved with reagent grade sulfuric acid and appropriately labeled.

After the samples have been collected and preserved, the sampler prepares the chain of custody and updates the field log book. Samples that are to be taken to Code 40 laboratory are delivered immediately. Samples that are to be shipped to the contract laboratory are taken to Building 3260 and stored in the sample refrigerator. Samples are usually shipped to the contract lab once each week.

IV-11 Outfall 501 (Building 2521)

IV-11.1 Sampling Requirements

Flow
pH
Oil and Grease

Outfall 501 pertains to the small arms coating facility at Building 2521. The sample site is designated by the NPDES Permit. The effluent waters are connected to a single discharge pipe.

Flow - The flow is measured by bucket and stop watch.

pH - Measurement of pH is done at the site. The sampler calibrates the meter according the recommendations of the manufacturer. Procedures for pH measurement are described in this manual.

Oil and Grease - The sampler uses the one liter glass sample container as the sampling apparatus. The bottle is positioned under the discharging flow and does not touch the discharge pipe during the collection. The sample is immediately preserved with reagent grade sulfuric acid.

IV-12 Quality Control

Quality control samples are collected on each sampling event. The purpose is to demonstrate that the samples of interest have not become contaminated by chemical preservatives, sample collection techniques, sampling equipment, transportation, or storage. Figure IV-12-1 shows the frequency sampling quality control analysis that will be performed.

IV-12.1 Travel Blanks

Travel blanks are only used to test for volatile contamination.

IV-12.2 Field Duplicates

Field duplicates are taken to determine the repeatability of data. One field duplicate is submitted for each 10 test samples.

QUALITY CONTROL SAMPLING FREQUENCY

PARAMETER		TRAVEL BLANKS	FIELD BLANKS	FIELD DUPLICATES	EQUIPMENT BLANKS
Ammonia as Nitrogen			One per Shipment	One out of Each Ten Tested	One out of Each Ten
Heavy Metals*			One per Shipment	One out of Each Ten Tested	One out of Each Ten
Hex Chrome			One per Shipment	One out of Each Ten Tested	One out of Each Ten
Nitrates			One per shipment	One out of Each Ten Tested	One out of Each Ten
Nitrites			One per shipment	One out of Each Ten Tested	One out of Each Ten
Oil and Grease			One per shipment	One out of Each Ten Tested	One out of Each Ten
PCB			One per shipment	One out of Each Ten Tested	One out of Each Ten
Phosphorous			One per shipment	One out of Each Ten Tested	One out of Each Ten
TKN			One per shipment	One out of Each Ten Tested	One out of Each Ten

SAMPLE TYPE		PREPARED BY	PRESERVED BY	PROCEDURE	FREQUENCY
TRAVEL BLANKS		CODE 40	CODE 40	PICK UP AT BLDG. 2707	EACH SHIPMENT
FIELD BLANKS		CODE 40	FIELD SAMPLER	PICK UP AT BLDG. 2707	EACH SHIPMENT
FIELD		FIELD SAMPLER	FIELD SAMPLER	PERFORMED IN THE	1 PER 10 SAMPLES
EQUIPMENT		CODE 40	FIELD SAMPLER	PERFORMED IN THE	1 PER 10 SAMPLES

* HEAVY METALS INCLUDE CADMIUM, COPPER, CHROMIUM, LEAD, MERCURY, NICKEL, SILVER AND ZINC. THESE METALS USE THE SAME PRESERVATIVE AND ARE COLLECTED IN THE SAME BOTTLE.

FIGURE IV-12-1

IV-13 Sample Holding

IV-13.1 Instructions

- Sample shipment is usually done once a week unless there is an emergency situation. If it is necessary for the sample to be preserved and stored at 4 ^{0} C the sample is placed in a cooler with ice packs at the sample site.

- All samples are entered on the sample record form at the site.

- Samples are taken to the laboratory at Building 3260, removed from the sample cooler, and placed in the sample refrigerator (4° C) as soon as possible.

- Figure IV-13-1 is an example of a sample label. Figure IV-13-2 is an example of a sampling record. Figures IV-13-3 through IV-13-7 are examples of chain of custody forms.

SAMPLE LABEL

SYNERGIC/ATC/CODE 40

CRANE DIVISION
NAVAL SURFACE WARFARE CENTER
ENVIRONMENTAL PROTECTION DEPT. (812) 854-3114

SPLE NO._____AN-LAB No._____

COLLECTOR_____

SPLE LOCATION_____

_____

SPLE DATE_____TIME_____

PRESERVATIVE_____

PARAMETERS_____

FIGURE IV-13-1

ENVIRONMENTAL PROTECTION SAMPLING RECORD
NWSCC 6280/7 (4/86)

Department of the Navy
Naval Weapons Support Center
Crane, Indiana 47522

OUTFALL NUMBER	LOCATION
DATE OF SAMPLING	TIME

ANALYTICAL PARAMETERS

FLOW RATE	gpm

TYPE OF SAMPLE* (Grab/Composite)

DESCRIBE FILTRATION METHOD, IF APPLICABLE

OBSERVATIONS/COMMENTS

SIGNATURE (Sampler's)	CODE	TELEPHONE EXTENSION

DATE SAMPLES SHIPPED/TRANSFERRED

REMARKS

NOTE: Holding time for samples requiring analysis for Hexavalent Chromium, Nitrate and/or BOD is 48 hours.

*Oil and grease, pH, residual chlorine parameters will always be Grab. In this space indicate what the sampling method was for other analytical parameters listed above.

FIGURE IV-13-2

NSWC, CRANE
CHAIN OF CUSTODY FORM
WasteWater

Control Number _____

Client:
NAVSURFWARCENDIV CRANE
ADDRESS
COMMANDER
CODE 09513 BLDG. 3260
NAVSURFWARCENDIV CRANE
300 HIGHWAY 361, CRANE IN 47522

Report to:
Jim Markel
Phone No. (812)-854-6161
Fax No. (812)-854-4177

Parameters	Bid Item Number	Preservative Used	Hold Time	Name of Collector	Time of Collection	Sample Date	Sample ID	Name of Collector	Time of Collection	Sample Date	Sample ID	No. Shipped	Rush 0008AA	Rush 0008AB
NH_3-(N)	0008AD	H_2SO_4	28 Days											
Cadmium	0008AH	HNO_3	6 Mo											
Chromium	0008AH	HNO_3	6 Mo											
Copper	0008AH	HNO_3	6 Mo											
Lead	0008AH	HNO_3	6 Mo											
Nickel	0008AH	HNO_3	6 Mo											
Silver	0008AH	HNO_3	6 Mo											
Zinc	0008AH	HNO_3	6 Mo											
Cyanide	0008AF	NaOH	14 Days											
Mercury	0008AG	HNO_3	6 mo											
Oil and Grease	0008AJ	H_2SO_4	28 Days											
NO_3-N	0008AK	Not Required	48 hours											
(TNT, HMX, RDX)	0008AL	Not Required	30 Days											
$CBOD_5$	0008AA	Not Required	48 Hours											
TSS	0008AB	Not Required	5 Days											
Hex Chrome	0008AE	Not Required	24 hours											
Biomonitoring Ceriodaphnia	0008AP													
Biomonitoring Pimephales P.	0008AP													
Phosphorus	0008AR	H_2SO_4	28 Days											
PCB	0008AQ	Not Required	7 Days											

Relinquished by:	Date/Time	Received by:	Relinquished by:	Date/Time	Received by:	Comments:
Relinquished by:	Date/Time	Received by:	Relinquished by:	Date/Time	Received by:	

FIGURE IV-13-3

Revision: Original
Effective Date: August 1, 1997

NSWC, CRANE
CHAIN OF CUSTODY FORM
SLUDGE AND SOIL SAMPLING

Control Number _____

Client:
NAVSURFWARCENDIV CRANE
Address
COMMANDER
CODE 09513 BLDG 3260
NAVSURFWARCENDIV
300 HIGHWAY 361, CRANE IN 47522

Report to: Jim Market
Phone No. (812)-854-6161
Fax No. (812)-854-4177

Parameters	Code	Preservative Used	HOLD TIME	Name of Collector	Time of Collection	Sample ID	Plastic or Glass	No. Shipped	Rush 0008AA	Rush 0008AB
% Total Solids	0002AA	Not Required	7 Days							
Cadmium	0002AA	HNO_3	6 mo.				Plastic			
Chromium	0002AA	HNO_3	6 mo.				Plastic			
Copper	0002AA	HNO_3	6 mo				Plastic			
Lead	0002AA	HNO_3	6 mo.				Plastic			
Nickel	0002AA	HNO_3	6 mo.				Plastic			
Silver	0002AA	HNO_3	6 mo.				Plastic			
Zinc	0002AA	HNO_3	6 mo				Plastic			
Potassium	0002AA	HNO_3	6 mo				Plastic			
NO_3-N	0002AB	Not Required	48 hrs.				Plastic			
Ammonia-N	0002AB	H_2SO_4	28 Days				Plastic			
Arsenic	0002AC	HNO_3	6 mo				Plastic			
Mercury	0002AC	H_2SO_4	14 Days				Plastic			
Molybdenum	0002AC	HNO_3	6 mo.				Plastic			
Phosphorous	0002AC	H_2SO_4	28 Days				Plastic			
Selenium	0002AC	HNO_3	6 mo.				Plastic			
TKN	0002AD	H_2SO_4	48 hrs.				Plastic			
PCB	0002AE	Not Required	7 Days				Glass (Teflon lid)			
pH (Soil)	0002AF	Not Required	ASAP				Plastic			
CEC (Soil)	0002AG	Not Required	ASAP				Plastic			

Relinquished by:	Date/Time	Received by:	Relinquished by:	Date/Time	Received by:
Relinquished by:	Date/Time	Received by:	Relinquished by:	Date/Time	Received by:

FIGURE IV-13-4

Revision: Original
Effective Date: August 1, 1997

NSWC, CRANE
CHAIN OF CUSTODY FORM
Waste-Oil

Control Number _____

Client:
NAVSURFWARCENDIV CRANE
Address
COMMANDER
CODE 09513 BLDG 3260
NAVSURFWARCENDIV
300 HIGHWAY 361, CRANE IN 47522

Report to: Jim Market
Phone No. (812)-854-6161
Fax No. (812)-854-4177

Parameters	Code	Preservative Used	Name of Collector	Time of Collection	Sample ID	Plastic or Glass	No. Shipped	Rush 0008AA	Rush 000AB
TCLP Metals Ignitability, TOH, PCB's including Arochlor 1268	0005AA	N/A				Glass			
Volitile Compounds EPA Method 8260	0005AB	N/A				Glass			
Semi-Volatile Compounds EPA Method 8270	0005AC	N/A				Glass			
PCB's (including Arochlor 1268)	0005AD	N/A				Glass			
Analyses of Soil PCB's	0005AE	N/A				Glass			

Relinquished by:	Date/Time	Received by:	Relinquished by:	Date/Time	Received by:
Relinquished by:	Date/Time	Received by:	Relinquished by:	Date/Time	Received by:

FIGURE IV-13-5

Revision: Original
Effective Date: August 1, 1997

NSWC, CRANE
CHAIN OF CUSTODY FORM
GENERAL

Control Number

Client:
NAVSURFWARCENDIV CRANE
Address
COMMANDER
CODE 09513 BLDG 3260
NAVSURFWARCENDIV
300 HIGHWAY 361, CRANE IN 47522

Report to: Jim Market
Phone No. (812)-854-6161
Fax No. (812)-854-4177

Parameters	Code	Preservative Used	Hold Time	Name of Collector	Time of Collection	Sample ID	Plastic or Glass	No. Shipped	Rush 0008AA	Rush 0008AB

Relinquished by:	Date/Time	Received by:	Relinquished by:	Date/Time	Received by:
Relinquished by:	Date/Time	Received by:	Relinquished by:	Date/Time	Received by:

FIGURE IV-13-6

Revision: Original
Effective Date: August 1, 1997

For IN-HOUSE Sampling
CODE 40

NSWC, CRANE
BLDG 2707 LABORATORY
CHAIN OF CUSTODY FORM

NPDES ☐

OTHER ☐

Relinquished by _____ Date _____ Time _____

Relinquished by _____ Date _____ Time _____

Date Shipped _____ By _____ Time _____ Date Rec'd _____ By _____ Time _____

Parameters	Code	Preservative Used	Name of Collector	Time of Collection	Sample ID	Preservative Used	Name of Collector	Time of Collection	Sample ID	No. Shipped	Rush
NH3-N		H2S04				H2S04					
Cadmium		HNO3				HNO3					
Chromium		HNO3				HNO3					
Hex Chrome		NONE				NONE					
Copper		HNO3				HNO3					
Lead		HNO3				HNO3					
Nickel		HNO3				HNO3					
Silver		HNO3				HNO3					
Zinc		HNO3				HNO3					
Cyanide		NaOH				NaOH					
Mercury		HNO3				HNO3					
Oil and Grease		H2S04				H2S04					
NO3-N		Not Required				Not Required					
NO2-N		Not Required				Not Required					
Explosives		Not Required				Not Required					
TNT		Not Required				Not Required					
RDX		Not Required				Not Required					
HMX		Not Required				Not Required					
% Solids		Not Required				Not Required					
PCB		Not Required				Not Required					

_____
Control No.

FIGURE IV-13-7

Revision: Original
Effective Date: August 1, 1997

IV-14 Sample Shipment

After the samples have been collected it is important that they are shipped to the contract laboratory as soon as possible. The sample collector reviews the samples to be sure that the samples that are shipped match the samples written on the chain of custody forms.

The sample collector places ice packs in the cooler and places the samples on top of the ice packs. Sample packing is placed around the samples to keep the samples from shifting and breaking. The chain of custody forms are placed inside a document protector and placed on top of the sample packing inside the cooler. The sample collector prepares an 1149 shipping document and takes the samples and the shipping document to Building 41 for shipment.

When the sampler/cooler relinquishes the sample cooler to Building 41 personnel, the sample cooler is prepared for shipment to the laboratory. The cooler is addressed and a custody seal is applied. The cooler is set aside to be picked up by Federal Express personnel before 1300 hours. Federal Express has custody of the sample cooler until it is delivered to the contract laboratory.

IV-15 Laboratory Equipment

The following is a list of laboratory equipment at building 3260. Table IV-15-1 is a list of reagents kept at building 3260.

1 ea. Orion digital pH/millivolt meter model 611 with Cole-Parmer pH electrode
2 ea. Cole-Parmer digital pH meter model 612
2 ea. Cole-Parmer pH wand model 5840-00
3 ea. 500 ml graduated cylinder
1 ea. 250 ml graduated cylinder
1 ea. Orion electrode holder
1 pkg. 2 ml pipet
1 pkg. 5 ml pipet
1 ea. Pipet bulb
3 ea. Wash bottles (distilled water rinse)
3 ea. Chemical reagent bottles (plastic) with pour spout
1 ea. Kelvinator sample refrigerator
1 ea. Refrigerator thermometer
1 pkg. Rubber gloves
1 pkg. Rubber gloves (green)
1 ea. Portable safety eye wash
1 ea. Safety glass

TABLE IV-15-1

	Sodium Hydroxide 50%	Sulfuric Acid	Nitric Acid Trace Metal Grade	Nitric Acid Standard Grade
Quantity	1 Each	5 Each	5 Each	5 Each
Volume	5 Gallons	2.5 Liters	2.5 Liters	2.5 Liters
Brand Name	Chempure	Fisher Scientific	Fisher Scientific	EM Science
	pH buffer 7	pH buffer 4	pH buffer 10	

IV-16 Laboratory and Sampling Equipment Clean-up

IV-16.1 Labware, Bucket, and Bailers

When sample collection is performed in the field it is important to decontaminate sampling equipment and any other equipment involved in the sampling processes. Sampling equipment is brought to the lab at Building 3260 and cleaned with a commercial laboratory detergent. After cleaning the sampling equipment, it is rinsed with tap water and given a final rinse with type II or III grade distilled water.

IV-16.2 Automatic Samplers

Automatic samplers are cleaned after each use at a given site. All equipment parts that had made contact with waste water samples are thoroughly cleaned with laboratory detergent and rinsed with distilled water. Pump tubing is either cleaned with laboratory detergent or it is replaced with new. The field sampler is aware of the importance of clean field sampling methods and uses his best judgement pertaining to the cleaning or replacement of the pump tubing.

IV-16.3 Working Areas

Work areas and work benches should be cleaned with laboratory detergent after each use and are to be kept clean at all times. Work areas should be free from anything that could cause contamination of sample bottles, preservatives, or any samples that are placed on the surface area.

IV-17 Personnel Safety

- The sampler/collector shall wear safety eye wear when using chemical preservatives during sampling. For additional safety, the sampler shall carry a portable eyewash in the vehicle used for sampling.

- Rubber gloves are used to protect the sample and to protect the sampler while handling waste water samples. Gloves are to be discarded after use at the particular sample site.

- Special protective clothing is not a requirement for the collection of compliance sampling but it is required that safety shoes or boots are worn.

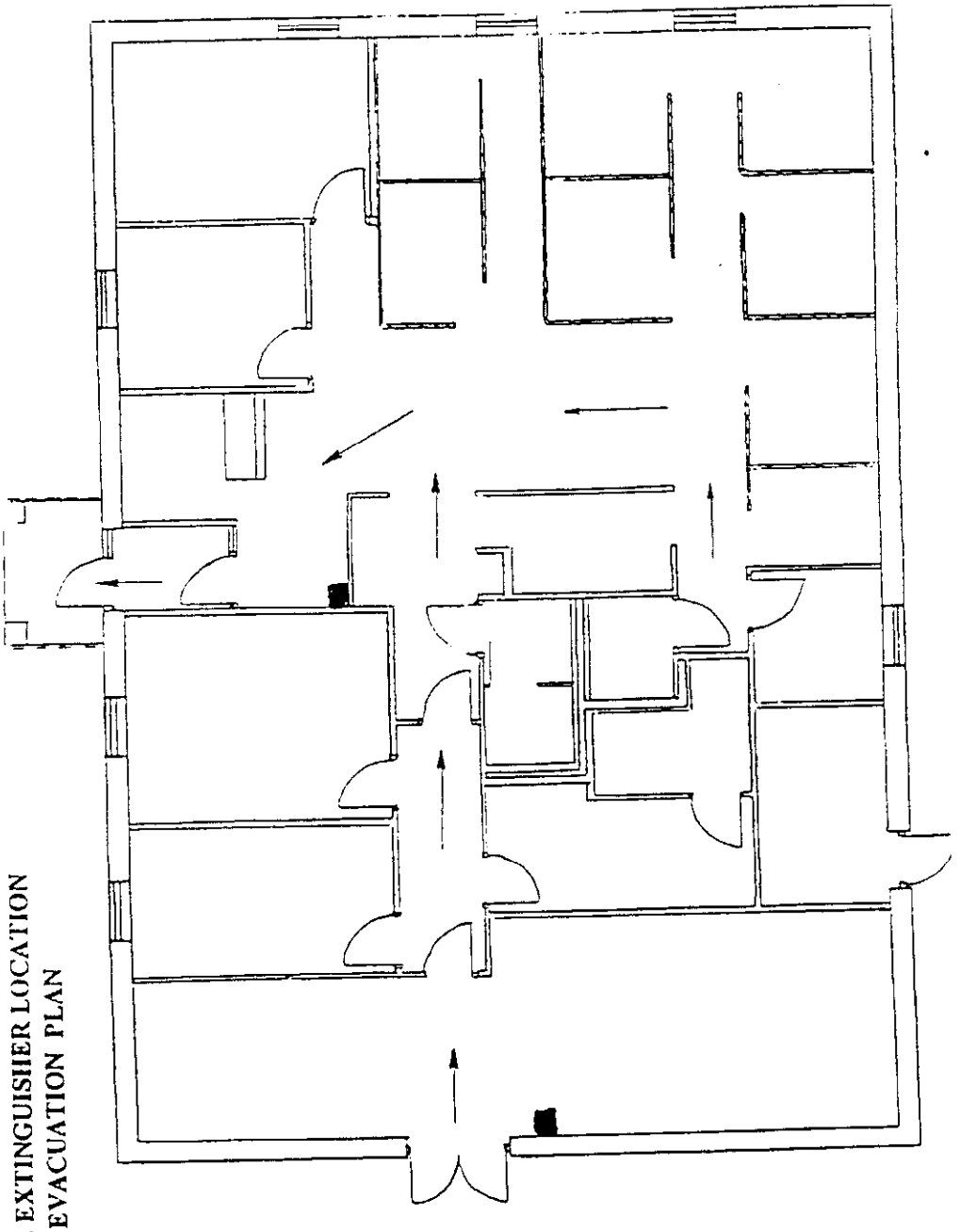
- Sample collectors are rarely in a position where they would require respiratory protection for compliance or other sampling. However, if the sampler should ever find it necessary to enter a confined space or perform other work outside of normal operation routines, the sampler follows the rules and regulations of the " Occupational Safety and Health Manual" (NAVWPNSUPPCENNINST ~5100.22C).

- Table IV-17-1 is a list of Crane's emergency phone numbers. Figure IV-17-1 is a diagram of building 3260's layout.

TABLE IV-17-1
EMERGENCY CONTACTS

THE EMERGENCY RESPONSE PLAN IS LOCATED IN THE CONFERENCE ROOM OF BUILDING 3260 REFERENCE NUMBER 5090.5

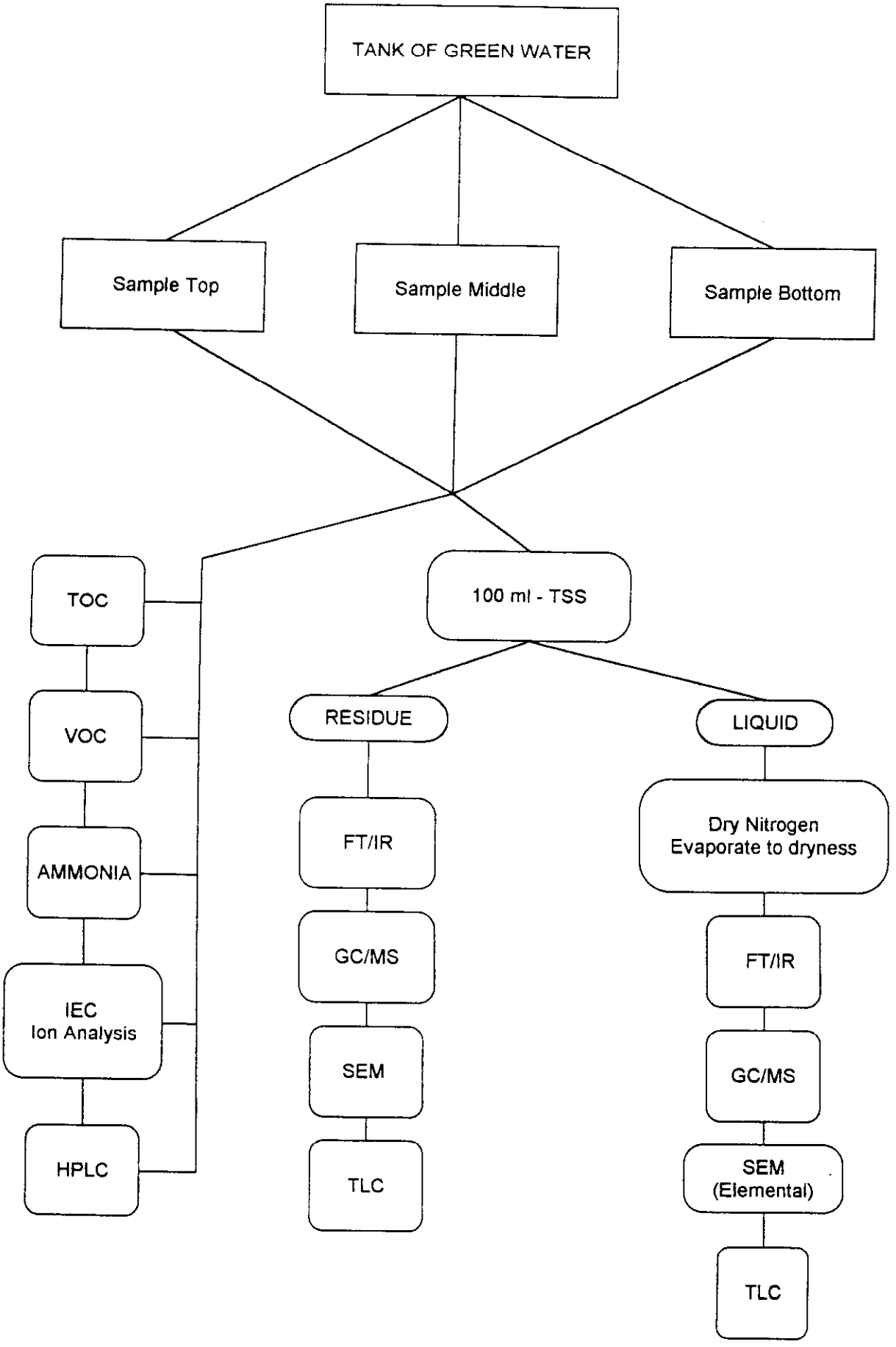
EMERGENCY GROUP	TELEPHONE NUMBER
AMBULANCE	1100
EMERGENCY	1333
FIRE DEPT.	1333
HOSPITAL	(812) 336-9578
SECURITY	3300



FIRE EXTINGUISHER LOCATION
AND EVACUATION PLAN

BUILDING 3260
FIGURE IV-17-1

APPENDIX F: DYE WATER EVALUATION FLOW CHART


TANK OF GREEN WATER
Sample Top
Sample Middle
Sample Bottom
TOC
VOC
AMMONIA
IEC
Ion Analysis
HPLC
100 ml - TSS
RESIDUE
FT/IR
GC/MS
SEM
TLC
LIQUID
Dry Nitrogen
Evaporate to dryness
FT/IR
GC/MS
SEM
(Elemental)
TLC

APPENDIX G: TOC ANALYSIS TECHNIQUE

CR 4052-EOP-0029

OPERATING PROCEDURE
FOR THE
DC-80 TOTAL ORGANIC CARBON (TOC) ANALYZER SYSTEM

PREPARED BY _____ 8/7/97
Don Miller Date

APPROVED BY _____ 13 Aug 97
Nancey Maegerlein Date

Analysis of Total Organic Carbon (TOC) Using the DC-80 Total Organic Carbon System

The information contained below provides directions to supplement the instructions provided in the DC-80 TOC operating manual.

Equipment Required:
Dohrmann DC-80 TOC System Analyzer
100 ml volumetric flasks
Injection syringes (must be able to dispense 40 μl, 200 μl, or 1000 μl)
Small test tubes

Chemicals Required:
Distilled water (for reactor reagent and carbon standards)
Sodium Persulfate, 96% or better purity (for reactor reagent)
Potassium Hydrogen Phthalate (for carbon standards)
Concentrated Nitric Acid (for reactor reagent, carbon standards, and samples)

Sample preparation -

(Water samples, for reactor analysis): Filter water samples to remove particulate. Allow samples to come to room temperature before analysis. Adjust pH of samples to 2-3 for inorganic carbon removal. Heavy soiled samples do not get filtered and should be analyzed using the combustion furnace.

(Soil and heavily soiled samples, for sludge/sediment analysis): Recommended sample size for solid samples is 10-50 mg. Heavy soiled liquid samples are dispensed in 40 μl volumes.

DC-80 system setup -

The detector unit of the DC-80 system must be powered on for at least 24 hours prior to sample analysis. For samples that require TOC analysis in the 1-40 ppm range, connect oxygen for the carrier gas, vs nitrogen. Power up the DC-80 reactor and pumps for a minimum of one hour before sample analysis. Set detector DET/PPM switch to the DET position, remove bottom plate of detector front, and dial zero control so that digital readout is 0.01. Adjusting the readout to anything less than 0.01 could result in a negative detect signal, which will generate an error reading on your sample concentration. Ensure digital readout does not change its reading by ± 0.0002 for two minutes before proceeding with any calibration procedures. After zeroing, change switch position back to PPM.

When needed, new reagent solution should be made up with 2% sodium persulfate (enclosure 1), not the 2% potassium persulfate identified in the operating manual. The sodium persulfate is pure enough that it will not add any background carbon to the sample and standard.

Water sample TOC analysis -

If the carbon (C) standard solutions are older than 30 days, prepare fresh standards as outlined in DC-80 operating systems manual (pages 6-1 through 6-2). Inject the middle range carbon standard (400 ppm) and calibrate system to that standard. Run one sample to determine range that the sample is in and if needed, recalibrate with lower or higher range standard. Consult DC-80 operating system manual for specific calibration techniques (pages 3-6 through 3-9). If performing manual injections, acidify and sparge water samples for 5-6 minutes prior to injection. The sparging (in addition to the pH adjustment) removes the carbonates and bicarbonates from the samples). Upon completion of sparging, press the green START button and inject specific amount:

40 μl for 2000 ppm C calibration
200 μl for 400 ppm C calibration
1000 μl for 10 ppm C calibration

of sample into DC-80 reactor. Wait for tape printout of sample concentration to print and the green READY light to come on before injecting another sample. Run a system blank with the samples, which consists of withdrawing an aliquot of reagent water from the reactor system and injecting to determine bachkground value. Try to inject samples at the same rate during manual sample injection. If using the autosampler, consult the DC-80 operating manual for auto sampler carousel setup and operating procedures (pages 4-1 through 4-14). Ensure that calibration to the standards is performed manually even when the autosampler is connected for use in analyzing samples.

Solid and heavy soiled water sample TOC analysis -

First, oxygen must be used. Do Not use nitrogen for the analysis of solid/soiled samples. Prepare fresh standards as indicated for the water sample analysis. For this procedure the UV lamp and the pump should be turned off at the reactor portion of the system. The sample volume select should be set at the 40 μl mark. Observe the detector baseline (DET/PPM switch in the DET position) on the digital display (should be stable to within ± 0.0002 for several minutes before initiating sample analysis). Push the empty sample boat into the combustion zone and leave for two minutes to bake off any residue. Pull back boat to Flip-Top inlet block and allow to cool for 30 seconds. Check DET digital reading, reading should be somewhat stable before proceeding. When stable, change DET position to PPM. Align boat with liquid injection sample port and inject 40 μl of blank. Press "START" and slide boat back into furnace at rate of 2 inches per second. Repeat again for the 2000 ppm C standard. Blank and standard analysis should take approximately 3-4 minutes. After detector has printout of the concentration, remove boat form the furnace. Allow 30 seconds to cool and remove remaining liquid. Push boat back into combustion zone and leave for two minutes. Pull back boat to Flip-Top inlet block and allow to cool for 30 seconds. Insert solid sample into boat and close Flip Top. Allow two minutes for the

baseline to return to normal, push the START button and slide boat back into furnace at rate of 2 inches per second.

DC-80 TOC System Shutdown -

If the DC-80 system will be used within the next day or two shut off the carrier gas to the system and power off the reactor pump, lamp ,and power. Leave the power to the detector unit on. If the system will not be used for an extended period of time, also power off the detector. Move carbon standards and reactor reagent to the refrigerator for storage.

APPENDIX H: TSS ANALYSIS

EXPLOSIVE SCIENCES BRANCH
CODE 4052
NAVAL SURFACE WARFARE CENTER
CRANE, INDIANA 47522

PROCEDURE FOR NON-FILTERABLE RESIDUE IN DRINKING OR WASTE WATER

CR 4052-EOP-0052

PREPARED BY
Louis Schwenk
LOUIS SCHWENK

DATE
8-14-97

APPROVED BY
Nancey J. Maegerlein
NANCEY J. MAEGERLEIN

DATE
14 Aug 97

METHOD #: 160.2 Approved for NPDES (Issued 1971)

TITLE: Residue, Non-Filterable (Gravimetric, Dried at 103-105-C)

ANALYTE:

Residue ,Non-Filterable

INSTRUMENTATION: Drying Oven

STORET No. 00530

1.0 Scope and Application

1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
1.2 The practical range of the determination is 4 mg/L to 20,000 mg/L.

2.0 Summary of Method

2.1 A well-mixed sample is filtered through a glass fiber filter, and the residue retained on the filter is dried to constant weight at 103-105-C.
2.2 The filtrate from this method may be used for Residue, Filterable.

3.0 Definitions

3.1 Residue, non-filterable, is defined as those solids which are retained by a glass fiber filter and dried to constant weight at 103 - 105-C.

4.0 Sample Handling and Preservation

4.1 Non-representative particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result.
4.2 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4-C, to minimize microbiological decomposition of solids, is recommended.

5.0 Interferences

5.1 Filtration apparatus, filter material, pre-washing, post-washing, and drying temperature are specified because these variables have been shown to affect the results.
5.2 Samples high in Filterable Residue (dissolved solids), such as saline waters, brines and some wastes, may be subject to a positive interference. Care must be taken in selecting the filtering apparatus so that washing of the filter and any dissolved solids in the filter (7.5) minimizes this potential interference.

6.0 Apparatus

6.1 Glass fiber filter discs, without organic binder, such as Millipore AP-40, Reeves Angel 934-AH, Gelman type A/E, or equivalent.
NOTE: Because of the physical nature of glass fiber filters, the absolute pore size cannot be controlled or measured. Terms such as "pore size", collection efficiencies and effective retention are used to define this property in glass fiber filters. Values for these parameters vary for the filters listed above.
6.2 Filter support: filtering apparatus with reservoir and a coarse (40-60

microns) fritted disc as a filter support.

NOTE: Many funnel designs are available in glass or porcelain. Some of the most common are Hirsch or Buchner funnels, membrane filter holders and Gooch crucibles. All are available with coarse fritted disc.

6.3 Suction flask.
6.4 Drying oven, 103-105-C.
6.5 Desiccator.
6.6 Analytical balance, capable of weighing to 0.1 mg.

7.0 Procedure

7.1 Preparation of glass fiber filter disc: Place the glass fiber filter on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible with 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 or both crucible and filter if Gooch crucible is used, and dry in an oven at 103-105-C for one hour. 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.

7.2 Selection of Sample Volume for a 4.7 cm diameter filter, filter 100 mL of sample. If weight of captured residue is less than 1.0 mg, the sample volume must be increased to provide at least 1.0 mg of residue. If other filter diameters are used, start with a sample volume equal to 7 mL/cm2 of filter area and collect at least a weight of residue proportional to the 1.0 mg stated above.

NOTE: If during filtration of this initial volume the filtration rate drops rapidly, or if filtration time exceeds 5 to 10 minutes, the following scheme is recommended: Use an unweighed glass fiber filter of choice affixed in the filter assembly. Add a known volume of sample to the filter funnel and record the time elapsed after selected volumes have passed through the filter. Twenty-five mL increments for timing are suggested. Continue to record the time and volume increments until filtration rate drops rapidly. Add additional sample if the filter funnel volume is inadequate to reach a reduced rate. Plot the observed time versus volume filtered. Select the proper filtration volume as that just short of the time a significant change in filtration rate occurred.

7.3 Assemble the filtering apparatus and begin suction. Wet the filter with a small volume of distilled water to seat it against the fritted support.

7.4 Shake the sample vigorously and quantitatively transfer the predetermined sample volume selected in 7.2 to the filter using a graduated cylinder. Remove all traces of water by continuing to apply vacuum after sample has passed through.

7.5 With suction on, wash the graduated cylinder, filter, non-filterable residue and filter funnel wall with three portions of distilled water allowing complete drainage between washing. Remove all traces of water by continuing to apply vacuum after water has passed through. NOTE: Total volume of wash water used should equal approximately 2 mL per

cm2. For a 4.7 cm filter the total volume is 30 mL.

7.6 Carefully remove the filter from the filter support. Alternatively, remove crucible and filter from crucible adapter. Dry at least one hour at 103-105 C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg).

8.0 Calculations

8.1 Calculate non-filterable residue as follows:

$$\text{Non-filterable residue, mg/L} = \frac{(A - B) \times 1{,}000}{C}$$

where:

A = weight of filter (or filter and crucible) + residue in mg
B = weight of filter (or filter and crucible) in mg
C = mL of sample filtered

9.0 Precision and Accuracy

9.1 Precision data are not available at this time.
9.2 Accuracy data on actual samples cannot be obtained.

Bibliography

1. NCASI Technical Bulletin No. 291, March 1977. National Council of the Paper Industry for Air and Stream Improvement, Inc., 260 Madison Ave., NY.

APPENDIX I: IEC ANALYSIS PROCEDURE

EXPLOSIVE SCIENCES BRANCH
CODE 4052
NAVAL SURFACE WARFARE CENTER
CRANE, INDIANA 47522

DETERMINATION OF INORGANIC ANIONS

BY

LIQUID ION CHROMATOGRAPHY

CR 4052-EOP-0010

PREPARED BY: BRAD KINDRED

PREPARED BY Brad Kindred BRAD KINDRED	DATE 8-11-97
REVIEWED BY Louis Schwenk LOUIS SCHWENK	DATE 8-11-97
APPROVED BY Nancey J. Maegerlein NANCEY J. MAEGERLEIN	DATE 13 Aug 97

EQUIPMENT REQUIRED FOR LIQUID ION CHROMATOGRAPHY ANALYSIS

(a) Waters Model 590 HPLC pump or equivalent

(b) Waters Model 430 Conductivity Detector or equivalent

© Waters Model 740 Data Module or equivalent

(d) Shimadzu Model SIL-9A Auto Injector or equivalent

REFERENCES

(a) Waters Model 590 HPLC pump Instruction Manual

(b) Waters Model 430 Conductivity Detector Instruction Manual

(c) Waters Model 740 Data Module Instruction Manual

(d) Shimadzu Model SIL-9A Auto Injector Instruction Manual

(e) EPA Method 300

MODIFICATIONS OF PROCEDURE

(a) No significant modification.

METHOD #: 300.0 Recommended for Approval for NPDES (November 1991)

TITLE: The Determination Of Inorganic Anions In Water By Ion Chromatography

IALYTE:	CAS #
Bromate BrO3	
Bromide Br	7726-95-6
Chlorate ClO3	
Chloride Cl	7782-50-5
Chlorite ClO2	
Fluoride F	7782-41-4
Nitrate NO3	
Nitrite NO2	
Phosphate HPO4	
Sulfate SO4	

INSTRUMENTATION: IC

0 Scope and Application

1.1 This method covers the determination of the following inorganic anions.

Method A.	Storet No. (Total)
Bromide	71870
Chloride	00940
Fluoride	00951
Nitrate-N	00620
Nitrite-N	00615
Ortho-Phosphate-P	70507
Sulfate	00945

Method B.	Storet No. (Total)
Chlorite	50074
Chlorate	
Bromate	

1.2 The matrices applicable to each method are shown below:

A. Drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, solids (after extraction 2.3), leachates (when no acetic acid is used 2.4)

B. Drinking water and reagent waters.

1.3 The Single Laboratory Method Detection Limit (MDL, defined in Section

13) for the above analytes is listed in Tables 1A and 1B. The MDL for a specific matrix may differ from those listed, depending upon the nature of the sample.

1.4 Method A is recommended for drinking and waste waters. The multilaboratory range tested for each anion is as follows in mg/L:

Bromide	0.63 - 21.0
Chloride	0.78 - 26.0
Fluoride	0.26 - 8.49
Nitrate-N	0.42 - 14.0
Nitrite-N	0.36 - 12.0
Ortho-P	0.69 - 23.1
Sulfate	2.85 - 95.0

1.5 This method is recommended for use only by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatogram. Each analyst must demonstrate the ability to generate acceptable results with this method, using the procedure described in Section 10.2.

1.6 When this method is used to analyze unfamiliar samples for any of the above anions, anion identification should be supported by the use of fortified sample matrix covering the anions of interest. The forttification procedure is described in Section 11.6.

2.0 Summary of Method

2.1 A small volume of sample, typically 2 to 3 mL, is introduced into an ion chromatograph. The anions of interest are separated and measured, using a system comprised of a guard column, separator column, suppressor device, and conductivity detector.

2.2 The main differences between Method A and B are the separator columns, guard columns and eluents. Sections 6 and 7 will elicit the differences.

2.3 In order to use this method for solids an extraction procedure must be performed (See 11.7).

3.0 Definitions

3.1 Stock standard solution - a concentrated solution containing a single certified standard that is a method analyte. Stock standard solutions are used to prepare calibration standards.

3.2 Calibration standards (CAL) - a solution of analytes prepared in the laboratory from stock standard solutions and diluted as needed and used to calibrate the instrument response with respect to analytic concentration.

3.3 Quality control sample (QCS) - a solution containing known concentrations of analytes, prepared by a laboratory other than the laboratory performing the analysis. The analyzing laboratory uses this solution to demonstrate that it can obtain acceptable identifications and measurements with a method.

3.4 Performance evaluation sample (PE) - a solution of method analytes distributed by the Quality Assurance Research Division (QARD), Environmental Monitoring Systems Laboratory (EMSL-Cincinnati), USEPA, Cincinnati, Ohio, to multiple laboratories for analysis. A volume of the solution is added to a known volume of reagent water and analyzed with procedures used for samples. Results of analyses used by the QARD to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. Analyte true values are unknown to the analyst.

3.5 Laboratory performance check standards (LPC) - a solution of analytes

prepared in the laboratory by adding appropriate volumes of the stock standard solutions to reagent water used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.6 Laboratory duplicates (LD) - two aliquots of the same sample that are treated exactly the same throughout laboratory analytical procedures. Analyses of laboratory duplicates indicate precision associated with laboratory procedures but not the sample collection, preservation, or storage procedures.

3.7 Field duplicates (FD) - two samples taken at the same time and placed under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of field duplicates indicate the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.8 Laboratory fortified sample matrix (LFM) - An aliquot of an environmental sample to whkh known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.9 Laboratory fonified blank (LFB) An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

4.0 Interferences

.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or spiking can be used to solve most interference problems.

4.2 The water dip or negative peak that elutes near and can interfere with the fluoride peak can usually be eliminated by the addition of the equivalent of 1 mL of concentrated eluent (7.3 100X) to 100 mL of each standard and sample.

4.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

4.4 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

4.5 Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known coelution is caused by carbonate and other small organic anions. At concentrations of fluoride above 1.5 mg/L this interference may not be significant, however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.

4.6 The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

7 The quantitation of unretained peaks should be avoided, such as low molecular weight organic acids (formate, acetate, propionate, etc.) which are conductive and coelute with or near fluoride and would bias the fluoride quantitation in some drinking and most waste waters.

5.0 Safety

5.1 Normal, accepted laboratory safety practices should be followed during reagent preparation and instrument operation. No known carcinogenic materials are used in this method.

6.0 Apparatus and Materials

6.1 Balance - Analytical, capable of accurately weighinq to the nearest 0.0001 g.

6.2 Ion chromatograph - Analytical system complete with ion chromatograph and all required accessories including syringes, analytical columns, compressed gasses and detectors.

6.2.1 Anion guard column: A protector of the separator column. If omitted from the system the retention limes will be shorter. Usually packed with a substrate the same as that in the separator column.

6.2.2 Anion separator column: This column producos the separation shown in Fgures 1 and 2.

6.2.2.1 Anion separator column (Method A): The separation shown in Figure 1 was generated using a Dionex AS4A column (P/N 37041). An optional column may be used if comparable resolution of peaks is obtained, and the requirements of section 10.2 can be met.

6.2.2.2 Anion separator column (Method B). The separation shown in Figure 2 was generated using a Dionex AS9 column (P/N 42025). An optional column may be used if comparable resolution of peaks is obtained and the requirements of section 10.2 can be met.

6.2.3 Anion suppressor device: The data presented in this method was generated using a Dionex Anion MicroMembrane Suppressor (P/N 37106).

6.2.4 Detector - Conductivity cell: approximately 1.25 uL internal volume, (Dionex, or equivalent) capable of providing data as required in section 10.2.

6.3 The Dionex AI-450 Data Chromatography Software was used to generate all the data in the attached tables. Systems using a stripchart recorder and integrator or other computer based data system may achbve approximately the same MDL's but the user should demonstrate this by the procedure outlined in Section 10.2.

7.0 Reagents and Consumable Materials

7.1 Sample bottles: Glass or polyethylene of sufficient volume to allow replicate anaiyses of anions of interest.

7.2 Reagent water: Distilled or deionized water, free of the anions of interest. Water should contain particles no larger than 0.20 microns.

7.3 Eluent solution (Method A and Method B): Sodium bicarbonate (CAS RN 144-55-8) 1.7 mM, sodium carbonate (CAS RN 497-19-8) 1.8 mM. Dissolve 0.2856 g sodium bicarbonate ($NaHCO_3$) and 0.3816 g of sodium carbonate (Na_2CO_3) in reagent water (7.2) and dilute to 2 liters.

7.4 Regeneration solution (MicroMembrane Suppressor): Sulfuric acid (CA RN-7664-93-9) 0.025N. Dilute 2.8 mL conc. sulfuric acid (H_2SO_4) to 4 liters with reagent water.

7.5 Stock standard solutions, 1000 mg/L (1 mg/mL): Stock standard

solutions may be purchased as certified solutions or prepared from ACS reagent grade materials (dried at 105-C for 30 min.) as listed below.

7.5.1 Bromide (Br) 1000 mg/L: Dissolve 1.2876 g sodium bromide (NaBr, CAS RN 7647-15-6) in reagent water and dilute to 1 liter.

7.5.2 Bromate (BrO3-) 1000 mg/L: Dissolve 1.3057 g of potassium bromate (KBrO3, CAS RN 7758-01-2) in reagent water and dilute to 1 liter.

7.5.3 Chlorate (ClO3-) 1000 mg/L: Dissolve 1.2753 9g sodium chlorate (NaClO3, CAS RN 7775-09-9) in reagent water and dilute to 1 liter.

7.5.4 Chloride (Cl-) 1000 mg/L: Dissolve 1.6485 g sodium chloride (NaCl, CAS RN 7647-14-5) in reagent water and dilute to 1 liter.

7.5.5 Chlorite (ClO2-) 1000 mg/L: Dissolve 1.3410 g of sodium chlorite (NaClO2, CAS RN 7758-19-2) in reagent water and dilute to 1 liter.

7.5.6 Fluoride (F-) 1000 mg/L: Dissolve 2.2100 g sodium fluoride (NaF, CAS RN 7681-49-4) in reagent water and dilute to 1 liter.

7.5.7 Nitrate (NO3- -N) 1000 mg/L: Dissolve 6.0679 g sodium nitrate (NaNO3, CAS RN 7631-994) in reagent water and dilute to 1 liter.

7.5.8 Nitrite (NO2- -N) 1000 mg/L: Dissolve 4.9257 g sodium nitrite (NaNO2, CAS RN 7632-00-0) in reagent water and dilute to 1 liter.

7.5.9 Phosphate (HPO4 2- -P) 1000 mg/ L: Dissolve 4.3937 g potassium phosphate, monobasic (KH2PO4, CAS RN 7778-77-0) in reagent water and dilute to 1 liter.

7.5.10 Sulfate (SO4 2-) 1000 mg/L: Dissolve 1.8141 g potassium sulfate (K2SO4, CAS RN 7773-80-5) in reagent water and dilute to 1 liter.

Note: Stability of standards: Stock standards (7.5) are stable for at least one month when stored at 4-C. Dilute working standards should be prepared weekly, except those that contain nitrite and phosphate should be prepared fresh daily.

8.0 Sample Collection, Preservation and Storage

8.1 Samples should be collected in scrupubusly clean glass or polyethylene bottles.

8.2 Sample preservation and holding times for the anions that can be determined by this method are as follows.

Analyte	Preservation	Holding Time
Bromate	None required	28 days
Bromide	None required	28 days
Chlorate	None required	28 days
Chloride	None required	28 days
Chlorite	Cool to 4-C	immed.
Fluoride	None required	28 days
Nitrate-N		
chlorinated	Cool to 4-C	28 days
nonchlorinated	conc. H2SO4 pH < 2	14 days
Nitrite-N	Cool to 4-C	48 hours
o-Phosphate-P	Cool to 4-C	48 hours

Sulfate	Cool to 4-C	28 days

8.3 The method of preservation and the holding time for samples analyzed by this method are determined by the anions of interest. In a given sample, the anion that requires the most preservation treatment and the shortest holding time will determine the preservation treatment It is recommended that all samples be cooled to 4-C and held no longer than 28 days for Method A and analyzed immediately for Method B.

9.0 Calibration and Standardization

9.1 Establish ion chromatographic operating parameters equivalent to those indicated in Table 1A or 1B.

9.2 For each analyte of interest, prepare calibration standards at a minimum of three concentration levels and a blank by adding accurately measured volumes of one or more stock standards (7.5) to a volumetric flask and diluting to volume with reagent water. If a sample analyte concentration exceeds the calibration range the sample may be diluted to fall within the ranse. H this is not possible then three new calibration concentrations must be chosen, two of which must bracket the concentration of the sample analyte of interest. Each attenuation range of the instrument used to analyze a sample must be calibrated individually.

9.3 Using injections of 0.1 to 1.0 mL (determined by injection loop volume) of each calibration standard, tabulate peak height or area responses against the concentration. The results are used to prepare a calibration curve for each analyte. During this procedure, retention times must be recorded.

9.4 The calibration curve must be verified on each working day, or whenever the anion eluent is changed, and after every 20 samples. If the response or retention time for any analyte varies from the expected values by more than +/- 10%, the test must be repeated, using fresh calibratbn standards. If the results are still more than +/- 10%, a new calibration curve must be prepared for that analyte.

9.5 Non-linear response can result when the separator column capacity is exceeded (overloading). The response of the detector to the sample when diluted 1 :1, and when not diluted, should be compared. If the calculated responses are the same, samples of this total anionic concentration need not be diluted.

10.0 Quality Control

10.1 Each laboratory using this method should have a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability (10.2) and the analysis of fortified samples as a continuing check on performance. The laboratory should maintain performance records to define and document the quality ot data that are generated.

10.1.1 In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options to improve the separations or bwer the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Section 10.2.

10.1.2 The laboratory should fortify and analyze a minimum of 10% of all samples to monitor continuing laboratory performance. A minimum of 10% of all samples should be run in duplicate.

10.2 Before performing any analyses, the analyst should demonstrate the ability to generate acceptable accuracy and precision with this

method, using a laboratory performance standard.

10.2.1 Select a representative check concentration for each analyte to be measured. Using stock standards, prepare a laboratory performance check sample concentrate in reagent water 100 times more concentrated than the selected concentrations.

10.2.2 Using a pipet, add 1.00 mL ot the check sample concentrate (10.2.1) to each of a minimum of four 100-mL aliquots of reagent water. Analyze the aliquots according to the procedure in Section 11.

10.2.3 Calculate the average percent recovery, (R), and the standard deviation(s) of the percent recovery, for the results.

10.2.4 Using the appropriate data from Table 2, determine the recovery and single operator precision expected for the method, and compare these results to the values cakulated in Section 10.2.3. If the data are not comparable within control limits (10.3.1), review potential problem areas and repeat the test.

10.3 The analyst must calculate method performance criteria and define the performance of the laboratory for each spike concentration of analyte being measured.

10.3.1 Calculate upper and bwer control limits for method performance as follows:

Upper Control Limit (UCL) = R + 3s
Lower Control Limit (LCL) = R - 3s

where R and s are calculated as in Section 10.2.3. The UCL and LCL can be used to construct control charts that are useful in observing trends in performance.

10.4 The laboratory should develop and maintain separate accuracy statements of laboratory performance for each matrix being analyzed by the laboratory. An accuracy statement for the method is defined as R +/- s. The accuracy statement should be developed by the analyses of four aliquots of water or wastewater, as described in Section 10.2.2, followed by the calculation of R and s.

10.5 Before processing any samples, the analyst must demonstrate through the analysis of an aliquot of reagent water that all glassware and reagent interferences are under control. Each time there is a change in reagents, a laboratory reagent blank must be processed as a safeguard against laboratory contamination.

10.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. When doubt exists over the identification of a peak in the chromatogram, confirmatory techniques such as sample dilution and fortification, must be used. Whenever possible, the laboratory should perform analysis of quality control check samples and participate in relevant performance evaluation sample studies.

10.7 In order to verify that standards have been prepared conectly a reference standard check should be performed using a standard of known concentration prepared by an independent source.

0.8 With each batch of samples processed analyze a single laboratory fortified blank containing each analyte of concern at a concentration at or near those used in the reagent water data in Tables 2A or 2B. If more than 20 samples are run in a batch analyze one LFB for every 20

samples. Evaluate the accuracy by comparing to Tables 2A of 2B. If acceptable data cannot be obtained, locate the problem and correct it.

10.9 At least quarterly, replicates of LFBs should be analyzed to determine the precision of the laboratory measurements. Add these results to the ongoing control charts to document data quality.

10.10 When using Part B, the analyst should be aware of the purity of the reagents used to prepare standards. Allowances must be made when the solid materials are less than 99% pure.

11.0 Procedure

11.1 Tables 1A and 1B summarize the recommended operating conditions for\ the ion chromatograph. Included in this table are estimated retention times that can be achieved by this method. Other columns, chromatographic conditions, or detectors may be used if the requirements of Section 10.2 are met.

11.2 Check system calibration daily and, if required, recalibrate as described in Section 9.

11.3 Load and inject a fixed amount of well mixed sample. Flush injection loop thoroughly, using each new sample. Use the same size loop for standards and samples. Record the resulting peak size in area or peak height units. An automated constant volume injection system may also be used.

11.4 The width of the retentbn time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for each analyte. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.5 If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

11.6 If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, fortify the sample with an appropriate amount of standard and reanalyze.

Note: Retention time is inversely proportional to concentration. Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. In some cases this peak migration may produce poor resolution or identification.

11.7 The following extraction should be used for solid materials. Add an amount of reagent water equal to ten times the weight of dry solid material taken as a sample. This slurry is mixed together for ten minutes using a magnetk stirring device. Filter the resulting slurry before injecting using a 0.45 u membrane type filter. This can be the type that attaches directly to the end of the syringe. Care should be taken to show that good recovery and identification of peaks is obtained with the users matrix through the use of spikes.

12.0 Calculation

12.1 Prepare separate calibration curves for each anion of interest by plotting peak size in area, or peak height units of standards against concentration values. Compute sample concentration by comparing sample peak response with the standard curve.

12.2 Report results in mg/L.

12.3 Report

NO_2^- as N

NO3- as N
HPO4 2- as P

13.0 Precision and Accuracy - Method Detection Limit

13.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1A and 1B were obtained using reagent waters.

13.2 Single operator accuracy and precision for reagent, drinking and surface water, and mixed domestic and industrial wastewater are listed in Table 2A and 2B.

13.3 Multiple laboratory accuracy and precision data for reagent, drinking and waste water using method A ue given for each anion in tables 3 through 9. Data from nineteen laboratories were used for this data.

13.4 Some of the bias statements, for example chloride and sulfate, may be misleading due to spiking small increments of the anion into large naturally occuring concentrations of the same anion.

14.0 References

14.1 "Determination of Inorganic Disinfection By-Products by Ion Chromatography", J. Pfaff, C. Brockhoff. J. Am. Water Works Assoc., Vol 82, NO. 4, p. 192.

14.2 Standard Methods for the Examination of Water and Wastewater, Method 4110B, "Anions by Ion Chromatography" proposed for the supplement 1 7th Edition of Standard Methods.

14.3 Dionex, System 4000 Operation and Maintenance Manual, Dionex Corp., Sunnyvale, California 94086. 1988.

14.4 Method Detection Limit (MDL) as described in "Trace Analyses for Wastewater," J. Glaser, D. Foerst, G. McKee, S. Quave, W. Budde, Environmental Science and Technology, Vol. 15, Number 12, page 1426, December 1981.

Table 1A. Chromatographic Conditions and Detection Limits In Reagent Water (Method A)

Analyte	Peak # (*)	Retention Time (min)	MDL (mg/L)
Fluoride	1	1.2	0.01
Chloride	2	1.7	0.02
Nitrite-N	3	2.0	0.004
Bromide	4	2.9	0.01
Nitrate-N	5	3.2	0.002
o-Phosphate-P	6	5.4	0.003
Sulfate	7	6.9	0.02

Standard Conditions:

Columns:	as specified in 6.2.2.1
Detector:	as specified in 6.2.4
Pump Rate:	2.0 mL/min.
Eluent:	as specified in 7.3.1
Sample Loop:	50 uL

MDL calculated from data system using a y-axis selection of 1000 ns and with a stripchart recorder with an attenuator setting of 1 uMHO full scale.

(*) See figure 1

Table 1B. Chromatographic Conditions and Detection Limits In Reagent Water (Method B)

Analyte	Peak # (*)	Retention Time (min)	MDL (mg/L)
Chlorite	1	2.8	0.01
Bromate	2	3.2	0.02
Chlorate	4	7.1	0.003

Standard Conditions:

Column:	as specified in 6.2.2.2
Detector:	as specified in 6.2.4
Pump Rate:	1.0 mL/min.
Eluent:	as specified in 7.3
Sample Loop:	50 uL
Attentuation:	1
y - axis:	500 ns

(*)See figure 2

Table 2A. Single Operator Accuracy and Precision of Standard Anions (Method A)

Analyte	Sample Type	Spike (mg/L)	Number of Replicates	Mean Recovery %	Standard Deviation (mg/L)
Bromide	RW	5.0	7	99	0.08
	DW	5.0	7	105	0.10
	SW	5.0	7	95	0.13
	WW	5.0	7	105	0.34
	SD	2.0	7	82	0.06
Chloride	RW	20.0	7	96	0.35
	DW	20.0	7	108	1.19
	SW	10.0	7	86	0.33
	WW	20.0	7	101	5.2
	GW	20.0	7	114	1.3
	SD	20.0	7	90	0.32
Fluoride	RW	2.0	7	91	0.05
	DW	1.0	7	92	0.06
	SW	1.0	7	73	0.05
	WW	1.0	7	87	0.07
	GW	0.4	7	95	0.07
	SD	5.0	7	101	0.35
rate-N	RW	10.0	7	103	0.21
	DW	10.0	7	104	0.27
	SW	10 0	7	93	0.17
	WW	10.0	7	101	0.82

	GW	10.0	7	97	0.47
	SD	10.0	7	82	0.28
Nitrite-N	RW	10.0	7	97	0.14
	DW	10.0	7	121	0.25
	SW	5.0	7	92	0.14
	WW	5.0	7	91	0.50
	GW	10.0	7	96	0.35
	SD	2.0	7	98	0.08
o-Phosphate-P	RW	10.0	7	99	0.17
	DW	10.0	7	99	0.26
	SW	10.0	7	98	0.22
	WW	10.0	7	106	0.85
	GW	10.0	7	95	0.33
Sulfate	RW	20.0	7	99	0.40
	DW	50.0	7	105	3.35
	SW	40.0	7	95	1.7
	WW	40.0	7	102	6.4
	GW	40.0	7	112	3.2

RW = Reagent Water
DW = Drinking Water
SW = Surface Water
WW = Mixed Domestic and Industrial Wastewater
GW = Groundwater
SD = USEPA ac Solid (Shale)

Table 2B. Single-Operator Accuracy and precision of By-Products (Method B)

Analyte	Sample Spike Type	Spike (mg/L)	Number of Replicates	Mean Recovery %	Standard Deviation (mg/L)
Bromate	RW	5.0	7	103	0.07
		1.0	7	98	0.04
		0.1	7	155	0.005
		0.05	7	122	0.01
	DW	5.0	7	95	0.04
		1.0	7	85	0.02
		0.1	7	98	0.005
		0.05	7	98	0.005
Chlorate	RW	5.0	7	101	0.06
		1.0	7	97	0.01
		0.1	7	100	0.01
		0.05	7	119	0.05
	DW	5.0	7	101	0.04
		1.0	7	115	0.01
		0.1	7	121	0.005
		0.05	7	110	0.01
Chlorite	RW	5.0	7	100	0.04
		1.0	7	98	0.01
		0.1	7	86	0.01
		0.05	7	94	0.01
	DW	5.0	7	96	0.03
		1.0	7	100	0.02
		0.1	7	76	0.00
		0.05	7	96	0.01

RW = Reagent Water
DW = Drinking Water

Table 3. Determination of Bias for Fluoride

Water	Am't Added mg/L	Am't Found mg/L	S(t)	S(o)	Bias %
Reagent	0.26	0.25	0.08	0.11	-3.8
	0.34	0.29	0.11		-14.7
	2.12	2.12	0.07	0.12	0.0
	2.55	2.48	0.14		-2.7
	6.79	6.76	0.20	0.19	-0.4
	8.49	8.46	0.30		-0.4
Drinking	0.26	0.24	0.08	0.05	-7.7
	0.34	0.34	0.11		0.0
	2.12	2.09	0.18	0.06	-1.4
	2.55	2.55	0.16		0.0
	6.79	6.84	0.54	0.25	+0.7
	8.49	8.37	0.75		-1.4
Waste	0.26	0.25	0.15	0.06	-3.8
	0.34	0.32	0.08		-5.9
	2.12	2.13	0.22	0.15	+0.5
	2.55	2.48	0.16		-2.7
	6.79	6.65	0.41	0.20	-2.1
	8.49	8.27	0.36		-2.6

Table 4. Determination of Bias for Chloride

Water	Am't Added mg/L	Am't Found mg/L	S(t)	S(o)	Bias %
Reagent	0.78	0.79	0.17	0.29	+1.3
	1.04	1.12	0.46		+7.7
	6.50	6.31	0.27	0.14	-2.9
	7.80	7.76	0.39		-0.5
	20.8	20.7	0.54	0.62	-0.5
	26.0	25.9	0.58		-0.4
Drinking	0.78	0.54	0.35	0.20	-30.8
	1.04	0.51	0.38		-51.0
	6.50	5.24	1.35	1.48	-19.4
	7.80	6.02	1.90		-22.8
	20.8	20.0	2.26	1.14	-3.8
	26.0	24.0	2.65		-7.7
Waste	0.78	0.43	0.32	0.39	-44.9
	1.04	0.65	0.48		-37.5
	6.50	4.59	1.82	0.83	-29.4
	7.80	5.45	2.02		-30.1
	20.8	18.3	2.41	1.57	-11.8
	26.0	23.0	2.50		-11.5

Table 5. Determination of Bias for Nitrite - Nitrogen

Water	Am't Added mg/L	Am't Found mg/L	S(t)	S(o)	Bias %
Reagent	0.36	0.37	0.04	0.04	+2.8
	0.48	0.48	0.06		0.0
	3.00	3.18	0.12	0.06	+6.0
	3.60	3.83	0.12		+6.4
	9.60	9.84	0.36	0.26	+2.5
	12.0	12.1	0.27		+0.6
Drinking	0.36	0.30	0.13	0.03	-16.7
	0.48	0.40	0.14		-16.7
	3.00	3.02	0.23	0.12	+0.7
	3.60	3.62	0.22		+0.6
	9.60	9.59	0.44	0.28	-0.1
	12.0	11.6	0.59		-3.1
Waste	0.36	0.34	0.06	0.04	-5.6
	0.48	0.46	0.07		-4.2
	3.00	3.18	0.13	0.10	+6.0
	3.60	3.76	0.18		+4.4
	9.60	9.74	0.49	0.26	+1.5
	12.0	12.0	0.56		+0.3

Table 6. Determination of Bias for Bromide

Water	Am't Added mg/L	Am't Found mg/L	S(t)	S(o)	Bias %
Reagent	0.63	0.69	0.11	0.05	+9.5
	0.84	0.85	0.12		+1.2
	5.24	5.21	0.22	0.21	-0.6
	6.29	6.17	0.35		-1.9
	16.8	17.1	0.70	0.36	+1.6
	21.0	21.3	0.93		+1.5
Drinking	0.63	0.63	0.13	0.04	0.0
	0.84	0.81	0.13		-3.6
	5.24	5.11	0.23	0.13	-2.5
	6.29	6.18	0.30		-1.7
	16.8	17.0	0.55	0.57	+0.9
	21.0	20.9	0.65		-0.4
Waste	0.63	0.63	0.15	0.09	0.0
	0.84	0.85	0.15		+1.2
	5.24	5.23	0.36	0.11	-0.2
	6.29	6.27	0.46		-0.3
	16.8	16.6	0.69	0.43	-1.0
	21.0	21.1	0.63		+0.3

Table 7. Determination of Bias for Nitrite - Nitrogen

Water	Am't Added mg/L	Am't Found mg/L	S(t)	S(o)	Bias %
Reagent	0.42	0.42	0.04	0.02	0.0
	0.56	0.56	0.06		0.0
	3.51	3.34	0.15	0.08	-4.8
	4.21	4.05	0.28		-3.8
	11.2	11.1	0.47	0.34	-1.1
	14.0	14.4	0.61		+2.6
Drinking	0.42	0.46	0.08	0.03	+9.5
	0.56	0.58	0.09		+3.6
	3.51	3.45	0.27	0.10	-1.7
	4.21	4.21	0.38		0.0
	11.2	11.5	0.50	0.48	+2.3
	14.0	14.2	0.70		+1.6
Waste	0.42	0.36	0.07	0.06	-14.6
	0.56	0.40	0.16		-28.6
	3.51	3.19	0.31	0.07	-9.1
	4.21	3.84	0.28		-8.8
	11.2	10.9	0.35	0.51	-3.0
	14.0	14.1	0.74		+0.4

Table 8. Determination of Bias for Ortho-Phosphate

Water	Am't Added mg/L	Am't Found mg/L	S(t)	S(o)	Bias %
Reagent	0.69	0.69	0.06	0.06	0.0
	0.92	0.98	0.15		+6.5
	5.77	5.72	0.36	0.18	-0.9
	6.92	6.78	0.42		-2.0
	18.4	18.8	1.04	0.63	+2.1
	23.1	23.2	0.35		+0.4
Drinking	0.69	0.70	0.17	0.17	+1.4
	0.92	0.96	0.20		+4.3
	5.77	5.43	0.52	0.40	-5.9
	6.92	6.29	0.72		-9.1
	18.4	18.0	0.68	0.59	-2.2
	23.1	22.6	1.07		-2.0
Waste	0.68	0.64	0.26	0.09	-7.2
	0.92	0.82	0.28		-10.9
	5.77	5.18	0.66	0.34	-10.2
	6.92	6.24	0.74		-9.8
	18.4	17.6	2.08	1.27	-4.1
	23.1	22.4	0.87		-3.0

ble 9. Determination of Bias for Sulfate

ter	Am't Added mg/L	Am't Found mg/L	S(t)	S(o)	Bias %

APPENDIX J: GC/MS ANALYSIS OF UNKNOWNS

EXPLOSIVE SCIENCES BRANCH
CODE 4052
NAVAL SURFACE WARFARE CENTER
CRANE, INDIANA 47522

PROCEDURE FOR FAILURE ANALYSIS USING THE MASS SPECTROMETER

CR 4052-EOP-0014

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7 Aug 97

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13 Aug 97

TITLE: Qualitative Analysis Of Materials By Desorption, Gas Chromatography, Mass Spectrometry (DGCMS)

1.0 SCOPE AND APPLICATION

1.1 This method is intended for the comparison and identification of organic materials encountered during routine failure analysis. The method is primarily intended for solids and high boiling point liquids that are not corrosive samples. It is useful as an exploratory tool for samples of unknown or uncertain composition. Making comparisons of samples to identify differences is also a use for the method.

1.2 The matrices applicable to the method are shown below:

Plastics
Lubricants
Volatile Contaminants in Explosives
Rubbers
Paints
Residues on Metal Surfaces
Inclusions Taken From Samples

1.3 Samples may be pyrolyzed in the desorption oven to identify samples based on the pattern of decomposition products.

2.0 SUMMARY OF METHOD

2.1 A small weight of sample, typically 0.01 or 0.1 milligram, is introduced into the desorption oven. The oven is heated to transfer volatile sample components for trapping, separating and measuring, using a system comprised of two liquid nitrogen traps, a gas chromatograph and a mass spectrometer.

2.2 Larger samples, up to 100 milligrams may be used in the desorption oven if the analysis of smaller samples has shown that separation and detection system will not be overloaded and there is a requirement for more sensitivity.

2.3 Limited performance-based method modifications may be acceptable provided they are fully documented. For example, PETN and TNT explosives use a lower desorption temperature for volatiles analysis because their decomposition temperatures are lower.

3.0 PROCEDURE

3.1 Instrument Preparation

3.1.1 The Desorption unit, Gas Chromatograph and Mass Spectrometer are

checked to determine if the correct operating programs are installed in the units. Appendix ( ) shows the program parameters for the instruments

3.1.2 The mass spectrometer program (.RUOK) is run to check for system leaks and to confirm that the spectrum of the background gases in the instrument are in the general response documented in Appendix. The .RUOK progrom is turned off by typing (.SMOFF). Later during sample analysis, additional calibration checks can be made by examining the silicone GC column bleed peaks present in every analysis run. Calibration of the instrument is performed if the silicone background peaks do not appear correct.

3.1.3 Prior to beginning the days' analysis, the desorption system and the gas chromatograph are heat cycled to remove volatile material that may have accumulated during the time when the system was not in use. This would include out gassing from ferrules and septums.

3.2 Sample Preparation

3.2.1 The analyst should become familiar with approximating sample weight based on the visual size of the sample. Estimating the weight of a 0.01, 0.1 and 1 milligram sample size. Since this is a qualitative technique, the estimation of sample size is used to avoid additional handling of the sample and over loading the separation and detection system.

3.2.2 To avoid oven contamination, the samples are wrapped in aluminum foil sheets (3 inches long by 3/4 inches wide by 0.00045 inches thick) prior to oven insertion. Sample preparation equipment is wiped off after each sample to avoid cross contamination between samples.

INSTRUMENT PARAMETER FOR THE DGCSM SYSTEM

Enclosure (1)

Parameters for TSQ-70 mass spectrometer system

Pyrolysis Unit: Chemical Data Systems, Inc. Model 122 Pyroprobe

Probe Type: Platinum Coil
Function: Run
Heating Interval: 10 seconds
Heating Ramp: Off (ballistic heating)
Cleaning Temperature: 990C
Sample Final Temperature: Variable (100C, 150C, 300C, 600C, 900C)
Remote Start by Concentrator

Desorber Unit: Chemical Data Systems, Inc. Model 330 Concentrator

Oven Helium Flow Rate: 30 cubic centimeters per minute
Controls Gas Chromatograph column flow rate at 3 cubic centimeters per minute
Trap A and B: Liquid nitrogen cooled
Concentrator Heating Program:

Function	Temperature degrees Celsius	Time, minutes
DR	60	0
DH	150	10
SP	0	0
VO	220	-
TL	220	-
RA	100	8
IA	-100	10
DA	0	0
FA	180	10
BA	225	5
RB	200	8
IB	-100	10
FB	220	10

Gas Chromatograph Unit: Varian model 3400

Column: J&W Scientific Capillary Column DB-5, 0.25 millimeters inside diameter, 30 meters long, 1 micrometer film thickness of 95% dimethypolysiloxane and 5% phenyl-methylpolysiloxane

Column Temperature: Programmed from mass spectrometer

Mass Spectrometer Unit: Finnigan Mat model TSQ-70

Transfer Line Temperature: 200 degrees Celsius
Gas Chromatograph Oven Program:
Inlet Program Name: GC50TO300
Hold 2 minutes at 50C
Heating rate 20C per minute to 300C
Hold at 300C for 10 minutes
ICL Procedure: DELAYON(0.1,200,1200)
DS Procedure: CHRO $
Scan Range: 32 to 650 atomic weight units
Sample File Naming: TSQ0---- (sequential numbering)

Parameters for 4500 mass spectrometer system

Pyrolysis Unit: Chemical Data Systems, Inc. Model 2000 Pyroprobe

Probe Type: Platinum Coil
Function: Run
Heating Interval: 10 seconds
Heating Ramp: Off (ballistic heating)
Cleaning Temperature: 990C
Sample Final Temperature: Variable (100C, 150C, 300C, 600C, 900C)
Remote Start by Concentrator

Desorber Unit: Chemical Data Systems, Inc. Peakmaster Concentrator

Oven Helium Flow Rate: 30 cubic centimeters per minute
Controls Gas Chromatograph column flow rate at 3 cubic centimeters per minute
Trap A: Tenax GC packing
Trap B: Liquid nitrogen cooled
Concentrator Heating Program:

Function	Temperature degrees Celsius	Time, minutes
CR	41	0
CP	130	10
VO	200	-
TL	220	-
TR	100	8
TI	41	10
DP	41	0
DT	200	10
BT	220	5
FR	220	8
FI	-100	10
FT	220	10

Gas Chromatograph Unit: Finnigan Mat Gas Chromatograph

Column: J&W Scientific Capillary Column DB-1, 0.25 millimeters inside diameter, 30 meters long, 1 micrometer film thickness of 100% dimethypolysiloxane
Column Temperature: Programmed from gas chromatograph control panel

Mass Spectrometer Unit: Finnigan Mat model 4500

Injection Port: 200 degrees Celsius
Transfer Line Temperature: 200 degrees Celsius
Gas Chromatograph Oven Program:
Inlet Program Name: GC50TO250
Hold 2 minutes at 50C
Heating rate 20C per minute to 300C
Hold at 300C for 10 minutes
Scan Range: 32 to 650 atomic weight units
Sample File Naming: GLX0---- (sequential numbering)

APPENDIX K: AMMONIA-NITROGEN ANALYSIS

EXPLOSIVE SCIENCES BRANCH
CODE 4052
NAVAL SURFACE WARFARE CENTER
CRANE, INDIANA 47522

PROCEDURE FOR THE OPERATION OF ION SELECTIVE ELECTRODE FOR AMMONIA-NITROGEN ANALYSIS

CR 4052-EOP-0009

PREPARED BY: BRAD KINDRED

PREPARED BY Brad Kindred BRAD KINDRED	DATE 8-11-97
REVIEWED BY Louis Schwenk LOUIS SCHWENK	DATE 8-11-97
APPROVED BY Nancey J. Maegerlein NANCEY J. MAEGERLEIN	DATE 13 Aug 97

EQUIPMENT REQUIRED FOR ION SELECTIVE ELECTRODE AMMONIA-NITROGEN ANALYSIS

(a) Corning pH/Ion Analyzer, model 250 or equivalent

(c) Orion Ammonia Selective Ion Electrode Model 96-12 or equivalent

REFERENCES

(a) Corning pH/Ion analyzer instruction manual

(c) Orion Ammonia Selective Ion Electrode Model 96-12 instruction manual

(b) EPA method 350.3

MODIFICATIONS OF PROCEDURE

(a) No significant modification

METHOD #: 350.3 Approved for NPDES (Issued 1974)

TITLE: Nitrogen, Ammonia (Potentiometric, Ion Selective Electrode)

ANALYTE:	CAS #
Nitrogen N	7727-37-9
Ammonia NH3	7664-41-7

INSTRUMENTATION: ISE

STORET No.

Total	00610
Dissolved	00608

1.0 Scope and Application

1.1 This method is applicable to the measurement of ammonia-nitrogen in drinking, surface and saline waters, domestic and industrial wastes.

1.2 This method covers the range from 0.03 to 1400 mg NH3-N/L. Color and turbidity have no effect on the measurements, thus, distillation may not be necessary.

2.0 Summary of Method

2.1 The ammonia is determined potentiometrically using an ion selective ammonia electrode and a pH meter having an expanded millivolt scale or a specific ion meter.

2.2 The ammonia electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from an ammonium chloride internal solution. Ammonia in the sample diffuses through the membrane and alters the pH of the internal solution, which is sensed by a pH electrode. The constant level of chloride in the internal solution is sensed by a chloride selective ion electrode which acts as the reference electrode.

3.0 Sample Handling and Preservation

3.1 Samples may be preserved with 2 mL of conc. H2SO4 per liter and stored at 4-C.

4.0 Interferences

4.1 Volatile amines act as a positive interference.

4.2 Mercury interferes by forming a strong complex with ammonia. Thus the samples cannot be preserved with mercuric chloride.

5.0 Apparatus

5.1 Electrometer (pH meter) with expanded mV scale or a specific ion meter.

5.2 Ammonia selective electrode, such as Orion Model 95-10 or EIL Model 8002-2.

5.3 Magnetic stirrer, thermally insulated, and Teflon-coated stirring bar.

6.0 Reagents

6.1 Distilled water: Special precautions must be taken to insure that the

distilled water is free of ammonia. This is accomplished by passing distilled water through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin.

6.2 Sodium hydroxide, 10N: Dissolve 400 g of sodium hydroxide in 800 mL of distilled water. Cool and dilute to 1 liter with distilled water (6.1).

6.3 Ammonium chloride, stock solution: 1.0 mL = 1.0 mg NH3-N. Dissolve 3.819 g NH4Cl in water and bring to volume in a 1 liter volumetric flask using distilled water (6.1).

6.4 Ammonium chloride, standard solution: 1.0 mL = 0.01 mg NH3-N. Dilute 10.0 mL of the stock solution (6. 3) to 1 liter with distilled water (6.1) in a volumetric flask.

NOTE 1: When analyzing saline waters, standards must be made up in synthetic ocean water (SOW); found in Nitrogen, Ammonia: Colorimetric, Automated Phenate Method (350. 1).

7.0 Procedure

7.1 Preparation of standards: Prepare a series of standard solutions covering the concentration range of the samples by diluting either the stock or standard solutions of ammonium chloride.

7.2 Calibration of electrometer: Place 100 mL of each standard solution in clean 150 mL beakers. Immerse electrode into standard of lowest concentration and add 1 mL of 10N sodium hydroxide solution while mixing. Keep electrode in the solution until a stable reading is obtained.

NOTE 2: The pH of the solution after the addition of NaOH must be above 11. Caution: Sodium hydroxide must not be added pri to electrode immersion, for ammonia may be lost from a bas solution.

7.3 Repeat this procedure with the remaining standards, going from lowest to highest concentration. Using semilogarithmic graph paper, plot the concentration of ammonia in mg NH3-N/L on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale.

7.4 Calibration of a specific ion meter: Follow the directions of the manufacturer for the operation of the instrument.

7.5 Sample measurement: Follow the procedure in (7.2) for 100 mL of sample in 150 mL beakers. Record the stabilized potential of each unknown sample and convert the potential reading to the ammonia concentration using the standard curve. If a specific ion meter is used, read the ammonia level directly in mg NH3-N/L.

8.0 Precision and Accuracy

8.1 In a single laboratory (EMSL), using surface water samples at concentrations of 1.00, 0.77, 0.19, and 0.13 mg NH3-N/L, standard deviations were +/- 0.038, +/- 0.017, +/- 0.007, and +/- 0.003, respectively.

8.2 In a single laboratory (EMSL), using surface water samples at concentrations of 0.19 and 0.13 mg NH3-N/L, recoveries were 96% and 91%, respectively.

Bibliography

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