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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 095/9192
~~11 JUN 1999~~
6-1-1999

U.S. Environmental Protection Agency, Region V
Waste, Pesticides, & Toxics Division
Waste Management Branch
Illinois, Indiana, and Michigan Section
ATTN: Mr. Peter Ramanauskas (DW-8J)
77 West Jackson Blvd.
Chicago, IL 60604

Dear Mr. Ramanauskas:

Crane Division, Naval Surface Warfare Center (NAVSURFWARCENDIV Crane) submits enclosure (1), Quality Assurance Project Plan for Insect Collection and Analysis at the Ammunition Burning Grounds. A response to U.S. Environmental Protection Agency Comments is provided as enclosure (2). Enclosure (3) contains the required Certification Statement.

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

Sincerely,

Thomas J. Brent
for JAMES M. HUNSICKER

Encl:
(1) Quality Assurance Project Plan
(2) Response to Comments
(3) Certification Statement

Copy to:
USACE WES (CEWES-EE-C)
USACE WES(CEWES-ERD-A)
USEPA (Allen Debus)
USFWS (Scott Pruitt)
ADMINISTRATIVE RECORD (w/2 copies)
COMNAVSEASYSCOM (SEA OOT) (w/o encl)
SOUTHNAVFACENGCOM (Code 1864) (w/o encl)

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.

Thomas J. Brent, acting
SIGNATURE

Environmental Protection Specialist
TITLE

11 JUN 1999
DATE

Enclosure (3)

QUALITY ASSURANCE PROJECT PLAN
FOR
INSECT COLLECTION AND ANALYSIS AT THE AMMUNITION BURNING GROUNDS
CRANE DIVISION, NAVAL SURFACE WARFARE CENTER

REVISION 2
DATE
JUNE 1999

Enclosure (1)

From: Allen A. Debus, IL/IN/MI Section

To: Carol Witt-Smith, IL/IN/MI Section

Date: January 6, 1998

Subject: Comments Concerning the QAPP, (Rev. 0 dated Dec. 1997), for the Insect Collection & Analysis at U.S. Navy Crane

Introduction

I have reviewed the portions of the QAPP referenced above. It has been thoughtfully prepared, with careful consideration of the specific project objectives. Presently, I have not had an opportunity to review either the field sampling plan or the individual SOPs. However, I will attempt to complete these reviews in the immediate future.

It is difficult to interpret the chronological structure of the plan, as I am uncertain whether or not the insects have been sorted yet, and, if so, what bearing this sorting will have on the subsequent analyses to be performed as an outcome of the cricket study. Also, it is unclear whether or not the cricket analytical study has been completed yet. There is little value in submitting a QAPP for the insect sample study if the cricket data hasn't been generated.

Specific Comments

1. Title page: A title page is needed which includes signature spaces.

A title page with signature spaces has been added to the front of the QAPP.

2. Page 3: Referring to the second paragraph, out of curiousity, what do the bats eat during the other nine months of the year?

FYI, bats are thought to forage from March/April until September/October, depending on the weather any given year. After that, the bats are either in hibernation living off fat stores, or have migrated. The text is a little misleading but meant to indicate that the heaviest foraging is when the insect populations are at their greatest number.

3. Page 6, Section 1.4.1.a.2.a: Clarify what the toxicity values will refer to. (Presumably this is a reference to the bat species, not the insects.)

The purpose is to see if there is any existing data on toxicity levels with reference to the bat. Hence, what do the values gained from the insect analyses tell us about what impact the site might be having to the bat? The text has been revised for clarification.

4. Page 7, Section 1.4.1.c.2: Note that to a large extent, 1.4.1.a.2.a is a prerequisite for this item. Until these activities have been adequately researched it may not be possible to approve this QAPP. What are the relevant values?

See revised text.

5. Page 7, Section 1.4.2.2: It should also be stated whether or not the U.S. EPA concurs with Ms. Chaffee's recommendations, if even on a preliminary basis. (I realize it is rather late in the game to begin "second guessing" the nature of the project.)

See revised text.

6. Page 8, Section 1.4.2.2: In the first paragraph, the rationale for analyzing phosphorous should be more clearly explained. I vaguely recall there were some extended conversations concerning this test parameter.

The reason for analyzing phosphorus is because it has been treated at the site (i.e., red phosphorus). Furthermore, phosphorus is toxic to mammals. The intent is to determine if phosphorus is present in the insects, above a concentration normally found in the insects, and at concentrations that have been proven toxic to the bat. The text will be revised accordingly.

7. Page 8, Table 1: Should the Method 8330 breakdown products be added to this list? (i.e. the "extra" compounds included in the groundwater study).

The Table has been revised.

8. Page 8, Section 1.4.3: The use of the term, "impacting" is rather vague and should be clarified. What is the decision rule associated with this goal? The answer to this question is heavily dependent on ecological information which may not have been obtained.

Ultimately, the goal of the research is to determine if the operations are affecting the health of the Indiana Bat. However, this task is an intermediate step and only determines if there are elevated levels of contaminants in the insects (which are the food source – or potential food source – for the bat). The term, "impacting" is probably an inappropriate choice. An impact here is defined as detecting the presence, through analytical methods, of explosives or elevated levels of metals, in the insect matrix. The elevated levels of metals will be determined, as explained elsewhere in the QAPP, by research into existing literature on the "background" levels of metals in insects. The phrase "present (and if so, at what concentration) in" will replace "impacting" here in the QAPP.

9. Page 9, Section 1.7: Although I haven't yet read the FSP referenced here, note that the matter of "Sorting" is of primary importance to this project. Has a sample network/design table been prepared yet?

A sample network/design table is now included in the QAPP.

10. Page 9, Section 2: This paragraph is written in future tense which is confusing considering the status of the project. Based on my understanding of project schedule, shouldn't the correct tense be both past and possibly future?

The text has been revised as suggested.

11. Page 10, Table 2: There should be some discussion concerning QA responsibilities of each identified individual and, given the unusual project scope, explanation of expertise required to perform special functions.

The text has been revised.

11. Page 10, Section 3: Referring to the next to last sentence, note that the SOPs must be modified prior to approval of this QAPP. This section of the QAPP indicates that approval may be premature. Also, this section should be tailored more exactly to the specific project objectives mentioned in section 1.4.1,

See revised text.

12. Page 11, Section3.1: This section's terminology should correspond more closely to discussion found on page 7, Section 1.4.1.c.4. Then, in the last sentence, if control limits are not available, will they be generated during the course of analysis? Otherwise, why are these RPDs being calculated? What are they supposed to indicate for this project?

See revised text.

13. Page 11, Section 3.2: There is a type in the first line. Insert the word "be" in between words of the phrase, "may difficult".

The text has been changed accordingly.

14. Page 12, Section 3.2: If limits are unavailable for insect matrices, then explain why there is any value in measuring % accuracy. Perhaps the word "limits" is too strong for what is intended here. At least the measurements will indicate something of importance to the study. What might that be, and are there any "default" values which would be consdiered reasonable target "limits" until a sufficient body of data has beene generated? Won't the cricket study provide these default limits? If this is the case, why aren't these listed here?

See revised text.

15. Page 12, Section 3.3: Is it the case that the number and type of analyses (including QC sample types) remains presently unknown? When will sorting be accomplished? Again, I haven't read the FSP.

Yes. The Chemist presented a table trying to estimate the amount of sample required for each of the analysis proposed. The sorting was completed in December 1998. She sent a hard copy, that

is attached to this document. The Chemist and Entomologists have entered the information in a spreadsheet in order to sort and combine to help determine the best mix. However, a conference call would be prudent to agree upon the optimum combination.

16. Page 14, Section 5.2: In the last paragraph, the phrase, "may be" should be changed to "shall be" or "should be".

The text has been changed accordingly.

17. Page 14, Section 5.3: What information will the final evidence file be comprised of? Who should retain it?

See revised text.

18. Page 15, Section 6.2: In the second paragraph, rationale should be provided for why 3,4 DNT will be selected as the surrogate. How does the % recovery of 3,5 DNT compare with that of 3,4 DNT in an insect matrix? Referring to the last sentence of this paragraph, hasn't the cricket study been concluded yet? If not, this is all very preliminary.

See revised text.

19. Page 15, Section 6.2: In the third paragraph, the reference to SW-846 is incorrectly stated as "SW-486". Will the ICP analysis proposed be a 'trace" ICP analysis? Referring to the last sentence in this paragraph, it sounds as if this study is of a very preliminary nature, and that this QAPP cannot be approved in its present state.

The ICP is a Perkin Elmer Optima 3000DV, not a Jerral Ash "trace" ICP. Standard protocol in the lab is to analyze samples first on the ICP and then on the ICP-MS or GFAA. The QAPP was drafted before the cricket work was completed. Based upon the Chemist's findings and work done by her for others during the past year, the insects will initially be analyzed by ICP-MS. Only those metals greater than the ICP-MS linear range will be analyzed by ICP.

20. Page 16, Section 7.3: Haven't the samples been sorted yet? This will significantly impact the number of QC samples to be tested (as well as achievable detection limits). Presumably the analytical options stated in Table 3 will be settled as an outcome of the cricket study. Note that the cricket data assessment study must be completed before an insect QAPP can be approved.

See revised text.

21. Page 17, Section 7.3: How will the low calibration standard compare to the cricket reporting limits? Only obervable reporting limits should be reported for the cricket study, which in turn will or may be used for the insect sample.

First, the reporting limits (LRLs) are calculated through the MDL process. As stated in the SOP, MDLs shall be matrix specific except for metals analysis which is only required to be performed

for a water matrix. The water MDLs are then used to calculate MDLs for other matrices. Generally, the low calibration standard is near the reporting limit. However, because the lab uses purchased multi-standard mixes for many analyses, this is not always achieved. In those cases, the Chemist analyzes a low level check standard during the analytical run.

22. Page 17, Section 8.1: This paragraph definitely illustrates the preliminary nature of this project. Also, note that it isn't truly possible to collect a valid field duplicate sample now. It seems logical to use the cricket study to generate default values ranges for the QC samples which cannot be analyzed in direct conjunction with the insect sample.

See revised text.

24. Page 18, Section 8.2: The status of the matrix duplicate should be indicated in Table 5.

The Table has been revised.

25. Page 18, Section 9: Is this section intended to apply to both the cricket and insect studies? Please clarify. Also, this should encompass review of sorting procedures for "field" or intermediate sorting step.

See revised text.

26. Page 20, Section 9.2.3: Which of the individuals identified in Table 2 will perform independent data validation?

See revised text.

27. Page 20, Section 9.3: What about review of notes generated during the sorting phase? This also counts as 'data".

See revised text.

28. Page 20, Section 9.3.2: Will there be an intermediate "end-cricket phase' report prior to the insect analysis? How will the U.S. EPA be notified when the insects will be analysed according to protocol defined in a successful cricket analytical demonstration? Here I have focused on the phrases "The final data packages" (which are these?), and "analyses" (in the last line).

See revised text.

QUALITY ASSURANCE PROJECT PLAN
FOR
INSECT COLLECTION AND ANALYSIS AT THE
AMMUNITION BURNING GROUNDS
CRANE DIVISION, NAVAL SURFACE WARFARE CENTER

REVISION 2
DATE
JUNE 1999

NSWC Crane Project Manager

_____

Laboratory Manager

_____

U.S. EPA RCRA Permit Writer

_____

U.S. EPA Regional Quality Assurance Manager

_____

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1. PROJECT DESCRIPTION

This project is for collecting and analyzing insects at the Ammunition Burning Grounds (ABG). This Quality Assurance Project Plan (QAPP) presents the organization, objectives, planned activities, and specific Quality Assurance/Quality Control (QA/QC) procedures for handling and storage, chain-of-custody, and laboratory and field analyses.

1. 1. INTRODUCTION

This QAPP presents the objectives, tasks, and QA/QC procedures associated with conducting sampling, preparation and analyses of insects for metals and explosives compounds.

1. 1. 1. OVERALL PROJECT OBJECTIVES

The project has three primary phases. The initial, or preliminary phase is to refine existing methods and document the procedures for analyzing explosives and metals in an insect matrix. The second objective is to collect macroinvertebrates samples associated with the food chain of the federally endangered Indiana Bat (*Myotis sodalis*) in the area of the ABG associated with the location of the capture of a single male bat. The third phase is to prepare and analyze the insect samples for the purpose of determining the levels, if present, of metals and explosives in the insect tissue. This information will then be used to determine the need for other studies which may entail additional sampling of bugs to determine possible contaminant effects to the bat.

Since the insect samples have already been collected, a limited sample volume is available for analyses. The limited sample size ultimately controls the extent the objectives can be pursued, especially with respect to the total number of analyses and quality control (QC) efforts. Therefore, crickets were obtained and used as surrogates for the initial phase of the project. Work with crickets assisted in determining changes to preparation and analytical procedures, interferences, detection limits, required sample volumes, and the extent of QC. The initial surrogate cricket work, along with the pre-obtained insect sample volume, determined the actual detection limits achievable for this project. Table 1 is the sample network/design.

Table 1 - **Sampling Network/Design**

Type of Sampling	Target Constituent	Objective	Limit of Detection
Cricket Surrogate	Metals Explosives	To determine changes to preparation and analytical procedures, interferences, detection limits, required sample volumes, and the extent of QC.	NA
Light Traps	Metals Explosives	❑ **Primary Objective:** To determine whether contaminants at the site are present in food sources for the Indiana Bat. ❑ **Secondary Objective:** To obtain representative samples of the Bat's food	Reporting limits low enough to determine potential harm to the Bat posed by the contaminants.
Malaise Trap	Metals Explosives		

1. 1. 2. PROJECT STATUS/PHASE

The project included three periods of insect collection in order to capture insects that emerge at different times during the season. Samples were collected in June, July, and August 1997. This allowed for a more representative sample of the bat's diet. The particulars of each sampling round included:

- Insect collection; and
- Sample preservation, packaging, and shipping.

Pending work includes:

- Sample preparation;
- Analysis for metals and explosives; and
- Data reporting.

Sample preparation, analysis and data reporting will not be accomplished until completion of the first phase of this project. The first phase of refining existing methods and documenting the procedures for analyzing explosives and metals in an insect matrix, was completed in December 1997. The second phase was actually completed prior to the first phase (June, July, and August 1997). The third phase will be completed following the approval of this QAPP. At the conclusion of the three phases of this project, data gaps may be identified. Data gaps may lead to additional work during the summer and fall of 1999 or 2000. If additional work is required beyond the phases of this project, a new Field Sampling Plan (FSP) with established objectives will be submitted for that work.

Samples were collected during the summer of 1997 in advance of the establishment of this QAPP in order to take advantage of the field season. The life cycle of organisms of interest required sampling during the summer months. Furthermore, the months of sampling parallel the timeframe of the endangered bats principal foraging at the ABG. Therefore, NSWC Crane chose to sample ahead of the establishment of some of the QAPP objectives in order to get as much information as possible in a timely manner.

1. 2. **LOCATION**

A brief description of the facility and project locations are presented in the following sections.

1. 2. 1. FACILITY LOCATION

NSWC Crane is located in southwestern Indiana, approximately 75 miles southwest of Indianapolis, and 71 miles northwest of Louisville, Kentucky. NSWC Crane occupies 62,463 acres (approximately 100 square miles) of the northern portion of Martin County and small portions of neighboring Greene, Daviess, and Lawrence Counties. The base is located in a rural agricultural and wooded area, and is situated on a topographic plateau known as the Crawford Upland, dissected by well-defined stream valleys, causing elevation differences of over 300 feet in some areas. Surficial geology consists of Pennsylvanian and Mississippian

age sandstones, shales, and limestones.

1. 2. 2. PROJECT LOCATION

Insect collection occurred in the vicinity of the capture of the single male Indiana Bat, south of the ABG. The ABG is located in the east-central portion of the facility (see Figure (1)) in the northwest corner of Section 28 and the southwest corner of Section 21, Township 5N, Range 3W. The ABG was identified as a Solid Waste Management Unit (SWMU) in the facility's operating permit. Covering approximately 50 acres, the ABG is located in a valley at the headwaters of Little Sulphur Creek (Figure (1)). The eastern boundary of the operating unit is the beginning of a pseudo-karst zone characterized by springs and a sinking stream.

1. 3. **SITE HISTORY**

NSWC Crane provides material, technical, and logistical support to the Navy for equipment, weapons systems, and expendable and nonexpendable ordnance items. The facility was opened in 1941 as the Naval Ammunition Depot (NAD), Burns City to serve as an inland munitions production and storage center. In 1943, the name was changed to NAD Crane in honor of Commodore William Montgomery Crane, the first chief of the Navy's Bureaus of Ordnance. The name changed again in 1975, to Naval Weapons Support Center, to reflect the facility's growing involvement in high-technology weapons systems. In 1977, it was decided by the Secretary of Defense to combine all conventional ammunition acquisition under the responsibility of a single service. The ammunition production and storage function was passed to the Army and the Crane Army Ammunition Activity (CAAA) was established as a Crane tenant to accomplish this task for Naval ammunition. CAAA has assumed ordnance production, storage, and related responsibilities under the single service management directive. All environmental activities on the installation, including permitting activities, remain the responsibility of the Navy. In 1992, the name was changed again to the Crane Division, Naval Surface Warfare Center. Although ordnance production and storage still resides at NSWC Crane, today, NSWC Crane serves a modern and sophisticated Navy as a recognized leader in diverse and highly technical product lines, such as microwave devices, acoustic sensors, small arms, microelectronic technology, and more.

1. 3. 1. PROJECT SITE HISTORY

The ABG has been used extensively since the 1940's for the thermal treatment of military pyrotechnics, propellants, and explosives (PEP), and materials potentially PEP contaminated. CAAA has operated the ABG since 1978. Thermal treatment is via open burning, conducted under interim status. NSWC Crane has applied to the U.S. EPA, Region V, for a Resource Conservation Recovery Act (RCRA) Subpart X Operating Permit for the open burning operations.

1. 3. 2. PAST DATA COLLECTION ACTIVITIES

A hydrogeological investigation of the ABG and surrounding area was conducted by Army

Corps of Engineers, Waterways Experiment Station (WES) in 1986-87. The Hunt (1988) report identified factors influencing or controlling the flow of potentially contaminated groundwater into and out of the ABG. Work included emplacement of 66 exploration borings and monitoring wells in three aquifers, geologic and hydrologic field mapping, literature survey and consultation with geologists at the Indiana Geological Survey, Bloomington. The study area included the area surrounding the ABG, especially that to the south.

The report by Hunt (1988) concluded that flow through solution passages in the Beech Creek limestone is the primary conduit for groundwater leaving the ABG and that flow through the conduits can be "rapid." The report recommended that increased emphasis be given to monitoring of springs and that injection of tracers (i.e., dye tracer test) be considered to confirm direction and rate of movement away from the ABG through solution conduits. In 1989, WES installed five additional monitoring wells (July and August 1989) in the vicinity of the ABG.

The Federal portion of the RCRA Permit, dated December 10, 1989, established the HSWA Corrective Action Requirements and Compliance Schedules (RCRA Section 3004). The compliance schedules obligated NSWC Crane to perform RCRA Facility Investigations (RFIs) at 30 SWMUs, and, if contamination was found, to conduct Corrective Measures Studies (CMSs) and implement Corrective Measures, if needed. The Permit's RFI compliance schedule for the ABG established work plan submittals for the following: (a) Modified RFI Phase III Release Characterization for Groundwater; (b) RFI Phase III Release Characterization for Soil; and (c) RFI Phase II Release Assessment for Surface Water Bodies. In April 1990, NSWC Crane submitted the Modified RFI Phase III Release Characterization Work Plan for Groundwater. The Work Plan scheduled the submittal of the Dye Tracer Report, the proposal to conduct a second Dye Tracer Test, progress reports, and the RFI Phase III Final Report for Groundwater. The RCRA Section 3004 Corrective Action Requirements of the Storage Permit have incorporated the Installation Restoration Program (IRP). RCRA will be the primary vehicle to further investigate and remediate the IRP sites.

As a part of the water sampling and chemical analysis program initiated by NSWC Crane in 1987, laboratory analysis and laboratory QA and QC data have been reported to NSWC Crane in a series of reports. The information from these reports formed the basis of a summary report, dated April 1, 1992, and prepared under contract by COMARCO, ESD of Bloomfield, Indiana. The groundwater was tested for a wide range of chemical parameters at various limits during the program. These parameters are discussed in 40 CFR 265.92, 265.93, and 265.94 Appendix III.

Murphy (1994) provided additional analyses of the groundwater data pertaining to RDX, TCE, and barium in the final RFI Phase III Groundwater Report for the ABG. Murphy concluded that four monitoring well sites within the ABG were notably higher in RDX and/or TCE than other wells.

To investigate background conditions and to characterize the source(s) of contamination in the soils, an RFI Phase III Part 1 soils investigation was conducted by WES in 1990. Twelve auger borings were placed and soil samples were collected. Chemical analysis of the soil

samples indicated contamination by explosives and metals.

Murphy and Wade (1998) conducted a Phase II Surface Water Assessment at the ABG and submitted a Final report. The report concluded that explosives, metals, and other inorganics, and certain volatile and semivolatile compounds have been released to the water and bottom sediments of streams at and below the ABG.

In 1993, Albertson (1998) conducted an RFI Phase III Part 2 soils investigation. Thirty-three surface (grab) soil samples were collected and 32 soil borings were made to determine the extent of soil contaminants identified in the RFI Phase III Part 1 soils investigation. The soils analyses indicated that ABG waste disposal activities have contributed residues of explosives compound and metal contaminants to the soils. PAHs and VOAs were also released, but in concentrations that were generally below 1 mg/kg. The explosives HMX, RDX, TNB, TNT, 2,4-DNT, 2,6-DNT, 2A-DNT, and 4A-DNT were detected. Explosives with the highest concentrations were HMX, RDX, and TNT. Several metals and inorganic constituents in ABG soils had consistently higher concentrations than nearby background soils. In some cases the concentrations of metals and inorganics were 100 times the background which suggested the release of these constituents to ABG soils. Constituents that were greater than 100 times background included cadmium, calcium, copper, lead, zinc, and tin.

1. 3. 3. CURRENT STATUS

NSWC Crane conducted an ecological risk assessment for RCRA corrective action activities and to support the RCRA Subpart X permit. A bat survey along the streams near the areas of concern was included as part of the ecological risk assessment and compliance with the Endangered Species Act. On June 25, 1996, a single male Indiana bat (*Myotis sodalis*) was caught. The capture occurred south of the ABG on Little Sulphur Creek approximately in the SE corner of Section 28, T5N, R3W, as shown on Figures (2) and (3). Following the capture, NSWC Crane proposed to the U.S. Fish and Wildlife Service, during informal consultation, to conduct a survey, such as a blacklight survey, of the available prey in the area the bat was captured, in order to determine if contaminants are mobilizing through the bat's food chain.

1. 4. **PROJECT OBJECTIVES**

1. 4. 1. SPECIFIC OBJECTIVES AND ASSOCIATED TASKS

The ultimate goal of this project is to gather sufficient information to evaluate the potential for contamination to be present in the food chain of *M. Sodalis* and to determine whether ecological risks are associated with the levels of contaminants, if found. It may not be possible to accomplish this objective fully during this project phase, however, because of the limited amount of insect tissue already collected.

1.4.1.aPreliminary tasks associated with this project are:

1.4.1.a.1. Collect a limited sample volume (reflecting a possible food source of the endangered bat) that will allow some specific objectives to be accomplished in this phase as outlined in (1.4.1.b) below.

1.4.1.a.2. Determine from literature reviews, toxicity levels for each analyte listed in Table 2.

1.4.1.a.3. Establish analytical procedures for insect tissue capable of providing acceptable recoveries for the analytes listed in Table 2.

1.4.1.a.3.a. Refine existing explosives methods to allow compound identification in the absence of major intereferences.

1.4.1.a.3.b. Refine existing metals digestion procedures to reduce or eliminate the effects of interferences from the insect matrix during metals analysis.

1.4.1.a.3.c. For explosives and metals, demonstrate method sensitivities [method detection limits (MDLs)] for each analyte in Table 2 for the cricket matrix.

1.4.1.a.3.d. Determine the sample size needed to achieve MDLs sensitive enough to meet the analytical requirements of this phase and future project phases.

1.4.1.b. Specific objectives for the analysis of potentially impacted insects are highly dependent on the outcome of (1.4.1.a) above. However, the following objectives should be accomplished in this phase.

1.4.1.b.1. Insect samples have been preliminarily sorted into fractions of the collected sample that reflect aquatic and terrestrial exposure food sources prior to preparation for analysis. Depending upon the minimum amount of sample required for each group of analytes listed in Table 2, additional sorting or combining of sorted lots may be required.

1.4.1.b.2. Each of the Table 2 analytes should be reported with a sensitivity ranging down to levels regarded as toxicologically significant as determined in (1.4.1.a.2) above, if available.

1.4.1.b.3. The data package resulting from the analyses in this phase shall be sufficiently comprehensive in its documentation to demonstrate the reliability of the data. The items to be included in the data package originating from the analytical laboratory are listed in (9.3.2) below.

1.4.1.b.4. Due to the limited amount of sample already collected, it is recognized that some of the standard SW846 QC protocols may have to be modified. At a minimum, the accuracy (percent recovery) data for the Table 2 analytes must be of an accurate nature. Precision measures must be regarded as acceptable. If adequate sample is available duplicate analyses (field duplicates and MSDs) will be performed. If the amount of sample is limited, the laboratory control samples (LCS) will be duplicated instead. The targeted analytical program for explosives will include MS/MSD and field duplicate analysis. At a minimum it will include MS recoveries and LCS recoveries. The analytical program for metals will include MS/MSD if sample size permits.

1. 4. 2. PROJECT TARGET PARAMETERS AND INTENDED DATA USAGES

The list of target parameters for this project is included in Table 2. Intended data usages are to ultimately determine whether or not the bat is affected by Table 2 analytes. However, data

usages may be limited by factors determined above. The data shall be compared to literature values for metals as developed above or to ecological based levels for explosives, and to ecological risk based levels established as part of the overall risk assessment for the ABG. Results of this study will be used as described in Section 1.1.1.

1. 4. 2. 1. Field Parameters

No field measurements will be collected for this project.

1. 4. 2. 2. Laboratory Parameters

The target compounds for this project are presented in Table 2 along with LD50 data for oral dosages in rats for those compounds for which it is available. Similar toxicity information is available for metal salts but not for the elemental metals.

Table 2 – **Target Compounds**

EXPLOSIVES		INORGANICS	
	ORL-Rat LD50		ORL-Rat LD50
1.RDX	Low toxicity when digested or inhaled	1. cadmium	Not available
2. TNT	High toxicity when digested or inhaled	2. lead	Not available
3. HMX	1500 mg/kg (mouse)	3. zinc	Not available
4. 1,3-DNB	83 mg/kg	4. mercury	Not available
5. Tetryl	Moderately toxic when digested or inhaled	5. copper	Not available
6. NB	640 mg/kg	6. barium	Not available
7. TNB	450 mg/kg	7. silver	Not available
8. 4-ADNT	Not available	8. aluminum	Not available
9. 2-ADNT	Not available	9. antimony	Not available
10. 2,6-DNT	177 mg/kg	10. arsenic	Not available
11. 2,4-DNT	268 mg/kg	11. chromium	Not available
12. 2-NT	891 mg/kg	12. manganese	Not available
13. 3-NT	1072 mg/kg	13. magnesium	Not available
14. 4-NT	1960 mg/kg	14. nickel	Not available
15. Azoxytoluene	Not available		
16. MNX	Not available		
17. TNX	Not available		

Analyte selection is based on previous investigations, as discussed in §1.3.2. The RFI ground water, surface water, sediment and soils reports were reviewed for contaminants of significance. This information was compared to the contaminants of potential ecological concern (COPEC) listed in the Current Contamination Conditions Risk Assessment (Tetra Tech NUS, 1999). The order of listing of the inorganic constituents in Table 2 is based upon

RFI multimedia prevalence, listing as a COPEC, and COPEC media prevalence. For example, cadmium was identified as a contaminant in all RFIs for all media, and was listed as a COPEC for all media. Whereas, nickel was identified as a contaminant in the two soil RFIs and the sediment RFI but was not listed as a COPEC. The second phase of this project may not contain enough sample volume to analyze for all of the inorganic constituents. As such, analysis will proceed in the order the compounds are listed as sample size allows. In addition to the above constituents, phosphorus will be analyzed in the first phase insect study as well as for one sample of insects during the second phase.

1. 4. 3. DATA QUALITY OBJECTIVES

Single operator precision and accuracy for the analytical methods selected will be demonstrated in the first phase of this project. Sensitivity will also be determined during the first phase.

The primary objective of this project is to obtain sufficient data of known quality to determine whether contaminants at the Ammunition Burning Ground are present (and if so, at what concentration) in food sources for the Indiana Bat. Table 3 compares the lower reporting limits (LRL) of explosives in an insect matrix to the known oral LD50 determined in rats. It also compares the method detection limits (MDL) of metals from the ICP-MS to the target detection limits obtained from the Fish and Wildlife.

Table 3 – Estimated reporting limits compared to known ORL-Rat LD50s or target MDLs					
EXPLOSIVES			INORGANICS		
Analyte	LRL(mg/kg)	LD50(mg/kg)	Analyte	MDL (mg/kg)	Target MDL (mg/kg)
HMX	3.2	1500	Silver	0.026	
RDX	0.8		Aluminum	0.078	5
TNB	1.2	450	Arsenic	0.073	0.5
1,3-DNB	1.0	83	Barium	0.009	1
Tetryl			Cadmium	0.005	0.1
NB	1.7	640	Chromium	0.065	0.5
TNT	1.3		Copper	0.05	0.5
4-ADNT	2.5		Magnesium	0.13	5
2-ADNT	1.2		Manganese	0.01	1
2,4-DNT	0.7	268	Nickel	0.032	0.5
2,6-DNT	1.3	177	Lead	0.007	0.5
2-NT	1.9	891	Antimony	0.014	
3-NT	1.6	1072	Zinc	0.19	1
4-NT	2.1	1960	Mercury	0.20	0.20
MNX					
TNX					
Azoxytoluene					

1. 5. SAMPLING LOCATION

The principle location for insect collection is shown on Figure (3). This is the same location as the previous capture of the Indiana Bat. Additional locations - in future phases, if needed - may be used in the vicinity, based on design of the sampling equipment, vegetation growth, etc. All sampling occurred at or near the Indiana Bat capture site along Little Sulphur Creek. It is assumed that the bat was foraging along Little Sulphur Creek at the time of the capture. Therefore, the intent of the sampling was to collect insects within the bats forage locale.

1. 6. PROJECT SCHEDULE

1. 6. 1. SAMPLE COLLECTION DATES

See the FSP provided in Appendix A.

1. 6. 2. ANTICIPATED ANALYTICAL TIMEFRAMES

Samples were submitted to WES for sorting in September 1997. The phase I study was completed December 1997. Following sorting and completion of phase I, the samples will be turned over to the analytical laboratory for analyses. Analyses will begin following QAPP approval with an analytical data package to follow.

1. 7. SORTING

For a discussion of sorting issues, refer to the FSP (Appendix A).

2. PROJECT ORGANIZATION AND RESPONSIBILITY

NSWC Crane has overall responsibility for all phases of this study. Personnel from WES provide field and analytical assistance. A WES entomologist supervised initial setup of the insect traps at the ABG, and WES is providing sampling and analysis support. Responsible personnel and their functions are shown in Table 4.

Table 4 - **Project Responsibilities**

Project Member	Function
Thomas J. Brent NSWC Crane Installation Restoration Project Manager	Overall project coordination, including scheduling, assistance in sample collection, and report writing. Assists in the development of the QA plans.
Karen Myers WES Chemist	Receives, stores, analyzes, and disposes of samples. Assists in the development of the QA plans. Also documents analytical methods used and reports analytical results.
Dr. Al Cofrancesco WES Entomologist	Established field collection, sorting, preservation, and shipping procedures, as well as report writing.
Allen Debus U.S. EPA Quality Assurance Expert	Review and approve the QAPP and overall support throughout the project. May also conduct audits of the WES laboratory as well as review analytical procedures.
Carol Witt-Smith U.S. EPA RCRA Corrective Action Expert	Overview of all site activities to ensure regulatory compliance. Reviews and approves all phases of the project.
Scott Pruitt USFWS Biologist	Overview of site activities to ensure compliance with the Endangered Species Act.

The laboratory chemist will have overall responsibility for ensuring analytical quality assurance. This responsibility includes, but is not limited to, receipt and inspection of the incoming sample containers, controlling and monitoring access and storage of samples and extracts, coordinate laboratory analyses, monitoring analytical and project QA requirements, conduct detailed review and verification of analytical data in reports prior to submission to NSWC Crane.

3. QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

The primary objective for this project is to gather sufficient defensible information to evaluate the potential for contamination to be present in the food chain of *M. Sodalis*. This will be accomplished by implementing field sampling, chain-of-custody, laboratory analysis, and reporting procedures that include adequate quality assurance/quality control to assure that the data are of known and verifiable quality. Specific procedures for sampling, chain-of-custody, laboratory instrument calibration, reporting of data, internal quality control, audits, preventive maintenance of field equipment, and corrective action are described in Appendix B of this QAPP. Because of the unique nature of the biological matrix, laboratory preparatory and determinative SOPs have been evaluated and modified for this project. Specific procedures for laboratory analysis have been determined from the cricket study and are included in Appendix B of this QAPP.

3. 1. Precision

Precision examines the distribution of the reported values about their mean, and is determined through duplicate measurements. Precision may be affected by the natural variation of the matrix or contamination within the matrix, as well as by errors made in field and/or laboratory handling or homogenization procedures. To minimize precision errors, preparatory methods will include adequate homogenization procedures.

Precision in the field is assessed through the collection and measurement of field duplicates. The preferred rate of field duplication is 1 duplicate in 10 samples. However, based upon the finite size of the sample collected and the possibility that the amount of sample required for analytical analysis may be large, true field duplication may not be possible.

Precision in the laboratory is assessed through the calculation of relative percent differences (RPD). For this project, due to finite sample amounts, MSDs will be substituted for matrix duplicates. If sample amount is insufficient for spike duplication, an LCS duplicate will be substituted.

Precision of duplicate samples is calculated using the equation below:

Relative percent difference:

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

where: S_1 and S_2 represent sample and duplicate sample results or MS/MSD results.

Precision measurements for this study must be regarded as acceptable. The default control limits given in Table 3 will be utilized for this study.

3. 2. Accuracy

Accuracy measures the bias in a measurement system. Accuracy may be difficult to measure for the entire data collection activity. Sources of error are the sampling process, field contamination, preservation, handling, sample matrix, sample preparation, and analysis techniques.

Laboratory analytical accuracy is assessed through the analysis of known QC samples such as LCS and external reference materials and through the analysis spiked samples such as MS and surrogate spikes. Accuracy is determined by calculating percent recoveries using the equations given below.

For LCS and surrogate spikes:

$$\% \text{ Recovery} = \frac{A}{B} \times 100$$

where: A = concentration of analyte measured
B = known true value

For MS/MSDs:

$$\% \text{ Recovery} = \frac{\{(\text{Sample} + \text{Spike Result}) - \text{Sample Result}\}}{\text{Spike Added}}$$

Accuracy control limits for LCS and surrogate spikes are given in the SOPs found in Appendix B. Although accuracy control limits are unavailable for insect matrices, analysis of MSs will serve as an indicator for any unexpected matrix effects. The default control limits given in Table 3 will be utilized for this study.

3. 3. Completeness

Laboratory completeness is a measure of the amount of valid measurements obtained from all the measurements taken in the project. For this project, the number of measurements to be made will depend upon the actual sample mass obtained after sorting (total, by month or by order) and upon the sample size required for each suite of analyses (determined from the cricket study). Laboratory completeness for this project will be greater than 95 percent. Following completion of analytical testing, the percent completeness will be calculated by the following equation:

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

3. 4. Representativeness

Representativeness expresses the degree to which sample data accurately and precisely represent the characteristics of a population of samples. Representativeness is a qualitative parameter that is most concerned with the proper design of the sampling program or subsampling of a given sample. Employing appropriate sampling strategies and techniques best satisfies the representativeness criterion.

Following the criteria set forth in the FSP ensures representativeness for this project. The sampling network was designed to provide data representative of facility conditions. During development of this network, consideration was given to habitat, foraging habits, and existing analytical data. The rationale of the sampling network is discussed in the detail in the FSP (Appendix A).

Representativeness in the laboratory is ensured by using the proper analytical procedures and meeting sample holding times. Representativeness is enhanced by making certain that all subsamples taken from a given sample are representative of the entire sample. To this end, special emphasis will be placed on initial homogenization of the sample before it is split for further processing.

3. 5. Method Detection Limits

Analytical reporting limits for the parameters targeted in this project must be lower than the target detection limits supplied by the Fish and Wildlife Service for metals and lower than the ORL-Rat LD50 for explosives (Table 3). Method detection limits are determined according to 40CFR, Appendix B to Part 136-Definition and Procedure for the Determination of the Method Detection Limit-Revision 1.11. The laboratory SOP for MDL determinations is found in Appendix C. The cricket, *Acheta domestica*, was used as a surrogate for the MDL study for explosives. As stated in the laboratory SOP, all metal MDLs are calculated from water spikes. Conversion into mass units is based upon the digestion weights and volumes. Reporting limits are calculated from the MDL values and are at or near the low standard.

3. 6. Level of Quality Control Effort

Method blank, duplicate, and spiked samples will be analyzed to assess the quality of the data resulting from the field sampling and analytical programs. Method blank samples are generated within the laboratory and used to assess contamination resulting from laboratory procedures. Duplicate samples are analyzed to check for sampling and analytical reproducibility. Duplicate samples may include field duplicates, MS/MSD or LCS/LCSD. Matrix spikes will be performed in duplicate where possible with one MS/MSD set collected for every 20 or fewer field samples. Field duplicates will be collected and analyzed where sample size permits (see section 3.1).

4. SAMPLING PROCEDURES

The insect trapping procedures are described in Appendix A. Trapping occurred three times during the summer season (June, July, and August) in order to capture insects with different emergent periods. Samples were frozen for preservation, packaged in coolers, and shipped to WES on September 16, 1997. The FSP (Appendix A) outlines all the sampling procedure information. No further sample collection is currently planned. Additional sampling will be preceded by a new sampling plan.

5. CUSTODY PROCEDURES

Records generated as a result of analytical sampling activities are quality records and will be processed in accordance with the requirements of this QAPP. Sampling and analytical documents are essential for ensuring the integrity and defensibility of data used to make decisions in determining impact upon the endangered species. Sample custody is addressed in three parts: field sample collection, laboratory analysis, and final evidence files. Evidence files include all originals of field notes, sorting logs, laboratory reports, notebooks, custody records and narratives. These original documents will be maintained under document control in a secure are or in the possession of the project member responsible for that phase of the project. Copies of the evidence files will be included in the final data submittals to the Navy.

5. 1. Field Sample Collection Documentation

The following information was recorded on the sampling record at the time of sampling:

- Trap type
- Trap site
- Sample date
- Time of trapping
- General observations (e.g., weather, status of lights in a.m., anesthetic used, etc.)

Copies of the sampling records are provided in Appendix A.

5. 2. Chain-of-Custody Documents

Samples are considered to be under a person's custody if:

- the item is in actual possession of a person; or
- the item is in the view of the person after being in actual possession of the person; or
- the item was in actual physical possession but is locked up to prevent tampering; or
- the item is in a designated and identified secure area.

Each sample was assigned a unique identification number and that number was entered on the chain-of-custody form. The chain-of-custody form includes the following information.

- Sample identification number
- Sample date
- Analysis required
- Sampler's name
- Release and acceptance information including date, location, and technician's signature.

Custody was relinquished from the site by using the signature blocks at the bottom of the custody form. The original chain-of-custody record accompanied the shipment to WES by a commercial carrier. The original chain-of -custody record and the commercial carrier waybill were kept as part of the project record files.

Upon receipt at WES, all samples proceeded through an orderly processing sequence specifically designed to ensure continuous integrity of both the sample and other information pertinent to the analysis. All samples were checked and verified for proper chain-of-custody records, preservation, leaking sample containers, proper label identification, and any associated discrepancies.

No discrepancies were identified and the sample chain-of-custody record was signed. After sorting the samples will be assigned unique identification numbers to reflect the sorting scheme, new chain-of-custody documents will be initiated if needed to reflect any changes in the numbering system before the samples are delivered to the analytical laboratory for preparation and analysis.

5. 3. Laboratory Sample Custody

When the samples are received in the laboratory, custody will be transferred to the chain-of-custody officer and a unique laboratory identification number will be assigned for tracking and filing purposes. Receipt of samples will be noted in a bound chain-of-custody log. The samples will be placed in a secured freezer or refrigerator until required for preparation or analysis, respectively. Custody will be transferred to the analysts as needed. Each transfer will be recorded sequentially in a bound log book. 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.

6. CALIBRATION PROCEDURES AND FREQUENCY

6. 1. Field Instrument Calibration

Not applicable

6. 2. Laboratory Instrument Calibration

Calibration of instruments is required to ensure that the analytical system is operating correctly and functioning at the proper sensitivity to meet the project-specific quantitation limits that will be determined upon the completion of the cricket study under way at WES. Instruments utilized for this study will be calibrated daily or prior to analysis. A detailed description of the calibration process is presented in the analytical SOPs found in Appendix B.

Explosives analysis will be performed by reversed phase high performance liquid chromatography (RPHPLC) following SOP number M-8330-00-WES-XX dated January 31, 1996. This SOP is based upon USEPA SW- 486 Method 8330, 1994. Primary source standards are prepared from neat crystalline stock explosives standards obtained from the Army Environmental Center at Aberdeen Proving Ground, MD. These standards are used to prepare the initial 5 point calibration curve, continuing calibration verification standard, surrogates, laboratory control sample and MSs. Secondary source stock standards are purchased as certified solutions for use as the initial calibration verification standard. Standards preparation is discussed in Section 7 of the SOP. Modifications to this SOP for this project are included with the SOP in Appendix B.

Metals analysis will be performed by either inductively coupled plasma - mass spectrometry (ICP/MS) following USEPA SW- 846 Method 6020, 1994 or by inductively coupled plasma - atomic emission spectroscopy (ICP) following SOP number M-6010-00-WES-XX dated January 31, 1996. This SOP is based upon USEPA SW- 486 Method 6010A, 1992. Primary source standards are prepared from both single and multi-element standards purchased from Alfa Aesar and SPEX Chemical. Initial calibration verification standards are prepared from second source stocks purchased specifically for that purpose. Certificates of analysis accompanying the purchased solutions state that concentrations are checked against NIST standard reference materials. Standards preparation is discussed in Section 7 of the SOP. Modifications to this SOP for this project are included with the SOP in Appendix B.

Mercury analysis will be performed by manual cold vapor with fluorescence detection following SOP number M-7471A-00-WES-XX. Standards preparation is discussed in Section 7 of the SOP. Primary and second source standards are purchased from SPEX Chemical. Certificates of analysis accompanying the purchased solutions state that concentrations are checked against NIST standard reference materials. Modifications to this SOP for this project are included with the SOP in Appendix B.

In all cases, analysts maintain logbooks identifying the calibration standards and date of calibration associated with each sample set analyzed on individual instruments.

7. ANALYTICAL PROCEDURES

7. 1. Field Analytical Procedures

Not applicable

7. 2. Laboratory Analytical Procedures

All analyses will be conducted by the USACE Waterways Experiment Station Environmental Chemistry Branch (ECB), 3909 Halls Ferry Road, Vicksburg, Mississippi, 39180. The laboratory director is Ann B. Strong, telephone - 601-634-2726. The sample custodian and chain-of-custody officer is Linda K. Stevenson, telephone - 601-634-3625.

A study was undertaken utilizing crickets (*Acheta domestica*) to determine the correct methods for sample preparation and extraction/digestion of both explosives and metals and to identify any modifications necessary to eliminate or minimize the effects of interferences extracted from the biological matrix. Because the sample size is finite and the amount of sample needed to obtain low detection limits is expected to be large, a method validation study cannot be performed on the actual sample matrix. The cricket, *Acheta domestica*, will be used as a surrogate for method validation. A single operator precision and accuracy study will be performed before the actual analysis is performed.

Table 5 lists the laboratory SOP numbers of the methods selected, their corresponding EPA reference method and the default target control limits for precision and accuracy for each of the analyte groups targeted for this project. As stated in Section 6, modifications to the SOPs are included in Appendix B.

Table 5 - **Analytical methods and data quality objectives.**

Analyte Group[1]	Laboratory SOP Number	Equivalent EPA Method Number[2]	Precision (RPD)	Accuracy (%R)
Explosives	M-8330-00-WES-XX	8330	35	75 - 125
Mercury	M-7471-00-WES-XX	7471	35	75 - 125
Metals digestion-microwave	M-3051-00-WES-XX	3051		
ICP/MS metals analysis (option 1)	in preparation	6020	35	75 - 125
ICP metals analysis (option 2)	M-6010-00-WES-XX	6010A	35	75 - 125

[1] See Table 2 for specific analytes within each group.
[2] SW-846

8. INTERNAL QUALITY CONTROL CHECKS

8. 1. Field Quality Control Checks

Because the insect samples have already been collected, it is not possible to identify and analyze a true field duplicate sample. If sufficient sample is available, a sample will be split and analyzed as a field duplicate.

8. 2. Laboratory Quality Control Checks

The ECB has a QC program in place to ensure the reliability and validity of the analysis performed in the laboratory. Analytical procedures are documented in SOPs, each of which includes a QC section that addresses the minimum QC requirements for the procedure. The internal quality control checks to be used in this investigation are listed in Table 6 below.

Table 6 – **Quality Control Checks**

QC Check	Explosives	Metals
Field Duplicate	?	?
Method Blank	X	X
Matrix Duplicate		X[1]
MS	X[1]	X[1]
MSD	X[1]	X[1]
LCS	X	X
LSD	X[2]	X[2]
Surrogate Spike	X	
Standard Reference Material		X

? Addition of this sample will depend upon the amount of sample available for analysis.
[1] Ability to prepare this control check depends upon amount of sample available and sample size. QC samples will be prepared and analyzed at a rate of 5%.
[2] The laboratory control sample will be duplicated only if there is insufficient sample to prepare a MSD.

The ECB will report the results of the QC samples with the analytical data for field samples. The data package will include a full deliverable package (without forms) capable of allowing the recipient to reconstruct QC information and compare it to QC criteria.

9. DATA REDUCTION, VALIDATION, AND REPORTING

9. 1. Data Reduction

9. 1. 1. Field data reduction procedures

Notebooks and chain-of-custody forms will be kept for all field activities.

9. 1. 2. Laboratory data reduction procedures

9. 1. 2. 1. Insect Sorting Procedures

Notebooks and chain-of-custody forms will be kept for the sorting process.

9. 1. 2. 2. Laboratory Analytical Procedures

All raw analytical data pertaining to sample and batch preparation will be recorded in numerically identified laboratory notebooks. Pertinent information recorded in these notebooks includes the laboratory sample identification number, the analytical method used, the data of preparation/analysis, the matrix sampled, solvents and lot numbers used, QC samples included in the batch, concentrations of spikes, and the name of the analyst.

For this project, the equations that will be employed in reducing the raw data into concentrations of mass of analyte per unit mass of sample are presented in Section 9 of the appropriate SOP.

9. 1. 2. 2. 1. For metals and explosives, the concentration of elements in solid matrices is reported in mg/kg (dry basis) of analyte and is calculated as follows:

$$\text{mg/kg analyte in sample} = \frac{A \times V}{W}$$

where: A = final concentration read from calibration curve in mg/L
V = final volume of processed sample (mL)
W = weight of sample digested (g)

where: W = (wet weight of sample) x (% solids / 100)

9. 1. 2. 2. 2. For mercury, the concentration is reported in mg/kg on a dry weight basis and is calculated as follows:

$$\text{mg/kg analyte in sample} = \underline{A}$$

W

where: A = μg mercury read from standard curve
W = weight of sample digested (g)

where: W = (wet weight of sample) x (% solids / 100)

9. 1. 2. 2. 3. Percent recovery:

For LCS, recovery is calculated using:

$$\% \text{ Recovery} = \frac{A}{B} \times 100$$

where: A = concentration of analyte measured
B = known true value

For MS/MSDs, recovery is calculated using:

$$\% \text{ Recovery} = \frac{\{(\text{Sample} + \text{Spike Result}) - \text{Sample Result}\}}{\text{Spike Added}}$$

9. 1. 2. 2. 4. Relative percent difference

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

where: S_1 and S_2 represent sample and duplicate sample results, or MS/MSD results.

9. 2. Data Review/Validation

9. 2. 1. Procedures Used to Evaluate Field Data

The project manager will keep field notebooks, data sheets and chain-of-custody forms for each sampling event. All field notes will be checked for accuracy, legibility and completeness.

9. 2. 2. Procedures to Review Laboratory Data

9. 2. 2. 1. Insect Sorting Procedures

Notebooks and chain-of-custody forms will be kept for the sorting process. All notes will be checked for accuracy, legibility and completeness.

9. 2. 2. 2. Laboratory Analytical Procedures

All analytical data generated by the ECB will be reviewed prior to report generation to assure the validity of the reported data. This data review process consists of a technical data review by the analyst to ensure: that sample preparation information is correct and complete; that analysis information is correct and complete; that the appropriate SOPs have been followed; that the analytical results are correct and complete; that QC samples are within established limits; and that documentation is complete. This data review will be documented by using a checklist form with a signature and data entered by the reviewer. After the data package is complete, it undergoes an administrative review performed by either the quality assurance officer or the program administrator.

9. 2. 3. Procedures to Validate Laboratory Data

An independent validation of the data will be required of the final data package. A contractor independent of the laboratory generating the data will perform this validation. All procedures will follow appropriate EPA Functional Guidelines for Data Validation based upon project objectives.

9. 3. **Data Reporting**

9. 3. 1. Field Data Reporting

Copies of all field records will be included in the files maintained by the Navy.

9. 3. 2. Laboratory Data Reporting

The final data package will be delivered to the Navy 60 days after analysis begins. The data package will include a full deliverable package (excluding forms) capable of allowing the validation process to be accomplished. The report package will consist of the record of chain-of-custody, a case narrative, and the chemical data package.

The narrative will contain the following information:

- Date of issuance
- Project name
- Condition of samples as received
- Laboratory analysis performed
- Any deviation from intended analytical strategy
- Number of samples and respective matrices
- Quality control procedures utilized and also references to the acceptance criteria (note that standard laboratory criteria may have to be suspended based upon interferences caused by the matrix)
- Discussion of technical problems or other observations which may have created analytical difficulties
- Discussion of any laboratory quality control checks which failed to meet project criteria

(note that standard laboratory criteria may have to be suspended based upon interferences caused by the matrix)
- Signature of the laboratory director

The chemical data package will consist of:
- Case narrative for each sample delivery group
- Summary page indicating dates of analyses for samples and laboratory quality control checks
- Cross-referencing of laboratory sample to project sample identification numbers
- Data qualifiers to be used should be adequately described
- Copies of sample preparation and analyses logbooks and bench sheets
- Sample results
- Raw data for sample results and laboratory quality control samples
- Matrix spike and MSD recoveries (or LCS and LCSD if insufficient sample for MSD), method blank results, calibration check compounds, and system performance check compounds
- Labeled and dated chromatograms/spectra of sample results and laboratory quality control checks

10. REFERENCES

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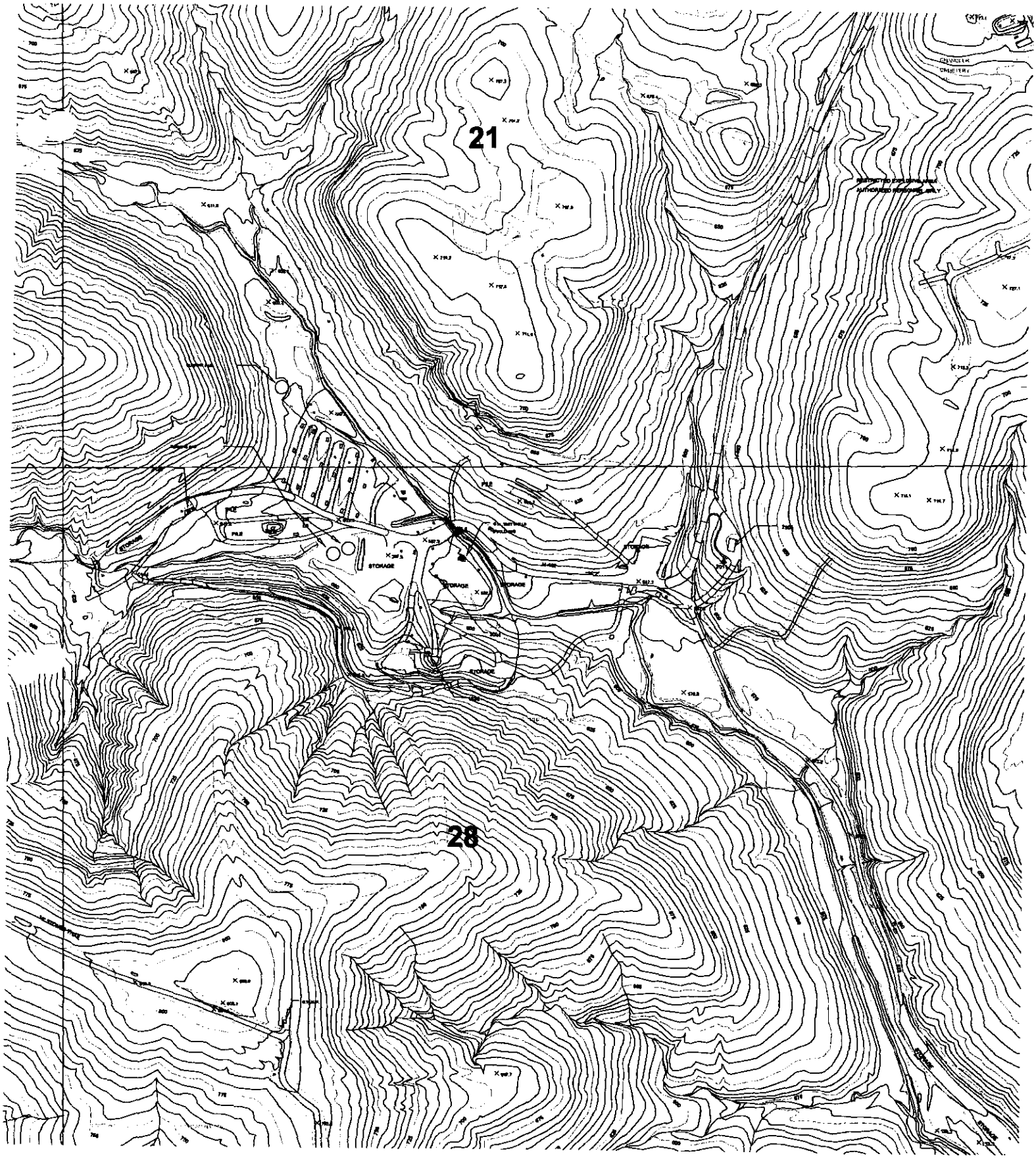
Tetra Tech NUS, 1999. Current Contamination Conditions Risk Assessment

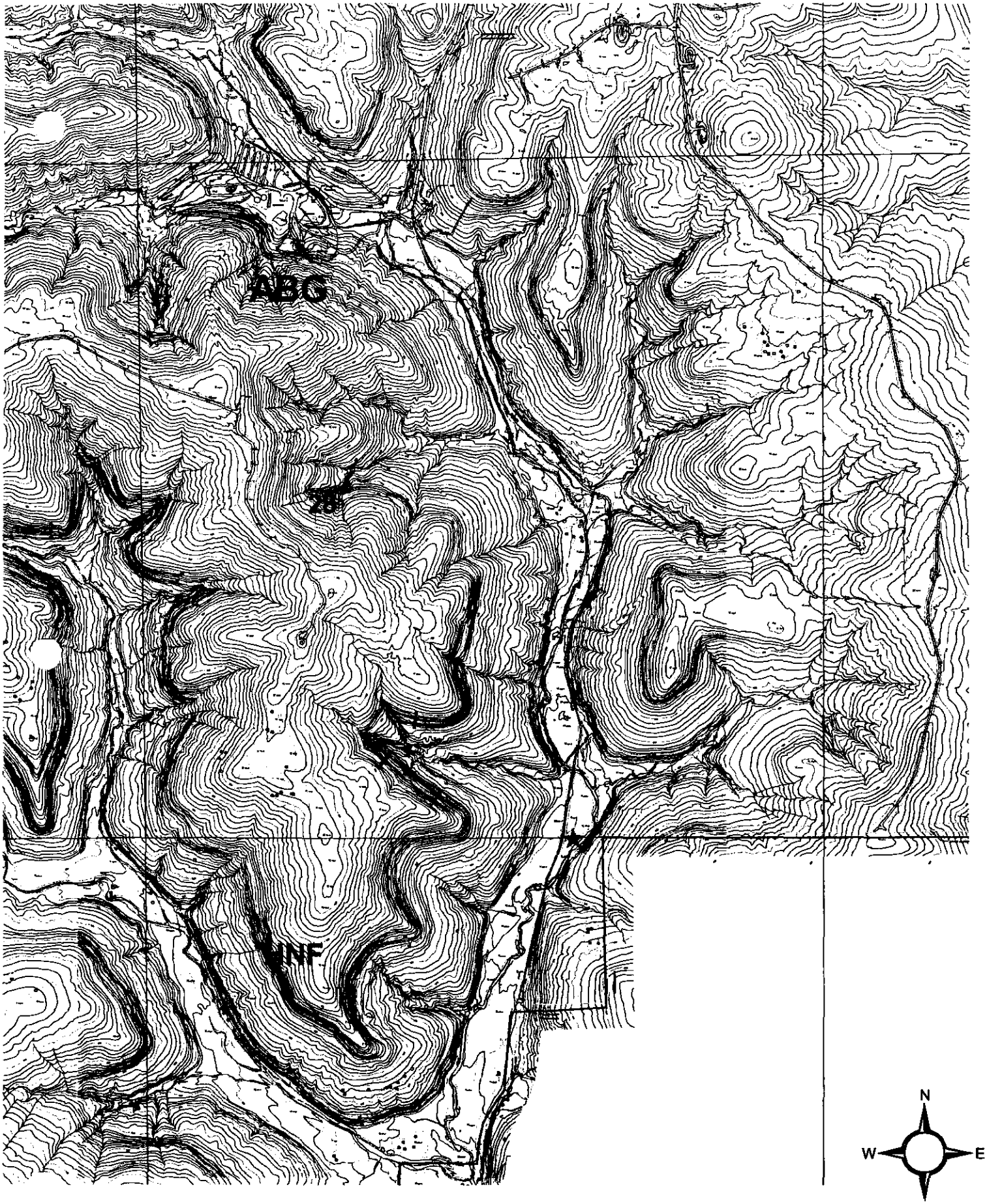


Ammunition Burning Grounds (ABG)

400 0 400 800 1200 Feet

N
W E
S

Figure (1)



★ Approximate location of M. sodalis

400 0 400 800 1200 Feet

Figure (2)

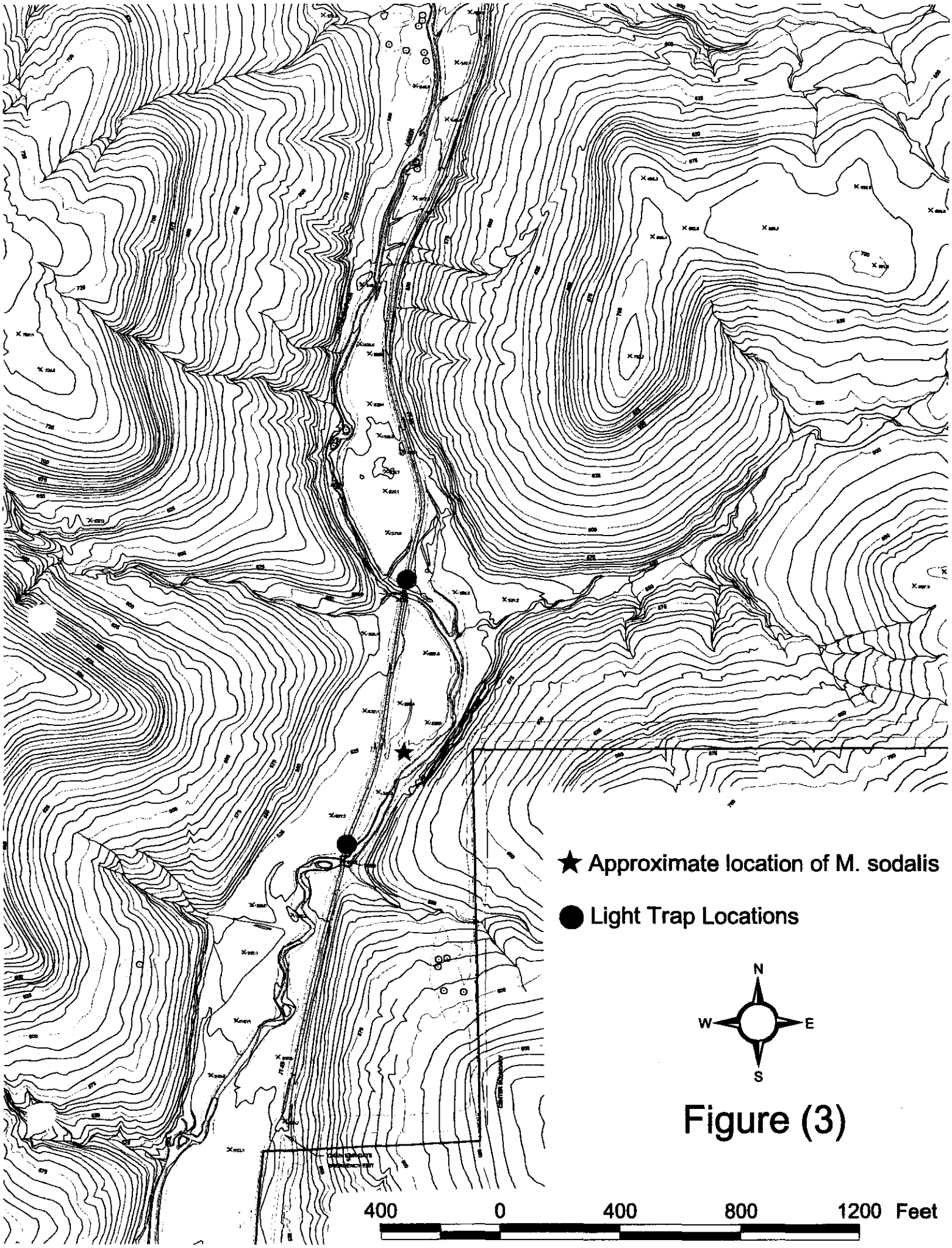

★ Approximate location of M. sodalis
● Light Trap Locations
N
W
E
S
400
0
400
800
1200 Feet

Figure (3)

APPENDIX A

FIELD SAMPLING PLAN

FIELD SAMPLING PLAN
FOR
INSECT COLLECTION AT THE
AMMUNITION BURNING GROUNDS
CRANE DIVISION, NAVAL SURFACE WARFARE CENTER

BACKGROUND

Crane Division, Naval Surface Warfare Center (NSWC Crane) is conducting an ecological risk assessment for Resource Conservation Recovery Act (RCRA) corrective action activities and to support a RCRA Subpart X (open burning-open detonation) permit. A bat survey along the streams near the areas of concern was included as part of the ecological risk assessment. On June 25, 1996, a single male Indiana bat (*Myotis sodalis*) was caught. The capture occurred south of the Ammunition Burning Grounds (ABG) on Little Sulphur Creek approximately in the SE corner of Section 28, T5N, R3W.

On June 28, 1996, Thomas J. Brent from NSWC Crane and Carol Witt-Smith of the U.S. EPA met with representatives from the U.S. Fish and Wildlife Service (USFWS) to discuss follow-up actions. NSWC Crane is in the process of determining if operations at the ABG are impacting *M. Sodalis*. Thus, NSWC Crane proposed to conduct a survey, such as a blacklight survey, of the available prey in the area the bat was captured, in order to determine if contaminants are mobilizing through the bat's food chain.

FIELD COLLECTION

NSWC Crane has contacted the U.S. Army Corps of Engineers, Waterways Experiment Station (WES) to assist in the project. Dr. Al Cofrancesco is a research entomologist who provided support in field collection and identification. Ms. Karen Myers will lead the analytical work.

Two types of traps were used for field collection. The first collecting apparatus was a large light trap that utilizes both black lights and a mercury vapor lamp. This trap attracts flying insects from a long distance. The different light sources give a wide spectrum of light stimulus that attracts the insects. The trap contained three large drawers. The bottom drawer contained a metal pan. Inside the pan, sheets of cotton were placed and then approximately 800 ml of ethyl acetate was poured over the cotton. The chemical would evaporate up through the two upper drawers and funnel area where the insects land. After breathing the chemical the insects would fall through the collecting funnel and into the top drawer. This drawer was composed of large mesh screen and the smaller insects dropped through to the second drawer. Two of these light traps were situated on the Jeep Trail below the ABG, one each at Bridges 3089 and 3090. Due to the remote location, the lights received power from gas-powered generators. The generators were fitted with an external gas supply to provide continuous fuel

through the night. The generators were placed on gravel to ensure that hot exhausts would not create a fire hazard for dry vegetation. Typically, the traps were setup at dusk and taken down and emptied around 8:00 a.m. Both generators and all lights were confirmed operable in the evening when started and morning when stopped.

Since light traps bias collection for light-attracted insects, a Malaise trap was also used. This type of trap consists of insect netting designed in a configuration to funnel flying insects into the collecting container. The Malaise trap was set up at dusk so as to not collect insects that fly only during daylight hours. The collecting container was operated dry at first, then later with a small amount of water.

All three traps were operated for three nights in each of the months of June, July, and August. The exceptions are the Malaise trap, which did not arrive on site until early July, and only two nights of trapping in June for the light traps (late start and technical difficulties). Therefore, 22 trap nights were conducted. This sampling strategy allowed for collecting insects with differing emergences, and provided for optimum sample volume. Following collection, all insects from one trap were placed into a container and frozen. For example, three nights of collection in July produced nine containers -- six from the two light traps and three from the Malaise trap. After sample numbers were applied and chain-of custodies completed, the samples were sent to Dr. Cofrancesco at WES for sorting and identification. Sorting will determine the differences between the collection devices, particularly the Malaise versus the light traps. No difference is anticipated between the light traps. However, since they tend to collect a larger volume of insects, samples from each light trap will be containerized separately.

SORTING

The entomologist began sorting the insects at WES in November 1997. In order to ensure continued preservation during the sorting process, only one container of insects was removed from the freezer at a time. Upon removal from the freezer, a timer was set for 10 minutes and at the end of that time, the insects were returned to the freezer and another container was pulled for sorting.

The entomologist is sorting the insects to order, by trap, by night, by aquatic versus terrestrial. Each container (except for the Malaise trap) represents one night from one trap. Thus, each container will be subdivided into orders and aquatic versus terrestrial. Sorting is expected to be completed by the end of December.

All of the sorted fractions will be weighed and turned over to the chemist. The chemist will determine the mass of sample necessary to obtain the analytical detection limits. In order to achieve appropriately low detection limits, it is likely that the analytical procedure will dictate a large sample size, thus requiring a recombination of some of the sorted fractions. Once the chemist receives and evaluates the status of the sorted samples, a conference call will be held with the WES chemist, the Navy, and the U.S. EPA to agree on the amount of sample pooling.

Note that, determining the capture differences between the two trap types (Malaise versus light) and the location of the traps (one bridge versus another - approximately 1000 feet apart) is mostly academic. The bat essentially does not care whether or not the insects are light attracted and captured, or near one bridge versus another, as long as all the traps collect insects representative of the bat's diet. As such, there is a lot of flexibility in determining the appropriate level of sorting. Minimizing the total number of samples for analysis is especially important since the project has a very limited budget.

INDIANA BAT FOOD CHAIN STUDY
SAMPLE LOG

Department of the Navy
Naval Surface Warfare Center
Crane, IN 47522

TRAP TYPE	TRAP SITE
LIGHT	BRIDGE 3089
SAMPLE DATE	**TIME OF TRAPPING**
6/18 - 6/19/97	2040 - 0815

OBSERVATIONS

Full moon. Partly cloudy.
all lights on p.m. & a.m.
800 - 1000 ml ethyl acetate used per trap. Cotton soaked in e.a. placed in collection container in a.m.

SAMPLE DATE	TIME OF TRAPPING
6/19 - 6/20/97	2100 - 0800

OBSERVATIONS

Full moon Clear to Partly cloudy.
all lights on p.m. & a.m.
800 ml. ethyl acetate used per trap. None in a.m.

SAMPLE DATE	TIME OF TRAPPING
7/15 - 7/16/97	2030 - 0730

OBSERVATIONS

2/3 moon. Clear.
no luna moths. ≈ 3-4 large greenish black beetles in each trap.
Traps not emptied until ≈ 1230. 1000 ml e.a. used per trap.
Cotton soaked in e.a. placed in collection bottles in a.m.

SAMPLE NUMBER	NUMBER OF CONTAINERS

SAMPLER'S SIGNATURE	CODE

DATE SAMPLES SENT	ANALYTICAL LAB

INDIANA BAT FOOD CHAIN STUDY
SAMPLE LOG

Department of the Navy
Naval Surface Warfare Center
Crane, IN 47522

TRAP TYPE	TRAP SITE
MALAISE	West side of JT. 25 between 3087 & 3090
SAMPLE DATE	**TIME OF TRAPPING**
7/15 - 7/16/97	2030 - 1230

OBSERVATIONS

Imp soil mp. Cotton soaked in ethyl acetate placed in collection head. Ethyl acetate ate through some of the plastic, and the adhesive joining parts of the head. Small amt. of insects.

SAMPLE DATE	TIME OF TRAPPING
7/16 - 7/17	2015 - 0745

OBSERVATIONS

Water used in lepan head. Seemed to be leaking. Small amt. of water left in c.m. Placed trap in freezer to kill the insects.

SAMPLE DATE	TIME OF TRAPPING

OBSERVATIONS

SAMPLE NUMBER	NUMBER OF CONTAINERS

SAMPLER'S SIGNATURE	CODE

DATE SAMPLES SENT	ANALYTICAL LAB

INDIANA BAT FOOD CHAIN STUDY
SAMPLE LOG

Department of the Navy
Naval Surface Warfare Center
Crane, IN 47522

TRAP TYPE	TRAP SITE
Light	3089 & 3090
SAMPLE DATE	**TIME OF TRAPPING**
7/16 - 7/17	2015 - 0745

OBSERVATIONS

Temp. 65-70°F Clear, 3/4 moon. 1000 ml e.g. ea trap.
~~[illegible]~~ e.g. used in collection bottles in a.m.

SAMPLE DATE	TIME OF TRAPPING
7/17 - 7/18	[illegible]00 - 0800

OBSERVATIONS

Nearly full-moon. Temp.: ~~[illegible]~~ upper 60s. 1000 mg e.g. ea trap.
e.g. used in collection bottles in a.m.

SAMPLE DATE	TIME OF TRAPPING

OBSERVATIONS

SAMPLE NUMBER	NUMBER OF CONTAINERS

SAMPLER'S SIGNATURE	CODE

DATE SAMPLES SENT	ANALYTICAL LAB

INDIANA BAT FOOD CHAIN STUDY
SAMPLE LOG

Department of the Navy
Naval Surface Warfare Center
Crane, IN 47522

TRAP TYPE	TRAP SITE
Light(s)	Bridges 3089 & 3090
SAMPLE DATE	**TIME OF TRAPPING**
8/5/97 - 8/6/97	2015 - 0730

OBSERVATIONS

Clear, crescent (new moon) moon. Very cool (≈ 50s °F).
All lights on p.m. + a.m. Used 1000 ml ethyl acetate

SAMPLE DATE	TIME OF TRAPPING
8/6/97 - 8/7/97	2000 - 0730

OBSERVATIONS

Clear, crescent moon. Cool (≈ 60s)
Used 800 ml ethyl acetate due to cooler temps.

SAMPLE DATE	TIME OF TRAPPING
8/7/97 - 8/8/97	2010 -

OBSERVATIONS

Used 800 ml ethyl acetate
Clear, crescent moon. Cool.

SAMPLE NUMBER	NUMBER OF CONTAINERS

SAMPLER'S SIGNATURE	CODE

DATE SAMPLES SENT	ANALYTICAL LAB

INDIANA BAT FOOD CHAIN STUDY
SAMPLE LOG

Department of the Navy
Naval Surface Warfare Center
Crane, IN 47522

TRAP TYPE	TRAP SITE
Malaise	J.J. 25 between 3089 & 3090
SAMPLE DATE	**TIME OF TRAPPING**
8/5-8/6/97	2015 ~~0815~~ - 0730

OBSERVATIONS

no water used. few insects. Cool night (≈50s °F).
clear, crescent moon (new moon). ~~[illegible] ethyl acetate.~~

SAMPLE DATE	TIME OF TRAPPING
8/6/97 - 8/7/97	2000 - 0730

OBSERVATIONS

Cool. Clear, crescent moon. No water used in trap.
~~[illegible] ethyl acetate (down from normal death jar temp)~~

SAMPLE DATE	TIME OF TRAPPING
8/7/97 - 8/8/97	

OBSERVATIONS

Cool, clear, crescent moon.
~~[illegible] ethyl acetate~~

SAMPLE NUMBER	NUMBER OF CONTAINERS

SAMPLER'S SIGNATURE	CODE

DATE SAMPLES SENT	ANALYTICAL LAB

APPENDIX B

LABORATORY SOPs

TITLE: Explosives
(SW-846 Method 8330)

SOP NUMBER: M-8330-00-WES-XX

PREPARED BY: _____
Date

REVIEWED BY: _____
Technical Specialist Date

_____
QA Officer Date

_____
Laboratory Director Date

SOP MANUAL CONTROL NO.: _____

1.0 Scope and Application

1.1 The procedures in this SOP are used for the extraction and trace analysis of explosive residue in water and soil/sediment matrices by high performance liquid chromatography (HPLC) using a UV detector. Table 1 lists the target compounds. ~~[Each laboratory should insert their specific list.]~~ The listing in Table 1 will be used in the absence of project-specific requirements.

Table 1. Target Compounds

Compound	Abbrev.	CAS No.
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	TNB	99-35-4
1,3-Dinitrobenzene	DNB	99-65-0
Methyl-2,4,6-trinitrophenylnitramine	Tetryl	479-45-8
Nitrobenzene	NB	98-95-3
2,4,6-Trinitrotoluene	TNT	118-96-7
4-Amino-2,6-dinitrotoluene	4-A-DNT	1946-51-0
2-Amino-4,6-dinitrotoluene	2-A-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

1.2 Appendix 1 provides MDLs and reporting limits for target analyte compounds in low- and high-level waters as well as soils. ~~[Each laboratory should add specific information.]~~

2.0 Method Summary

2.1 This SOP provides high performance liquid chromatographic (HPLC) conditions for the detection of ppb (µg/L) levels of certain explosives residues in water, soil and sediment. Samples must be appropriately extracted prior to HPLC analysis.

2.2 There are two appropriate sample preparation techniques for aqueous samples.

2.2.1 Low-level Salting-out Method With No Evaporation: Aqueous samples of low concentration are extracted by a salting-out extraction procedure using acetonitrile and sodium chloride. The small volume of acetonitrile which remains undissolved above the salt water is drawn off and transferred to a smaller volumetric flask. It is then back-extracted by vigorous stirring with a specific volume of salt water. After equilibration, the phases are allowed to separate and the small volume of acetonitrile residing in the narrow neck of the volumetric flask is removed using a Pasteur pipet. The concentrated extract is diluted 1:1 (v/v) with reagent grade water. An aliquot is separated on a Supelco C-18 reverse phase column, determined at 245 nm, and confirmed on a Supelco CN reverse phase column at 245 nm. ~~[Each laboratory should insert columns and wavelength used.]~~

2.2.2 Low-level Solid Phase Method With No Evaporation: Aqueous samples of low concentration are extracted by a solid phase extraction procedure using a vacuum manifold and solid phase cartridges (Waters SepPak Vac cc (500 mg) Porapak RDX, catalog # WAT047220). The water samples are concentrated onto the cartridges and are eluted off using a small volume of acetonitrile. The concentrated extract is diluted 1:1 (v/v) with reagent grade water. An aliquot is separated on a Supelco C-18 reverse phase column, determined at 245 nm, and confirmed on a Supelco CN reverse phase column at 245 nm.

2.2.3 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 Supelco C-18 reverse phase column, determined at 245 nm, and confirmed on a Supelco CN reverse phase column at 245 nm. If HMX is an important target analyte, methanol is preferred. ~~[Each laboratory should insert columns and wavelength used.]~~

2.3 Soil and sediment samples are extracted using acetonitrile in an ultrasonic bath, filtered, and treated as described in the high-level direct injection method.

3.0 Health and Safety

3.1 Soil samples as high as 2% 2,4,6-TNT have been safely ground. Samples containing higher concentrations must not be ground in the mortar and pestle.

3.2 A visual inspection of the sample shall be performed prior to analysis.

3.2.1 Lumps of material having a chemical appearance are considered suspect and shall not be ground.

3.2.2 Explosives are generally a very finely ground grayish-white material.

3.2.3 Pure TNT crystals can be straw colored or dark red or brown when exposed to sun light.

3.3 The toxicity or carcinogenicity of each compound or reagent used in this procedure has not been precisely determined. Each chemical should be treated as a potential health hazard and be handled in a fume hood. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. MSDS sheets are available in Room # 65D and Room # 59A and should be consulted as needed. ~~[Each Division laboratory uld insert location of MSDSs.]~~

3.4 This procedure employs organic solvents that are flammable and/or may pose a risk through inhalation. Therefore, exposure to these solvents should be reduced to the lowest possible level and must be handled in a hood with the analyst wearing the appropriate personal safety equipment (i.e., lab coat, gloves, goggles, etc.) at all times.

3.5 When preparing standard solutions from neat material, all weighing tools must be teflon coated. Weighings shall be performed behind an explosion-proof shield.

4.0 Sample Preservation, Containers, Handling, and Storage

4.1 Requirements for sample preservation, sample containers, and sample storage are detailed in SOP No. Q-005-XX-MCX-XX, Sample Receipt, Login, and Storage.

4.2 Sample extracts must be stored in the dark at 4 ± 2°C. Soil or sediment samples must be extracted within 14 days of collection, and analyzed within 40 days of extraction. Water samples must be extracted within 7 days of collection, and analyzed within 40 days of extraction.

5.0 Interferences and Potential Problems

5.1 Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing the misinterpretation of chromatograms. All of these materials must demonstrate freedom from interferences. Refer to SOP Nos. Q-012-XX-MCX-XX, Glassware Cleaning and Q-015-XX-MCX-XX, Reagent Control.

5.2 2,4-DNT and 2,6-DNT elute at similar retention times (retention time difference of 0.2 minutes.). ~~[Each laboratory should insert appropriate retention time difference.]~~ 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 must be reported.

5.3 Tetryl decomposes rapidly in methanol/water solutions, and also with heat. All aqueous samples expected to contain tetryl must be diluted with acetonitrile prior to filtration. All samples expected to contain tetryl must not be exposed to temperatures above 30°C.

5.4 Tetryl's degradation products 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.

6.0 Equipment/Apparatus

6.1 HPLC system

6.1.1 HPLC — an analytical system equipped with a Waters 610 Fluid Unit pump capable of achieving 5000 psi , a Waters 717 plus Autosampler including a 200 µl loop injector, and a Waters 486 Tunable UV Absorbance detector monitored at 245 nm and "Millenium" 2.1 Chromatography Software (Waters Chromatography Division, Milford, MA) ~~(Perkin-Elmer Series 3, or equivalent)~~. ~~[Each laboratory shall specify make and model of their specific equipment, including all associated options, components, and software.]~~

6.1.2 Primary column — Supelco LC-18 reverse phase HPLC column 25 cm x 4.6 mm (5 µm), Catalog # 5-8298. ~~[Each laboratory should insert the column used, along with the supplier and catalog number.]~~

6.1.3 Secondary (confirmatory) column — Supelco LC-CN reverse phase HPLC column 25 cm x 4.6 mm (5 µm), Catalog # 5-8231 ~~[Each laboratory should insert the column used, along with the supplier and catalog number.]~~

6.1.4 Filtration system to filter and degas HPLC mobile phase—Millipore Solvent and Degassing Unit (catalog # XX1504700) with 0.22 µm filter (catalog # GVWP04700) (attaches to vacuum) and helium sparging. ~~[each laboratory should specify system used]~~.

6.1.5 Pre-column — Novapak C-18 catalog # WAT015220 and Novapak CN catalog # WAT020800 (Waters Chromatography Division, Milford, MA)

6.1.6 Column heaters — Cera Column Heater 250 set at 30° C, catalog # 282-0252 (Cera, Inc., Baldwin Park, CA)

6.2 Refrigerator, Explosion-proof, capable of maintaining 4 ± 2°C.

6.3 Temperature-controlled ultrasonic bath, not to exceed 30° C. — Cole-Parmer Instrument Co., model # 8855-00 ~~[Each laboratory should specify make and model of bath.]~~

6.4 Vortex mixer (Glas-Col model VB2 or equivalent) — Scientific Industries Vortex

Genie 2, model G-560 ~~{Each laboratory should specify make and model of mixer.}~~

6.5 Balance capable of measuring to ± 0.0001g.

6.6 Magnetic stirrer with stirring pellets.

6.7 Tube Rotator – Scientific Equipment Products, catalog # 60448 ~~{each laboratory should specify make and model number}~~.

6.8 Oven — Forced air, without heating – GS Blue M Electric, Model 256 ~~{each laboratory should specify make and model}~~.

6.9 Filtration system and disposable cartridge filters (~~0.45 µm~~ 0.50 Teflon filter). Vacuum Filtration System from Millipore (catalog # XX1504700) with .22 µm filters (catalog #GVWP04700) to degas mobile phase; Millipore Millex-SR .50 µm teflon filters (catalog # SLSR025NB) for all samples. ~~{Each laboratory should describe system and specify supplier and catalog number of filters.}~~

6.10 Volumetric pipets — Class A 1-mL, 2.5-mL, 10-mL, or appropriate volume.

6.11 Disposable glass pasteur pipets.

6.12 Vials, scintillation, 20 mL.

6.13 Vials — 10-mL, 20-mL, 40-mL glass, Teflon-lined cap, or appropriate volume.

6.14 Volumetric flasks — Class A, round bottom, 10-mL, 25-mL, 100-mL, and 1L, or appropriate volume with tight fitting plastic snap caps, for use for the low level salting out procedure.

6.15 Volumetric flasks — Class A, 10-mL, 25-mL, 100-mL, and 1L, or appropriate volume for use for in standards preparation.

6.16 Vacuum desiccator.

6.17 Mortar and pestle — Steel or Ceramic. Adequate sample grinding can be accomplished in either type. When processing a large number of samples at a time, it is better to have several mortar and pestle sets available to facilitate sample processing.

6.18 Sieve — 30 mesh.

6.19 Graduated cylinders — Class A, 10-mL, 25-mL, 250-mL, 1-L, or appropriate volume.

6.20 Disposable Syringes - Plastipac, 3 mL and 10 mL, or equivalent. – 10 cc Luer-Lok syringe, VWR catalog # BD30-9604 ~~{Each laboratory should insert the~~

~~supplier and catalog number of disposable syringes.]~~

6.21 Automatic pipets with disposable tips.

6.22 Automatic diluter or dispenser.-15°± Hamilton MicroLab 500 Diluter

6.23 Freezer, Explosion-proof, capable of maintaining -15°± 5°C.

6.24 Solid Phase Cartridges — Waters SepPak Vac cc (500 mg) Porapak RDX cartridges, catalog # WAT047220

6.25 Solid Phase Extraction Vacuum Manifold (Supelco, catalog # 5-7250) with attached 4000 mL vacuum trap

6.26 15 mL Graduated conical bottomed centrifuge tubes (Fisher, catalog # 05-495R)

6.27 500 mL flasks (Fisher, catalog # 02-599-19

6.28 SepPak adapters (Supelco, catalog # 5-7020)

6.29 60 cc Luer-Lok syringe (used as reservoirs for solid phase extraction), VWR, catalog # BD309663

6.30 FreeZone 4.5 liter benchtop Freeze/Dry System, Model 77500

6.31 Omni Mixer ES Homogenizer, catalog # ES-115

6.32 Glass wool — muffle furnace extracted glass wool, Fisherbrand, catalog # 11-390

6.33 Florisil- Fisher Scientific, catalog # F100-500

6.34 Alumina- Fisher Scientific, catalog # A540-500

7.0 Reagents

7.1 Reagent grade inorganic chemicals must 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 the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first proven the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination.

7.2 Acetonitrile, CH_3CH — HPLC grade.

7.3 Methanol, CH_3OH — HPLC grade.

7.4 Calcium chloride, $CaCl_2$ — Prepare an aqueous solution of 5 g/L. Weigh 5 g to the nearest milligram and place in a 1-L volumetric flask. Dilute the solution to 1-L using reagent water. Stopper until use.

7.5 Sodium chloride, NaCl (salt) — Prepare a solution to contain 325 g NaCl per 1000 mL reagent water. Dissolve 325 g NaCl in 1 L of water to make a saturated sodium chloride. Place salt solution onto a magnetic stir plate, add a stir bar, and mix at maximum speed (using no heat) until NaCl is completely dissolved. Make enough for all samples to be extracted (~90 mL each). ~~[Each laboratory should describe how this solution is prepared.]~~

7.6 Organic-free reagent water — as defined in SOP No. Q-008-XX-MCX-XX, Reagent Water Generation and Quality Monitoring.

7.7 Stock Standard Solutions — Both primary and secondary source stock standards shall be stored in the dark at < 6°C. Follow supplier's instructions. These stock solutions may be used for up to one year.

7.7.1 Stock primary source standard solutions shall be made from neat or crystalline stock explosives standards obtained from the Army Environmental Center at Aberdeen Proving Ground. Stock solutions will be prepared as single analyte solutions of 1,000 µg/mL in acetonitrile. These stock solutions will be used to prepare the initial 5-point calibration curve, continuing calibration verification (CCV) standard, surrogates, laboratory control sample (LCS), and matrix spikes and their duplicates (MS/MSDs). See Sections 7.8, 7.9, 7.10, 7.11, and 7.12.

Each analyte is to be dried (at ambient temperature) to a constant weight in a vacuum dessicator in the dark. Weigh 0.100 g ± 0.001 g of the analyte into a 100 mL volumetric flask and dilute to volume with acetonitrile. Invert several times to dissolve. Store in an explosion proof refrigerator at < 6°C in the dark. Calculate the concentration from the actual weight used (see Section 9.1).

7.7.2 Secondary source standards shall be purchased as certified solutions for use as the initial calibration verification (ICV) standard. This standard shall be at a concentration near the mid-level calibration standard. (When these standards are purchased, flexibility from this criteria may be exercised.) Ultra Scientific, catalog # NAIM833C, contains 1000 µg/ml of HMX, RDX, TNB, NB, TNT, and 2,4-DNT (Diluted to 1.0 ppm for working secondary source) ~~[Each laboratory should insert supplier and catalog numbers and concentrations.]~~

7.8 Intermediate Standards

7.8.1 Intermediate standards are prepared from the above stock solution(s). These standards are then used to create the calibration standards for the initial 5-point calibration curve and the ICV.

7.8.2 If both 2,4-DNT and 2,6-DNT are to be determined, prepare two separate solutions; the first containing HMX, RDX, 1,3,5-TNB, 1,3-DNB, NB, 2,4,6-TNT, 4-A-DNT, and 2,4-DNT, and the second containing Tetryl, 2-A-DNT, 2,6-DNT, 2-NT, 3-NT, 4-A-DNT, and 4-NT. When analyzing soil samples, prepare solution in acetonitrile; use methanol when analyzing aqueous samples. Refer to Table 2. ~~[Each laboratory should specify the concentrations and preparation procedures for these intermediate standards.]~~

Table 2. Intermediate Standard Preparation

Compound	Intermediate 1			Intermediate 2		
	mL Stock	Final vol., mL	Conc., mg/L	mL Stock	Final vol., mL	Conc., mg/L
HMX	1	10	1			
RDX	1	10	1			
TNB	1	10	1			
DNB	1	10	1			
Tetryl				1	10	1
NB	1	10	1			
TNT	1	10	1			
4-A-DNT	1	10	1			
2-A-DNT				1	10	1
2,4-DNT	1	10	1			
2,6-DNT				1	10	1
2-NT				1	10	1
3-NT				1	10	1
4-NT				1	10	1

7.8.3 Intermediate Standards are to be stored at < 6°C in the dark. Standards should be allowed to come to room temperature and be thoroughly mixed prior to use. Standards can be used beyond 30 days if instrument response of CCV is monitored and compared to response of freshly prepared standard. Intermediate standards should be replaced if degradation occurs such that the CCV response exceeds ±15% of the original response.

7.9 Calibration Standards

7.9.1 The two intermediate standards in Section 7.8.2 are diluted to generate two sets of calibration standards at five concentration levels. The low

standard is set at a concentration approximately 3 to 5 times the MDL and the high standard is typically chosen to correspond to the linear range of the instrument. The calibration curve presented in Section 8.5.3 is used in the absence of project-specific information. Specific client requirements may dictate that a different curve be constructed.

7.9.2 Table 3 summarizes the solvents and diluents used in the preparation of the calibration standards.

Table 3. Diluents for Calibration Standards

Sample Type	Sample Matrix	Diluent	Factor	Std. Matrix	Diluent	Factor
Low Level Water	Acetonitrile	Reagent Water	1:1 (v:v)	Acetonitrile	Reagent Water	1:1 (v:v)
High-Level Water	Water	Acetonitrile	1:1 (v:v)	Acetonitrile	Reagent Water	1:1 (v:v)
Soil	Acetonitrile	5 g/L $CaCl_2$	1:1 (v:v)	Acetonitrile	5 g/L $CaCl_2$	1:1 (v:v)

Depending on the columns and eluent used in the HPLC analysis, as well as the types of samples received, the lab may vary the solvents and dilution ratios in order to achieve acceptable separation. ~~[Each laboratory should revise Table 3 as necessary.]~~

7.10 Surrogate Spiking Solution

Surrogate solutions are prepared from the primary stock standards. The use of one surrogate is mandatory; the use of additional surrogates is optional. **[Each laboratory should identify surrogate(s) used, the concentration of the spiking solution, the amount to be spiked, and the resulting concentration of the surrogate in the extract.]** See Table 4.

Table 4. Surrogate Spikes

Method	Surrogate Used	Surrogate Solution Concentration (mg/L)	Volume Surrogate Added (mL)	Per Sample Volume	Final Surrogate Concentration
Low-Level Water	3,4-DNT	40	0.050	700 mL	0.0026 mg/L
High-Level Water	3,4-DNT	200	0.050	5 mL	2.0 mg/L
Soil	3,4-DNT	200	0.050	2 g	5.0 mg/kg

7.11 Matrix spike (MS) standards

7.11.1 The matrix spike standard shall be prepared from the primary stock standards. Using Class A volumetrics, measure 5 mL from the 1000 ppm stock solutions of HMX, RDX, TNB, TNT, 4-A-DNT, and 2,4-DNT into a 50 mL volumetric (final solution is 100 ppm). Add acetonitrile to the line and vortex. Keep in the freezer at -15°C ± 5°C. ~~{Each laboratory shall specify how the MS standard is prepared.}~~

7.11.2 The spike should be at a level that would approximately double the concentration of the target analytes present, if known. In the absence of target analytes, the spike would be made at the site action level, assuming that this level did not also correspond to the value of the low standard used. If the action level is the same as the low standard used, then the spiking would occur at a slightly higher level, i.e., at the value of the next calibration standard used. If the action level is not known, the spiking level would then default between the low and mid-level initial calibration standards.

7.11.3 Ideally, all target analytes should be contained in the MS spike. Subset target analytes may be used based on project specific requirements. In the absence of project related information, a representative subset of the target analytes may be used. The following is a recommended default subset — HMX, RDX, TNB, ~~Tetryl~~, TNT, 4-A-DNT, 2,4-DNT, and ~~2-NT~~. ~~{Each laboratory should revise list as appropriate.}~~ See Table 5.

Table 5. Matrix Spiking Solutions

MS Std. Compounds	Method	MS Std. Conc. mg/L	Vol. MS Added mL	Sample Aliquot	Final MS Conc.
HMX RDX TNB TNT 4-A-DNT 2,4-DNT	Salt-Out	10	0.200	1 L	0.0020 mg/L
	SPE	5	0.100	500 mL	0.0020 mg/L
	High-Level Water	100	0.100	5mL	2.0 mg/L
	Soil	100	0.100	2 g	5 mg/kg

7.12 Laboratory Control Sample (LCS)

7.12.1 The LCS shall be prepared from the primary stock standard. The LCS is the same as the MS solution in section 7.11.1. ~~{Each laboratory should specify how the LCS standard is prepared.}~~

7.12.2 The LCS shall be prepared in the appropriate matrix (organic-free reagent water, or purified solid) depending upon the matrix within the batch; and contains all of the method target analytes. A subset of target analytes could be used based on the project

specific requirements. The spiking level used would be at the same level as the site-specific action limit. If site-specific action limits are not available, the spiking level shall be at a concentration between the low and the mid-level calibration standard.

7.13 HPLC Mobile Phase

To prepare 1 L of mobile phase (1:1 (v/v) methanol/reagent water), measure 500 mL of each using graduated cylinders and combine. Mix thoroughly. Filter the mixture through a ~~0.45~~ 0.50 micron filter and degas prior to use.

8.0 Procedure

The low-level method is used for aqueous samples with expected single component explosive concentrations below 50 μg/L. If expectant concentrations are not known, project-specific DQOs should be consulted. Project-specific minimum reporting limits will help determine whether the low or high-level method should be used. Process waste samples should be screened to determine which approach is appropriate. Extraction information should be recorded using Figure 1 or 2, as appropriate.

8.1 Preparation Of Aqueous Samples by Low-Level Method (salting-out extraction).

8.1.1 Using a 1-L graduated cylinder, measure out 770 mL of sample, and add it to a 1-L volumetric flask.

8.1.2 Spike samples and associated QC samples with surrogate spiking solution and matrix spike solution, (see Sections 7.10 and 7.11). After addition of the surrogate and matrix spiking solutions, the samples are to be swirled or shaken to allow complete mixing of the solutions within the sample.

8.1.3 Using a disposable weigh dish, weigh out 251.3 ± 0.5 g of sodium chloride (NaCl) and add to the sample.

8.1.4 Place sample on a magnetic stir plate, add a stir bar, and mix at maximum speed (using no heat) until NaCl is completely dissolved.

8.1.5 Using a 250-mL graduated cylinder, add 164 ± 2 mL of acetonitrile while the solution is being stirred and stir for an additional 15 min. Turn off the stirrer and allow the phases to separate for 10 min. Remove the acetonitrile (upper) layer (approximately 8 mL) with a disposable glass pasteur pipet and transfer it to a 100-mL volumetric flask with a plastic snap lid.

CAUTION: Incomplete mixing will result in low extraction efficiencies. In some cases the vortex doesn't reach the top of the liquid column in the neck of the flask. When that happens

the acetonitrile sits on top of the stirring sample and little to no extraction takes place. If the sample prep technician walks away for the 15 minutes, they may not notice this. They need to establish a complete mix and then monitor it, adjusting the flask as necessary in order to get a complete extraction.

8.1.6 Add 10 mL of fresh acetonitrile to the water sample in the 1-L flask. Again, stir the contents of the flask for 15 min., followed by 10 min. phase separation. Combine the second acetonitrile portion with the initial extract. The inclusion of a few drops of salt water at this point is unimportant.

8.1.7 Using a 100-mL graduated cylinder, add 84 mL ± 2 mL of NaCl solution (see Section 7.5) to the acetonitrile extract in the 100-mL volumetric flask. Cap the volumetric, clip onto the tube rotator, and mix for 15 min. Allow 10 min. for phase separation. Using a disposable glass pasteur pipet, carefully transfer the acetonitrile phase to a ~~10-mL graduated cylinder~~ 15 mL graduated centrifuge tube. At this stage, the amount of water transferred with the acetonitrile must be minimized. The water contains a high concentration of NaCl producing a large peak at the beginning of the chromatogram where it could interfere with the HMX determination.

8.1.8 Add an additional 1.0 mL (using a 1-mL volumetric pipet) of acetonitrile to the 100-mL ~~graduated cylinder~~ volumetric flask, recap and return to the tube rotator for 15 min., followed by 10 min. for phase separation. Combine the second acetonitrile portion with the initial extract in the 15 mL graduated centrifuge tube ~~10-mL graduated cylinder (transfer to a 25-mL graduated cylinders if the volume exceeds 5 mL)~~. ~~[The use of 10 or 25 mL graduated cylinders can be modified to meet laboratory specific requirements.]~~ Record the total volume of acetonitrile extract to the nearest 0.1 mL ~~on~~ in the Explosive extraction log book ~~(see Figure 1)~~. (Use this as the volume of total extract [V(t)] in the calculation of concentration after converting to uL). The resulting extract, about 5 - 6 mL, is then diluted 1:1 (v/v) with organic-free reagent water prior to analysis.

8.1.9 Filter the extract through a ~~0.45-µm~~ 0.50-µm Teflon filter using a plastic disposable syringe. Discard the first 0.5 mL of filtrate, and retain the remainder in a vial with a Teflon cap for HPLC analysis as in Section 8.6.

8.2 Preparation of Aqueous Samples by Low-Level Method (Solid Phase Extraction)

8.2.1 Using a 500 mL graduated cylinder, measure out 500 mL of sample, and add it to a 500 mL fleaker.

8.2.2 Spike samples and associated QC samples with surrogate spiking

solution and matrix spike solution (see Sections 7.10 and 7.11). After addition of the surrogate and matrix spiking solutions, the samples are to be swirled or shaken to allow complete mixing of the solutions within the sample.

8.2.3 Condition the cartridges:

8.2.3.1 Remove the internal rack from the vacuum manifold.

8.2.3.2 Insert a Sep-Pak adapter into each Propak RDX cartridge.

8.2.3.3 Connect the cartridges to the vacuum manifold.

8.2.3.4 Connect the 60 cc syringe reservoirs to the adapters.

8.2.3.5 Fill each reservoir with 15 mL acetonitrile. Pulse the vacuum pump to start the flow, then let the acetonitrile drip through under gravity alone.

8.2.3.6 Just before each reservoir runs dry, refille the reservoir with 30 mL organic free reagent water.

8.2.3.7 Turn on the vacuum pump and adjust the flow rate with the stopcock valves to draw the water through the cartridge. The flow rate should not exceed 10 mL/min. Close valves.

CAUTION: Once the packing material has been activated, do not expose it to air until all of the sample has been loaded. If the cartridge runs dry, repeat the conditioning procedure.

8.2.4 To load the sample onto the cartridge, fill the reservoirs with the water sample that is to be concentrated. Turn on the vacuum. Use the stopcocks to adjust the flow rate to about 10 mL/min. Refill the reservoir and empty the vacuum trap as needed. Be sure the bed does not run dry during loading.

8.2.5 After the 500 mL sample is loaded, remove the adapter and reservoir from the cartridge. Set up the vacuum manifold with clean 15 mL graduated centrifuge tubes and needles.

8.2.6 Put 5 mL acetonitrile into the cartridge. Pulse the vacuum pump to start the flow, then let the acetonitrile drip through under gravity alone. The flow rate should be about 1 mL/min. After acetonitrile stops dripping, turn on the vacuum briefly (too much vacuum will cause the sample to splatter) to draw the remaining acetonitrile through the cartridge.

8.2.7 Open the manifold and remove the centrifuge tubes. Fill the centrifuge tubes to the 5 mL mark with acetonitrile and vortex to mix thoroughly.

Record the total volume of acetonitrile extract to the nearest 0.1 mL in the Explosive Extraction Log Book. (Use this as the volume of total extract [V(t)] in the calculation of concentration after converting to μL). The resulting extract, about 5 mL, is then diluted 1:1 (v/v) with organic-free reagent water prior to analysis.

8.2.8 Filter the extract through a 0.50 μm Teflon filter using a plastic disposable syringe. Discard the first 0.5 mL of filtrate, and retain the remainder in a vial with a Teflon cap for HPLC analysis as in Section 8.6.

8.3 Preparation of Aqueous Samples by High-Level Method

8.3.1 Transfer 5-mL of sample volumetrically into a 20-mL glass vial.

8.3.2 Spike samples and associated QC samples with surrogate spiking solution, and matrix spike solution (see Sections 7.10 and 7.11). After addition of surrogate and matrix spiking solutions, the sample is to be shaken (by hand) to allow complete mixing of the solutions within the sample.

8.3.3 Volumetrically add 5 mL of acetonitrile. (HMX quantitation can be improved with the use of methanol rather than acetonitrile for dilution.)

8.3.4 Using a vortex mixer, mix sample for 2 minutes.

8.3.5 Filter through a ~~0.45 μm~~ 0.50 μm Teflon filter using a plastic disposable syringe. Discard the first 3 mL of filtrate, and retain the remainder in a 10-mL glass vial with Teflon-cap for HPLC analysis as in Section 8.6.

8.3.6 All radioactive samples will be prepared according to Section 8.3. The samples will be contained only in areas which are designated by the ECB Safety Officer for radioactive prep work.

8.4 Soil and Sediment Samples

8.4.1 Thoroughly mix sample as defined in SOP No. Q-021-XX-MCX-XX, Subsampling of Containers. Using disposable weigh dishes, weigh out 10 -20 grams of wet weight sample (that would yield a sample weight of 2.0 g after drying) and allow to air dry. A forced-air oven at room temperature may also be used.

8.4.2 After drying, grind and homogenize thoroughly in an acetonitrile-rinsed mortar (Section 6.17) to pass a 30 mesh sieve.

Weigh out 2.0 ± 0.5 g of each ground soil sample (record weight in the Explosive Prep Labbook ~~on extraction log in Figure 1~~) into a 20-mL glass vial with a Teflon lined cap.

8.4.3 Spike samples and associated QC samples with surrogate and matrix spike spiking solutions (see Sections 7.10 and 7.11).

8.4.4 Volumetrically add 10.0 mL of acetonitrile.

8.4.5 Using a vortex mixer, swirl for one minute, and place in a cooled ultrasonic bath for 18 hours.

8.4.6 After sonication, allow sample to settle for 30 minutes. Remove 5 mL of supernatant, using a 5-mL pipet with disposable tips, and put in a 20-mL vial. Volumetrically add ~~transfer~~ 5 mL of calcium chloride solution (Section 7.4) to the 5 mL of supernatant. Vortex for 2 minutes and let stand for 15 minutes.

8.4.7 Using a disposable glass pasteur pipet, place the supernatant in a disposable plastic syringe and filter through a ~~0.45 µm~~ 0.50 µm Teflon filter attached to the syringe. Discard the first 3 mL and retain remainder in a 10 mL glass Teflon-capped vial for HPLC analysis as in Section 8.6.

8.4.8 Sample Dilution - Samples are to be diluted in the same matrix as the prepared, filtered sample. Standards must be prepared in this same matrix (see Table 3). Samples are diluted using the automated Hamilton MicroLab 500 diluter for 1:10, 1:100, and 1:1000 dilutions. The accuracy of the diluter is checked periodically. Standards are diluted using Class A volumetrics. ~~[Each laboratory shall insert specifics on how dilutions are performed (i.e., using volumetric pipets, flasks, or automated diluters).]~~

8.4.9 All radioactive samples will be prepared according to Section 8.4. The samples will be contained only in areas which are designated by the ECB Safety Officer for radioactive prep work.

8.4.10 See Appendix 8 for Preparation of Compost and Plant Samples.

8.5 Calibration of HPLC

8.5.1 Chromatographic Conditions: The room is maintained at a constant temperature (between 65-70°F). The equipment is kept in a low humidity and relatively dust free environment. ~~[Each laboratory must enter their own optimal conditions, based on their specific instruments.]~~

Primary column: Supelco LC-18 reverse phase HPLC column 25 cm x 4.6 mm (5 µm) (Catalog # 5-8291 with a Novapak C-18 pre-column, Catalog # WAT020800. ~~[Each laboratory should insert]~~

Secondary column: Supelco LC-CN reverse phase HPLC column 25 cm x 4.6 mm (5 µm) (Catalog # 5-8291 with a Novapak CN pre-column, Catalog # WAT020800. ~~[Each laboratory should insert]~~

Mobile Phase: 1:1 (v/v) methanol/organic-free reagent water. ~~{Each laboratory should revise as necessary.}~~

Flow Rate: 1.2 mL/min ~~{Each laboratory should revise as necessary.}~~

Injection volume: 50 µL ~~{Each laboratory should revise as necessary.}~~

UV Detector: 245 nm ~~{Each laboratory should revise as necessary.}~~

8.5.2 All electronic equipment must warm up for 30 minutes. During this period, at least 15 void volumes of mobile phase are passed through the column (approximately 30 min at 1.2 mL/min) and continued until the baseline is level at the UV detector's greatest sensitivity. ~~{Each laboratory should revise as necessary.}~~

8.5.3 Initial Calibration — Prepare the calibration curve using the intermediate standards (see Section 7.8) as described in Table 6 below using volumetric flasks and either methanol or acetonitrile as the dilution solvent. Calibration is to be performed in singlet. A second source standard (ICV) is analyzed to verify the acceptability of the initial curve. Acceptance criteria are as discussed in Sections 11.1 and 11.2 for the initial curve and ICV, respectively.

Table 6. Initial Calibration Standards

Standard No.	Intermediate Std. Used	Volume of Std. Used	Final Volume	Final Standard Conc.
1	20 mg/L	10 mL	10 mL	20 mg/L
2	20 mg/L	5 mL	10 mL	10 mg/L
3	20 mg/L	2 mL	10 mL	4 mg/L
4	20 mg/L	0.5 mL	10 mL	1 mg/L
5	4 mg/L	1 mL	10 mL	0.40 mg/L
6	1 mg/L	1 mL	10 mL	0.10 mg/L
7	1 mg/L	0.5 mL	10 mL	0.050 mg/L
8	1 mg/L	0.2 mL	10 mL	0.020 mg/L

~~{Each laboratory shall specify specific calibration information.}~~

8.5.4 Peak heights are obtained for each analyte. Calculate the calibration factor (CF) for each analyte as described in Section 9.2. Calculate the % RSD as presented in Section 9.3.

8.5.5 Retention Time Windows

8.5.5.1 Before establishing windows, make sure the HPLC system is within optimum operating conditions. Make three injections of all standard mixtures throughout the course of a 72 hour period. Serial injections over less than a 72 hour period result in retention time windows that are too tight.

8.5.5.2 Plus or minus three times the standard deviation of the retention times for each analyte will be used to define the width of the retention time window; however, the experience of the analyst should weigh heavily in the interpretation of chromatographs.

8.5.5.3 In those cases where the standard deviation (SD) for a particular standard is zero, the analyst should refer to SW-846 Method 8000B for instruction. A zero SD is not acceptable.

8.5.5.4 The laboratory must calculate retention time windows for each analyte on each HPLC column and whenever a new HPLC column is installed. The data must be retained by the laboratory.

8.5.5.5 Establish the midpoint of the retention time window for each analyte and surrogate by using the absolute retention time established from the mid-level standard of the initial calibration. The absolute retention time window equals the midpoint ± 3SD (as determined above).

8.5.6 Daily Calibration — At a minimum, midpoint calibration standards (CCVs) are to analyzed in singlet, at the beginning of the analytical run, every 8 hours of continuing analysis, and after the last sample of the day. It is recommended that a CCV be analyzed after every 10 samples.

8.5.6.1 Obtain the calibration factor for each analyte from the peak height and compare it with the calibration factor obtained for the initial calibration. The % difference between the calibration factor for the daily calibration and the calibration factor of the initial calibration must be < 15%, or a new initial calibration must be performed (see Section 9.4). (The laboratory may perform a complete 5 point calibration each day if the analyst determines it is appropriate.)

8.5.6.2 The retention time of all target analytes and surrogates in the CCVs must fall within the absolute retention time windows calculated in 8.5.5.5. If the retention time of any target analyte does not fall within the ±3SD window, then a new initial calibration curve for the failed analytes is necessary unless system maintenance corrects the problem. Reanalysis of all affected sample extracts must also be performed for

those failed analytes. Appendix 2 summarizes the estimated retention times on the two columns for a number of analytes analyzable using this method. ~~[Each laboratory shall update RTs as appropriate.]~~

8.6 HPLC Analysis

Document appropriate information using the Explosive instrument log book ~~in Figure 3. [Each laboratory should insert form used.]~~

8.6.1 Samples are analyzed in a set referred to as an analytical sequence. The sequence begins with instrument calibration, ICV standard, method blank, and sample extracts interspersed with continuing calibration checks every 10 samples and at the end of the analysis. An analytical sequence is shown in Table 7.

Table 7. Analytical Sequence

Analysis	Purpose
Calibration standard(s)	Initial 5-point calibration or single-point calibration verification.
ICV	For the verification of the initial calibration curve only.
Method blank	Verify that carry over has not occurred from the calibration standard, and that the extraction and analytical system do not exhibit contamination above the detection limits of the procedure.
Samples	"Samples" includes all field samples, spiked samples, laboratory control samples, and dilutions.
Calibration verification (CCV) (See Section 8.4.6)	Single-point calibration verification standard, (mid-point standard).
Method blank	Verify that carry over has not occurred from the calibration standard, and that the analytical system does not exhibit contamination above the detection limits of the procedure.
Samples	"Samples" includes all field samples, spiked samples, laboratory control samples, and dilutions.
Calibration verification (CCV) (See Section 8.5.6)	Single-point calibration verification standard, (mid-point standard).

8.6.1.1 All samples analyzed must be bracketed by in-control calibration verification standards (± 15%). If the calibration verification standard is outside the control limits, all the samples analyzed within the out-of control brackets must be

reanalyzed.

8.6.1.2 The analytical sequence in Section 8.6.1 may be continued indefinitely, as long as QC acceptance criteria are met.

8.6.2 Each sample is injected by an auto-injector onto a 200 µl loop using 50 µl volume injection. All radioactive samples will be injected by an auto-injector (onto a 200 µl loop using 50 µl volume injection) which has been designated as "radioactive" by the ECB Safety Officer. ~~[Each laboratory shall insert specific method of injection and volume injected.]~~

8.6.3 If any analyte response exceeds the linear range of the system, dilute the extract and reanalyze. It is recommended that extracts be diluted so that all peaks are on scale. Overlapping peaks are not always evident when peaks are not on scale. Chromatograms should be reviewed at different attenuations via the computer screen after the analysis is complete, to ensure the validity all peaks.

8.6.4 Tentative identification of an analyte occurs when a peak from a sample extract falls within the absolute retention time window. Confirmation is required on a second HPLC column (see Section 8.7). Analyst experience is important in confirming the presence of target compounds.

8.6.5 Sample concentrations are calculated by comparing the sample responses with the initial calibration of the system. Record the resulting peak sizes in peak heights. Refer to Section 9.5 for calculation of analyte concentrations.

8.7 Second Column Confirmation

Any time target analytes are detected on the primary column, second column confirmation must be performed. These confirmation analyses are subject to the same requirements as the primary analyses (i.e., MDL studies, retention time windows, initial and continuing calibrations, etc.). Confirmation shall be based on both qualitative and quantitative agreement. Requirements for qualitative agreement are the same as for the primary analysis (Section 8.6.4). Regarding quantitative agreement, the concentrations determined on the two columns should be within 40% RPD. ~~[Each laboratory may revise this requirement as necessary based on data generated.]~~ Refer to Section 11.13 for additional information on confirmation requirements.

9.0 Calculations

9.1 The standard is calculated as:

$$mg/L\ Standard = \%\ Purity \times \left(\frac{mg\ Standard}{Solute\ vol,\ L}\right)$$

9.2 The calibration factor (CF) is calculated as:

$$CF = \frac{\text{Peak Height}}{\text{Std conc, ng}/\mu\text{L}}$$

9.3 To evaluate the linearity of the initial calibration, calculate the mean CF, the standard deviation (SD), and the RSD as follows:

$$\text{mean CF} = \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (CF_i - \overline{CF})^2}{n-1}}$$

$$RSD = \frac{SD}{\overline{CF}} \times 100$$

where n is the number of calibration standards and RSD is expressed as a percentage (%).

9.4 To evaluate the calibration verification, calculate the % difference as follows:

$$\%\ \text{Difference} = \frac{|\overline{CF} - CF_v|}{\overline{CF}} \times 100$$

where CF_v is the calibration factor from the analysis of the verification standard, and CF is the mean calibration factor from the initial calibration.

9.5 Target Analyte Concentrations

9.5.1 For aqueous samples

$$\text{Concentration (ug/L)} = \frac{(A_x)(V_t)(D)}{(\overline{CF})(V_s)}$$

where:

A_x = Height of the peak for the analyte in the sample.

V_t = Total volume of the concentrated extract (μL) before diluting 1:1 (v/v) as appropriate.

D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless.

$\overline{CF}$ = Mean calibration factor from the initial calibration (height/ng/μL).

V_s = Volume of the aqueous sample extracted in mL. If units of liters are used for this term, multiply the results by 1000.

Use of the units specified here for these terms will result in a concentration in units of ng/mL, which is equivalent to μg/L. Concentrations may be converted to mg/L by dividing by 1000.

9.5.2 For non-aqueous samples

$$\text{Concentration (ug/kg)} = \frac{(A_x)(V_t)(D)}{(\overline{CF})(W_s)}$$

where A_x, V_t, D, and $\overline{CF}$ are the same as for aqueous samples, and
W_s = Weight of sample extracted (g). The wet weight or dry weight may be used, depending upon the specific application of the data.

Use of the units specified here for these terms will result in a concentration in units of ng/g, which is equivalent to μg/kg. Concentrations may be converted to μg/g by dividing by 1000.

10.0 Quality Assurance/Quality Control

10.1 A preparation batch of samples is defined as a group of up to twenty field samples of similar matrix type that have been prepared at the same time or time sequence with the same lots of reagents for the same analysis. In addition to the twenty samples, each preparatory batch will contain at a minimum, a method blank, a laboratory control sample, a matrix spike, a matrix spike duplicate and a matrix duplicate. An analytical, or instrumental batch is defined

as samples that are analyzed together within the same time period or in continuous sequential time periods. Within the analytical batch time are included individual QC requirements as defined by the analytical (determinative) method. For instance, each injection sequence would begin with a CCV (or initial 5-point calibration and ICV), followed by a instrument, and up to ten QC (normally a method blank, LCS, MS, MSD, MD, etc.) and field samples, then calibration verification, instrument blank, and so on. Preparation batches of samples may be continuously strung together in these run sequences, as long as the analytical batch QC requirements meet the acceptance criteria established within the appropriate SOP. At the conclusion of the last sequence, a CCV is required. Each analytical sequence must be documented using the sample identification record (see inserted form) ~~run log in Figure 1~~. ~~[Each lab should insert their own form if necessary.]~~

10.2 Run a 5-point calibration curve using the primary source standards initially, each time major instrument maintenance occurs, or if the CCV does not meet acceptance criteria. Acceptance criteria are presented in Section 11.1.

10.3 After the analysis of an acceptable 5-point calibration curve, run a Initial Calibration Verification (ICV) standard (single injection) before sample analysis. The ICV standard must be prepared from a second source standard. Acceptance criteria are listed in Section 11.2.

10.4 Run a mid-point Continuing Calibration Verification (CCV) on a daily basis before sample analysis. Also run a CCV every 8 hours of continuous analysis, and at the end of the analytical sequence. It is recommended that a CCV be analyzed after every 10 samples. Acceptance criteria are listed in Section 11.3 and 11.9.1.

10.5 A method blank must be extracted with each batch of samples. The method blank should be prepared from either organic-free water or sand. Method blanks may be injected at any time in the sequence to verify absence of contamination. Acceptance criteria for these blanks are listed in Section 11.4.

10.6 A laboratory control sample must be prepared and analyzed with each batch of samples. The LCS would be prepared using the primary source standard and would contain all method target analytes. Monitoring of the LCS for all target analytes and surrogate spikes. (Refer to SOP No. Q-009-XX-MCX-XX, Control Chart Generation, Maintenance, and Usage.) Acceptance criteria are presented in Section 11.5.

10.7 The use of the matrix spike and matrix spike duplicate will depend in part on what role the laboratory is playing. When the laboratory serves the role as the primary laboratory, then site-specific documents should be consulted. The sample to be used for the MS/MSD may be specified in the field. This previously designated sample would then be spiked with the site-specific target analytes at a concentration equivalent to the site action level. The MS/MSD would be prepared using the primary source standards. If this information was not specified or unknown, then the laboratory would choose a representative

sample from each batch of samples analyzed. If samples from multiple sites were to be analyzed in the same batch, then multiple sets of MS/MSDs may be required. When the laboratory serves the role as the QA laboratory, the above scenario may not be practical to implement. If the site-specific requirements are unknown and samples from multiple sites are analyzed in the same batch, then the laboratory should select at least one sample for spiking. Each batch of samples would then contain at least one MS/MSD pair. Best professional judgement should be used to determine whether or not additional matrix spikes are appropriate. Acceptance criteria are presented in Section 11.6 for percent recovery and RPD.

10.8 The use of the matrix duplicate may also depend in part on the role the laboratory is playing. The selection of a matrix duplicate will be performed as described for the MS/MSD in Section 10.7. Acceptance criteria are presented in Section 11.7 for RPD.

10.9 Surrogate recoveries are calculated for each LCS, method blank, matrix spike, matrix duplicates, and field sample analyzed. Acceptance criteria are listed in Section 11.9.

10.10 The retention times (RTs) of identified compounds need to be checked for each identified compound in samples, and compared to absolute RTs. Refer to Section 11.9.

10.11 All sample analytical results used for final data reporting must be between the low standard and the high standard of the calibration curve. Results which fall below the low standard are to be reported as estimated (J value). Corrective actions are described in Section 11.10.

10.12 MDLs are determined in either reagent water or organic-free sand / soil and verified annually. Project specific requirements might require that an MDL study be performed in the site-specific matrix. Refer to SOP No. Q-019-XX-MCX-XX, Method Detection Limits (MDLs), Method Quantitation Limits (MQLs), and Laboratory Reporting Limits (LRLs). Whenever MDLs are updated, Appendix 1 values should also be updated.

10.13 The analyst must demonstrate proficiency in performing the analysis as outlined in SOP No. Q-016-XX-MCX-XX, Technical Training. Method proficiency must be redemonstrated anytime a major method modification is made, a major software revision is added, or a major instrument modification is made. Demonstration of method proficiency may also be required after major instrument maintenance. This is decided on a case by case basis through discussions with the Section Chief, Laboratory Director, and Laboratory QA Officer.

10.14 All target analytes detected on the primary column must be confirmed on a second column. Acceptance criteria are presented in Section 11.13.

11.0 Data Validation

Site-specific requirements must be checked and used, if known, for data review. The criteria presented in this section should be used as a default in the absence of site-specific requirements. The following items shall be verified and documented using the data review checklist in Figure 4 and 5.

11.1 After a five-point initial calibration curve is analyzed, ensure that the following criteria were met. For the CFs, the %RSD must be less than 20% for all target analytes. Alternatively, the correlation coefficient (r) for the calibration line must be > 0.995.

- If the %RSD of any target analyte is 20% or less, then the CF is assumed to be constant over the calibration range, and the average CF may be used for quantitation.

- If the %RSD of any method target analyte is greater than 20%, calibration curves must be constructed using first or higher order regression fits of the five calibration points. The corresponding correlation coefficients must be ≥ 0.995.

- If these acceptance criteria are not met, then the following corrective actions should be performed: (1) adjust the instrument and/or perform instrument maintenance; or (2) narrow the calibration range using five standards at different concentrations. The low end of the calibration curves must be carefully watched.

If an alternative calibration technique is necessary, refer to SOP No. M-8081-XX-MCX-XX, Organochlorine Pesticides and PCBs, for further information.

11.2 If a 5-point calibration was performed, verify that an ICV was analyzed. The ICV standard compound results must be within 15% of the known values for each compound. If this criterion is not met, perform the following corrective actions:

11.2.1 Check ICV preparation and standard curve preparation for accuracy. If either preparation is found to be in error, redo the appropriate standard preparation and reanalyze. Also, if the ICV does not check due to possible instrumental or injection errors, reanalyze and reassess.

Note: If either of the sources for the standards is being used for the first time, the analyst may gain useful information by referring to a third source standard.

11.2.2 If the ICV is still out of compliance, perform minor instrument maintenance and reinject and reassess.

11.2.3 If ICV is still out of compliance, perform new 5-point curve and ICV verification, remaking all standards from the beginning. If this still does

not correct the problem, perform major instrument maintenance or call instrument manufacturer for instruction.

11.3 After the continuing calibration verification (CCV) standard has been analyzed, ensure it was run at the required frequency (every 8 hours, at the end of the sequence, or initially before daily analysis). Calculate the percent difference as in Section 9.4.

If the percent difference for any compound is less than or equal to 15%, the initial calibration is assumed to be valid. If the criterion is not met (> 15% difference) for any compound, corrective action must be taken. For example:

- Assess the shape and size/area of the peaks and compare to historical data (if applicable)
- Change the guard column
- Check injection volumes
- Remake standards
- Ensure samples and standards are both cut and are in the same matrix.

If this still does not correct the situation, change column and recalibrate instrument with all 5 standards. This above criteria must be met before sample analysis begins and/or reanalysis of all samples up to the last acceptable CCV standard.

11.4 Assess the method blanks. The analyst shall confirm that this blank was extracted at the required frequency. The method blank should not exhibit any contamination above the MDL for any of the method target analytes. Corrective action should be performed any time method target analytes are detected above the MDL to reduce and control contamination. Corrective action will be required if site-specific target analytes are detected at greater than 5% of the regulatory limit for that analyte or if the concentration in the blank is greater than 5% of that in the sample. The first step of corrective action is to assess the effect on the samples. Corrective action would include reanalysis of field and QC samples in the batch if some or all of the samples also contained levels of target analytes that exceeded the above criteria. If none of the field samples had values above the stated criteria, then reanalysis may not be necessary. The source of contamination should still be investigated and reduced/eliminated.

11.5 Assess that LCSs were extracted at the required frequency. Plot the target compounds on appropriate control charts. (Refer to SOP No. Q-009-XX-MCX-XX, Control Chart Generation, Maintenance, and Usage.) If recoveries of all target compounds are not within control limits, the LCS extract is to be reanalyzed for verification. If acceptable, all affected sample extracts should be reanalyzed. If it is still out of control limits, then all field and QC samples in the batch must be reextracted and reanalyzed.

Note: Even though control charts must be maintained for the LCSs, the

acceptance criteria derived from these charts may not be appropriate if the charted ranges are too wide. A maximum default range should be used. It is recommended that the maximum default range be set to 80-120%. ~~{Each laboratory should specify maximum default ranges.}~~

The RPD of interbatch LCSs should fall within the control limits determined from the precision control charts. However, if the RPD is outside these control limits, the batch will not be rejected, as long as the LCS recovery is acceptable. This precision information should be evaluated to see if systematic problems can be identified. If problems are suspected, the method should be fully evaluated.

11.6 Assess that matrix spike/matrix spike duplicates were analyzed at required frequency. The analyst shall also verify that the samples were spiked at the appropriate level. The order of preference for spiking levels is as follows; 1) If the target analyte concentrations are known, spike to increase the background concentration by a factor of approximately two, 2) if an action level exists, spike at this level, or 3) if neither of the first two conditions apply, spike at a level that corresponds between the low and mid-level calibration standards. Acceptance criteria are that all % Recovery and/or RPD results meet project established goals. If no project goals are specified, then results must be within the indicated control limits on the appropriate LCS control charts (if the spike concentration increased the native analyte concentration by a factor of 2 or more). If these conditions are not met, perform the following corrective actions as appropriate.

- If both LCS and MS/MSD recoveries are unacceptable, then the entire batch of field and QC samples must be reextracted.

- If the MS/MSD is unacceptable, but the LCS is acceptable, then a potential matrix effect has been identified. Review the surrogate recovery data. If surrogates are acceptable, reanalyze the MS/MSD extracts to verify a matrix effect. If a matrix effect is still suspected, then the project manager must be contacted to discuss further alternatives and the potential impact on the project. Further alternatives may include reextraction and reanalysis. Reasonable attempts must be made to address a matrix interference.

Note: If the MS/MSD % recovery is outside LCS limits because the native analyte concentration is greater than the spike by a factor of 2 or more and the sample had to be diluted, a matrix effect is not demonstrated.

11.7 Assess matrix duplicates were analyzed at required frequency. Acceptance criteria are that all RPD results meet project established goals. If no project goals are specified, then results must be within the indicated control limits on the appropriate LCS precision control charts. Refer to SOP No. Q-009-XX-MCX-XX, Control Chart Generation, Maintenance, and Usage. The acceptance criteria derived from these charts may not be appropriate if the charted ranges are too wide. A maximum default range of 25% RPD should be used for samples with target analyte concentrations ≥ 10 times the MDL. ~~{Each~~

~~laboratory should specify maximum default ranges.]~~ If these conditions are not met, perform the following corrective actions as appropriate.

- Reanalyze the sample extract to verify a matrix effect.

- If the duplicate precision is still unacceptable, then a potential matrix effect has been identified. The project manager must be contacted to discuss further alternatives and the potential impact on the project. Further alternatives may include reextraction and reanalysis.

11.8 Check the surrogate calculations for correctness for all samples, blanks, LCS, MS, MSD, and MD. Check that the surrogate recoveries are properly control-charted for the LCS. The following acceptance criteria apply to surrogate recoveries.

- The surrogate recoveries for the method blank(s) and LCS(s) must be within control limits on the LCS control charts. If it is suspected that failure was due to instrumental malfunction, the sample extracts are reanalyzed. If recoveries fail reanalysis, then reextraction is necessary.

- Sample, MS, MSD, and MD surrogate recoveries are compared to the LCS control chart. A maximum default range of 60-125% should be used. ~~[Each laboratory should specify default ranges for each matrix.]~~ If results are outside these limits but the LCS surrogate recoveries are acceptable, the extracts of the sample(s), MS, MSD, or MD with the unacceptable surrogate recoveries shall be reanalyzed. If still out, the project manager is to be contacted to discuss further alternatives and the impact on the project. Further alternatives may include reextraction and reanalysis.

11.9 The retention times must be checked for all identified compounds in both standards and samples. The calibration standard absolute retention times should also be checked for all initial and continuing calibrations. Retention time noncompliances are attributed to changes in temperature during analysis if a column heater is not used, and to subtle changes in the ratio of aqueous phase to organic phases of the mobile phase over the course of the analysis. Unless a gradient is used or there is a leak, the flow rate seldom changes. The corrective actions are to isolate the cause of retention time noncompliances, correct the situation, and reinject the sample. Acceptance criteria are as follows:

11.9.1 The retention time of all target analytes and surrogates in the CCVs must fall within the absolute retention time windows calculated in 8.5.5.5. If the retention time of any target analyte does not fall within the ±3SD window, then a new initial calibration curve for the failed analytes is necessary unless system maintenance corrects the problem. Reanalysis of all affected sample extracts must also be performed for those failed analytes.

11.9.2 The analyte RT must fall within the absolute retention time window within (± 3 standard deviations of the RTs for each standard will be used to define the retention time window) (see Section 8.5.5). However, the experience of the analyst should weigh heavily in the interpretation of the chromatographs.

11.10 The analyst must verify all reported results are derived from analytical results that are either above the LRL or below the highest standard of the initial calibration curve. Verify the results are reported as follows:

- Sample concentrations that have been analyzed using the extract in its most concentrated form, and are below the MDL, should report the result as less than the LRL.

- Sample results (again using the extract in its most concentrated form) that are above the MDL but below the low standard need to be flagged as estimates, (J) values, when reported.

- For samples that exceed the calibration curve, dilute and analyze an appropriate sample aliquot.

11.11 Besides the items listed in Sections 11.1 through 11.10, the analyst should also verify the additional item as noted in Figures 3 and 5.

11.12 Additional levels of review are performed as described in SOP No. Q-024-XX-MCX-XX, Data Reduction and Review/Validation (In-House/Contractor Data) and can be documented on forms such as those presented in Figures 4 and 5.

11.13 For confirmation purposes, target analytes on the second column must fall within established retention time windows. Analyte concentrations on the two columns must be within 40% RPD. ~~[Each laboratory should insert default.]~~ It should be noted that coeluting compounds (e.g., TNB/DNB, 2,6-DNT, 2-A-DNT/4-A-DNT) may not have an accurate concentration for both columns when both compounds are present. Analyst experience is important when confirming the presence of target compounds.

12.0 Waste Disposal

This procedure generates organic solvent wastes. All waste disposal procedures must comply with all federal and local regulations. Refer to the Laboratory's Waste Management Plan. ~~Solvent wastes are collected in DOT approved containers in the Explosives Laboratory. When a container is full, a Hazardous Waste Profile Sheet (WES Form 1930) is completed and the waste is turned over to the ECB Hazardous Waste Officer. The waste is then transfered to the WES Logistics Management Office, Material Control Section. All radioactive waste is collected in contained areas that are designated by the ECB Safety Officer. The radioactive waste is given to the Radio-Isotope Lab for proper disposal. [Each laboratory should describe how solvent wastes are accumulated, stored, and disposed of.]~~

13.0 References

13.1 Nitroaromatics and Nitroamines by HPLC. Method 8330. (Test Method for Evaluating Solid Waste Physical/Chemical Methods), SW-846, 3rd Edition, Update II, September 1994.

13.2 Bauer, C.F., T.F. Jenkins, S.M. Koza, P.W. Schumacher, P.H. Miyares and M.E. Walsh (1989). Development of an analytical method for the determination of explosive residues in soil. Part 3. Collaborative test results and final performance evaluation. USA Cold Regions Research and Engineering Laboratory, CRREL Report 89-9.

13.3 Grant, C.L., A.D. Hewitt and T.F. Jenkins (1989) Comparison of low concentration measurement capability estimates in trace analysis: Method Detection Limits and Certified Reporting Limits. USA Cold Regions Research and Engineering Laboratory, Special Report 89-20.

13.4 Jenkins, T.F., C.F. Bauer, D.C. Leggett and C.L. Grant (1984) Reversed-phased HPLC method for analysis of TNT, RDX, HMX and 2,4-DNT in munitions wastewater. USA Cold Regions Research and Engineering Laboratory, CRREL Report 84-29.

13.5 Jenkins, T.F. and M.E. Walsh (1987) Development of an analytical method for explosive residues in soil. USA Cold Regions Research and Engineering Laboratory, CRREL Report 87-7.

13.6 Jenkins, T.F.,P.H. Miyares, and M.E. Walsh (1988a) An improved RP-HPLC method for determining nitroaromatics and nitramines in water. USA Cold Regions Research and Engineering Laboratory, Special Report 88-23.

13.7 Jenkins, T.F. and P.H. Miyares (1992) Comparison of Cartridge and Membrane Solid-Phase Extraction with Salting-out Solvent Extraction for Preconcentration of Nitroaromatic and Nitramine Explosives from Water. USA Cold Regions Research and Engineering Laboratory, Draft CRREL Special Report.

13.8 Jenkins, T.F., P.W. Schumacher, M.E. Walsh and C.F. Bauer (1988b) Development of an analytical method for the determination of explosive residues in soil. Part II: Further development and ruggedness testing. USA Cold Regions Research and Engineering Laboratory, CRREL Report 88-8.

13.9 Leggett, D.C., T.F. Jenkins and P.H. Miyares (1990) Salting-out solvent extraction for preconcentration of neutral polar organic solutes from water. Analytical Chemistry, 62: 1355-1356.

13.10 Miyares, P.H. and T.F. Jenkins (1990) Salting-out solvent extraction for determining low levels of nitroaromatics and nitramines in water. USA Cold

Regions Research and Engineering Laboratory, Special Report 90-30.

13.11 Gas Chromatography. Method 8000B. (Test Method for Evaluating Solid Waste Physical/Chemical Methods), SW-846, 3rd Edition, proposed Update III, January 1995.

13.12 SOP No. Q-005-XX-MCX-XX, Sample Receipt, Login, and Storage.

13.13 SOP No. Q-008-XX-MCX-XX, Reagent Water Generation and Quality Monitoring.

13.14 SOP No. Q-021-XX-MCX-XX, Subsampling of Containers.

13.15 SOP No. Q-019-XX-MCX-XX, Method Detection Limits (MDLs), Method Quantitation Limits (MQLs), and Laboratory Reporting Limits (LRLs).

13.16 SOP No. Q-016-XX-MCX-XX, Technical Training.

13.17 SOP No. Q-009-XX-MCX-XX, Control Chart Generation, Maintenance, and Usage.

13.18 SOP No. Q-024-XX-MCX-XX, Data Reduction and Review/Validation (In-House/Contractor Data).

13.19 SOP No. M-8081-XX-MCX-XX, Organochlorine Pesticides and PCBs.

13.20 WES Logistics Management Office, Material Control Section. ~~[Identify MSC laboratory]~~ Waste Management Plan.

Appendix 1
MDLs and Laboratory Reporting Limits (LRLs)

Compound	Water (mg/L)						Soil (mg/kg)	
	Low-Level Salt-Out		Low-Level SPE		High Level			
	MDL	LRL	MDL	LRL	MDL	LRL	MDL	LRL
HMX	0.00006	0.00030	0.00005	0.00018	0.004	0.02	0.02	0.2
RDX	0.00010	0.00050	0.00009	0.00021	0.005	0.02	0.02	0.2
TNB	0.00005	0.00025	0.00005	0.00017	0.004	0.02	0.02	0.1
DNB	0.00005	0.00025	0.00005	0.00016	0.003	0.02	0.02	0.1
Tetryl	0.00008	0.00040	0.00007	0.00023	0.006	0.02	0.03	0.2
NB	0.00013	0.00065	0.00012	0.00041	0.002	0.02	0.01	0.2
TNT	0.00005	0.00025	0.00005	0.00017	0.003	0.02	0.02	0.1
4-A-DNT	0.00006	0.00030	0.00006	0.00020	0.002	0.02	0.02	0.2
2-A-DNT	0.00007	0.00035	0.00005	0.00017	0.002	0.02	0.01	0.25
2,4-DNT	0.00009	0.00045	0.00009	0.00021	0.005	0.02	0.02	0.15
2,6-DNT	0.00014	0.00070	0.00013	0.00043	0.005	0.02	0.02	0.2
2-NT	0.00009	0.00045			0.004	0.02	0.04	0.2
3-NT	0.00012	0.00060			0.004	0.02	0.04	0.2
4-NT	0.00014	0.00070			0.004	0.02	0.04	0.2

~~[Each laboratory should revise table as appropriate.]~~

Appendix 2
Retention Times

Compound	Column 1	Column 2
HMX	3.25	12.12
RDX	4.53	8.05
TNB	8.13	5.15
DNB	7.32	5.15
Tetryl	8.08	9.87
NB	8.52	4.65
TNT	9.80	6.20
4-A-DNT	10.45	6.67
2-A-DNT	10.45	7.15
2,6-DNT	10.33	5.73
2,4-DNT	11.57	5.98
2-NT	14.05	5.22
4-NT	15.01	5.32
3-NT	15.89	5.22

~~[Each laboratory should revise table as appropriate.]~~

Soil Extraction Log
[Identify MSC Laboratory]

Batch No(s):	Extraction: ☐ SOP #
Extracted Date:	Clean-up: ☐ SOP #

Type	Lab ID No.	% Dry Weight	Sample Aliquot (g)	Final Vol. mL (pre-cleanup)	Clean Up Aliquot (mL)	Final Vol. mL (postcleanup)	Sample Comments
MB							
LCS							
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							
MD							
MS							
MSD							

rrogate Std #: _____ Amount: _____

S Std #: _____ Amount: _____

S/MSD Std #: _____ Amount: _____

tness: _____ Date: _____

lvents/Reagent Lots:

_____ _____

_____ _____

:raction Analyst(s): _____ KD Analyst(s): _____ Clean Up Analyst(s): _____

viewed by: _____ Date: _____

Figure 1.

USACE Logo

Soil Extraction Log
[Identify MSC Laboratory]

Batch No(s):	Extraction: ☐ SOP #
Extracted Date:	Clean-up: ☐ SOP #

Type	Lab ID No.	% Dry Weight	Sample Aliquot (g)	Final Vol. mL (pre-cleanup)	Clean Up Aliquot (mL)	Final Vol. mL (postcleanup)	Sample Comments
MB							
LCS							
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							
MD							
MS							
MSD							

rrogate Std #: _____ Amount: _____

S Std #: _____ Amount: _____

/MSD Std #: _____ Amount: _____

tness: _____ Date: _____

vents/Reagent Lots:

_____ _____

_____ _____

raction Analyst(s): _____ KD Analyst(s): _____ Clean Up Analyst(s): _____

iewed by: _____ Date: _____

Figure 1. Example.

USACE Logo

Aqueous Extraction Log
[Identify MSC Laboratory]

Batch No(s): | Extraction: ☐ SOP #

Extracted Date: | Clean-up: ☐ SOP #

Type	Lab ID No.	Sample Aliquot (g)	Final Vol. mL (pre-cleanup)	Clean Up Aliquot (mL)	Final Vol. mL (postcleanup)	Sample Comments
MB						
CS						
0						
1						
2						
3						
4						
5						
6						
7						
8						
9						
0						
D						
S						
SD						

rogate Std #: _____ Amount: _____

Std #: _____ Amount: _____

MSD Std #: _____ Amount: _____

ness: _____ Date: _____

ents/Reagent Lots:

_____ _____

_____ _____

action Analyst(s): _____ KD Analyst(s): _____ Clean Up Analyst(s): _____

Reviewed by: _____ Date: _____

Figure 2.

USACE Logo

Aqueous Extraction Log
[Identify MSC Laboratory]

Batch No(s):	Extraction: ☐ SOP #
Extracted Date:	Clean-up: ☐ SOP #

Type	Lab ID No.	Sample Aliquot (g)	Final Vol. mL (pre-cleanup)	Clean Up Aliquot (mL)	Final Vol. mL (postcleanup)	Sample Comments
MB						
LCS						
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
MD						
MS						
MSD						

rogate Std #: _____ Amount: _____

S Std #: _____ Amount: _____

/MSD Std #: _____ Amount: _____

ness: _____ Date: _____

vents/Reagent Lots:

_____ _____

_____ _____

raction Analyst(s): _____ KD Analyst(s): _____ Clean Up Analyst(s): _____

Reviewed by: _____ Date: _____

Figure 2. Example.

USACE Logo

HPLC Instrument Log (Explosives)
[Identify MSC Laboratory]

Instrument ID:

Column ID:

Injection Volume:

Batch No(s):

Start Date:

Flow Rate:

Detector:

Method:

SOP Number:

Lab ID	Instrument File ID	Low Level Method	High Level Method	Dilutions	Comments

V Lot #: _____ Conc. _____ Amount _____

/ Lot #: _____ Conc. _____ Amount _____

:ness: _____

LC Analyst: _____

/iewer: _____ Date: _____

Figure 3.

HPLC Instrument Log (Explosives)
[Identify MSC Laboratory]

Instrument ID: Flow Rate:

Column ID: Detector:

Injection Volume:

Batch No(s): Method:

Start Date: SOP Number:

Lab ID	Instrument File ID	Low Level Method	High Level Method	Dilutions	Comments

CCV Lot #: _____ Conc. _____ Amount _____

ICV Lot #: _____ Conc. _____ Amount _____

Witness: _____

HPLC Analyst: _____

Reviewer: _____ Date: _____

Figure 3. Example.

Lab Data Review Check List
Organic Extractions
[Identify MSC Laboratory]

Project Number(s)	
Batch Number(s)	
Extraction SOP No.	Clean-up SOP No. (if applicable)

Review Item	Yes (x)	No (x)	N/A (x)	2nd Level Review (x)
Were the project number, batch number, and sample identification number(s) properly recorded?				
Were the weight/volume of sample extracted and the final extract volume properly recorded?				
Were extraction sample dilutions or concentration factors properly recorded?				
Was a method blank prepared at the required frequency using a blank solid/liquid matrix?				
Was a Laboratory Control Sample (LCS) prepared at the required frequency?				
Were a matrix spike (MS) and matrix spike duplicate (MSD) prepared at the proper frequency?				
Were the matrix duplicates (MD) prepared at the proper frequency?				
Were correct surrogates used?				
Are there any Corrective Action Reports associated with this sample batch?				
Are copies of Corrective Action Reports attached?				
Were the spiking volume, stock source, and spike concentration properly recorded for the MS/MSD and LCS?				

NOTES: _____

_____

_____

nalyst: _____ Date: _____

nd Level Reviewer: _____ Date: _____

Figure 4.

Lab Data Review Check List
Organic Extractions
[Identify MSC Laboratory]

Project Number(s)	
Batch Number(s)	
Extraction SOP No.	Clean-up SOP No. (if applicable)

Review Item	Yes (x)	No (x)	N/A (x)	2nd Level Review (x)
Were the project number, batch number, and sample identification number(s) properly recorded?				
Were the weight/volume of sample extracted and the final extract volume properly recorded?				
Were extraction sample dilutions or concentration factors properly recorded?				
Was a method blank prepared at the required frequency using a blank solid/liquid matrix?				
Was a Laboratory Control Sample (LCS) prepared at the required frequency?				
Were a matrix spike (MS) and matrix spike duplicate (MSD) prepared at the proper frequency?				
Were the matrix duplicates (MD) prepared at the proper frequency?				
Were correct surrogates used?				
Are there any Corrective Action Reports associated with this sample batch?				
Are copies of Corrective Action Reports attached?				
Were the spiking volume, stock source, and spike concentration properly recorded for the MS/MSD and LCS?				

NOTES: _____

_____

_____

Analyst: _____ Date: _____

2nd Level Reviewer: _____ Date: _____

Figure 4. Example.

Lab Data Review Check List
HPLC
[Identify MSC Laboratory]

Project Number(s):

Batch Number(s):

Method:

Review Item	Yes (x)	No (x)	N/A (x)	2nd Level Review (x)
A. Initial Calibration 1. Does the curve consist of five Calibration Standards?				
2. Is the low standard near, but above, the MDL?				
3. Are calibration factors updated or were curves drawn and are CFs and %RSDs within QC limits?				
4. Are retention time windows established and updated?				
B. Continuing Calibration 1. Are the Continuing Calibration Verification (CCV) standards run every 8 hours and at the end of the analytical sequence?				
2. Is the % difference within QC limits?				
C. Sample Analysis 1. Are all sample holding times met?				
2. Are all samples with concentrations > the highest standard used for initial calibration diluted and reanalyzed?				
3. Are reported compounds within retention time windows?				
4. Are all hits confirmed on a second column?				
5. Are surrogate recoveries within QC limits?				
D. QC Samples 1. Is the Method Blank run at the desired frequency and is its concentration for target analytes less than the MDLs?				
2. Is the ICV from a second source and its recovery within QC limits?				
3. Is the Laboratory Control Sample percent recovery within QC limits?				
4. Is the Matrix Spike/Matrix Spike Duplicate run at the desired frequency and is the percent recovery/RPD within QC limits?				

Figure 5.

Lab Data Review Check List
HPLC
[Identify MSC Laboratory]

Review Item	Yes (x)	No (x)	N/A (x)	2nd Level Review (x)
4. Is the Matrix Duplicate run at the desired frequency and is the RPD within QC limits?				
E. Others 1. Are all nonconformances included and noted?				
2. Is the correct methodology used for sample prep and analysis?				
3. Are all calculations checked at the minimum frequency?				
4. Did analyst sign/date the appropriate printouts and report sheets?				
5. Are all sample ID and units checked for transcription errors?				

Comments on any "No" response:

_____

_____

_____

_____

_____

_____

Analyst: _____ Date: _____

Second-Level Review: _____ Date: _____

Figure 5. (Cont.)

Lab Data Review Check List
HPLC
[Identify MSC Laboratory]

Project Number(s):

Batch Number(s):

Method:

Review Item	Yes (x)	No (x)	N/A (x)	2nd Level Review (x)
A. Initial Calibration 1. Does the curve consist of five Calibration Standards?				
2. Is the low standard near, but above, the MDL?				
3. Are calibration factors updated or were curves drawn and are CFs and %RSDs within QC limits?				
4. Are retention time windows established and updated?				
B. Continuing Calibration 1. Are the Continuing Calibration Verification (CCV) standards run every 8 hours and at the end of the analytical sequence?				
2. Is the % difference within QC limits?				
C. Sample Analysis 1. Are all sample holding times met?				
2. Are all samples with concentrations > the highest standard used for initial calibration diluted and reanalyzed?				
3. Are reported compounds within retention time windows?				
4. Are all hits confirmed on a second column?				
5. Are surrogate recoveries within QC limits?				
D. QC Samples 1. Is the Method Blank run at the desired frequency and is its concentration for target analytes less than the MDLs?				
2. Is the ICV from a second source and its recovery with QC limits?				
3. Is the Laboratory Control Sample percent recovery within QC limits?				
4. Is the Matrix Spike/Matrix Spike Duplicate run at the desired frequency and is the percent recovery/RPD within QC limits?				

Figure 5. Example.

Lab Data Review Check List
HPLC
[Identify MSC Laboratory]

Review Item	Yes (x)	No (x)	N/A (x)	2nd Level Review (x)
4. Is the Matrix Duplicate run at the desired frequency and is the RPD within QC limits?				
E. Others 1. Are all nonconformances included and noted?				
2. Is the correct methodology used for sample prep and analysis?				
3. Are all calculations checked at the minimum frequency?				
4. Did analyst sign/date the appropriate printouts and report sheets?				
5. Are all sample ID and units checked for transcription errors?				

Comments on any "No" response:

_____

_____

_____

_____

_____

_____

Analyst: _____ Date: _____

Second-Level Review: _____ Date: _____

Appendix 3
Preparation of Compost and Plant Samples

1.0 Compost Samples

1.1 Thoroughly mix sample as defined in SOP No. 0-021-XX-MCX-XX, Subsampling of Containers. Weigh a disposable weigh dish and record the weight in the laboratory sample prep logbook. Weigh out 2-4 grams of the wet sample into the disposable weigh dish. Record the combined weight of the sample and disposable weigh dish into the sample prep logbook. Subtract the weight of the disposable weigh dish and record the wet weight of the sample. Allow the sample to dry. A forced air oven at room temperature may also be used.

1.2 After drying, weigh the sample in the disposable weigh dish and record the combined weight in the sample prep logbook. Subtract the weight of the pan and record the weight of the dry sample. Divide the weight of the dry sample by the weight of the wet sample to obtain the percent solid. Record the percent solid in the sample prep logbook.

1.3 Weigh out approximately 5.0 grams ± 0.5 g of each wet compost sample (record the weight in the laboratory sample prep logbook) into a 20 mL glass vial with a Teflon lined cap.

1.4 Calculate the dry weight of the compost by multiplying the weight wet and the percent solid. Subtract the calculated dry weight from the wet weight of the compost to obtain the percent moisture in the sample.

1.5 Spike samples and associated QC samples with surrogate and matrix spike spiking solutions (see Sections 7.10 and 7.11).

1.6 Volumetrically add 10.0 mL of acetonitrile.

1.7 Using a vortex mixer, swirl for one minute, and place in a cooled ultrasonic bath for 18 hours.

1.8 After sonication, allow sample to settle for 30 minutes. If the sample has not completely settled, place in the centrifuge at 2500 rpm for 5 minutes. Remove 5 mL of supernatant, using a 5 mL pipet with disposable tips, and put in a 20 mL vial. Volumetrically add 5 mL of calcium chloride solution (Section 7.4) to the 5 mL of supernatant. Vortex for 2 minutes and let stand for 15 minutes.

1.9 Using a disposable glass pasteur pipet, place the supernatant in a disposable plastic syringe and filter through a 0.50 µm Teflon filter attached to the syringe. Discard the first 3 mL and retain the remainder in a 10 mL glass Teflon capped vial for HPLC analysis as in Section 8.6.

1.10 Sample Dilution - See Section 8.4.8.

1.11 All radioactive samples will be prepared according to Appendix 3, Section 1. The samples will be contained only in areas which are designated by the ECB Safety Officer for radioactive prep work.

1.12 HPLC Calibration and Analysis - See Section 8.0.

1.13 Calculations of Analyte Concentration - See Section 9.5.2.

0 Plant Samples

2.1 Allow the samples to come to room temperature. Take a subsample of the plant and place it onto a clean papertowel to remove any excess moisture.

2.2 Using Table 8, weigh out the appropriate fresh weight ± 0.5 g of the plant species and record in the plant prep logbook.

2.3 Using scissors and/or knife, cut the fresh samples into small pieces.

2.4 Place the cut plant material into a homogenizing chamber. Add enough Milli-Q water to just cover the top of the sample. Homogenize using a sawtooth generator probe, beginning at 500 rpm. Once 500 rpm has been reached, increase in increments of 2500 rpm, 5000 rpm, and 7500 rpm. Homogenize at 10000 rpm until the sample is near a frothy paste.

2.5 After homogenizing the sample to a frothy paste, pour the sample into the 120 mL amber freeze-dried flasks. Cover the flask with parafilm and place in the freezer until frozen (approximately 1-2 hours).

2.6 Rinse the generator probe between samples by homogenizing Milli-Q water in a flask.

2.7 Insert a freeze dried adapter (not well-made freeze dried adapter) and rubber top. Place the flask upside down in the freezer flask and allow the frozen sample. Insert the exposed end into a valve on the freeze dried condenser.

2.8 Turn the plastic valve stem to the "vacuum" position. Once the vacuum reading has dropped to below 200, add the next sample.

2.9 Remove the sample from the freezer when the flask is no longer cool to touch and no ice chunks or crystals are left in the sample (approximately 2 days to dry most samples). Remove flask from freeze dried by turning the plastic valve stem to the "vent" position. Remove the rubber top from the sample flask.

2.10 Place a disposable weigh dish onto the balance and tare. Scoop out the freeze dried sample into the disposable weigh dish. Record the dry weight in the plant prep logbook.

2.11 Weigh out 0.25 grams of each freeze dried sample (record weight in plant prep logbook) into a 20-mL glass vial with a Teflon lined cap.

2.12 Spike samples and associated QC samples with surrogate and matrix spike spiking solutions (see Sections 7.10 and 7.11).

2.13 Volumetrically add 10.0 mL of acetonitrile.

2.14 Using a vortex mixer, swirl for one minute, and place in a cooled ultrasonic bath for 18 hours.

2.15 After sonication, place sample into the centrifuge at 2500 rpm for 5 minutes. Allow the sample to sit for approximately 1 hour.

2.16 Remove 5 mL of supernatant, using a 5-mL pipet with disposable tips, and put in a 20-mL vial.

2.17 Prepare enough filter columns to clean-up all of the samples.

2.17.1 Place a small piece of glass wool into a 5 3/4" glass disposable pipette.

2.17.2 Place 0.5 g of florisil into the pipette.

2.17.3 Place 0.5 g of alumina into pipette (on top of florisil).

2.18 Rinse the filter column with 5 mL of acetonitrile. Discard the filtrate.

2.19 Supernatant is added to the filter column using a glass disposable pipette. Collect the filtrate in a 20 mL glass vial.

2.20 After the supernatant has completely filtered through, filter 5 mL of acetonitrile through the column, collecting in the 20 mL glass vial containing the filtered supernatant.

2.21 Vortex the filtered supernatant for one minute.

2.22 Volumetrically transfer 2 mL of the filtered supernatant, using a 5-mL pipet with disposable tips, and put in a 20 mL vial. Volumetrically transfer 2 mL of Milli-Q water into the same 20 mL vial.

2.23 Using a disposable glass pasteur pipet, attach the supernatant to a disposable syringe and filter through a 0.45 [illegible] filter into the syringe. Discard the first 4 mL and retain the remainder in a 10 mL glass Teflon capped vial for HPLC analysis as in Section 8.6.

2.24 Sample Dilution - See Section 8.4.8.

2.25 All radioactive samples will be prepared according to Appendix 3, Section 2. The samples will be contained only in areas which are designated by the ECB Safety Officer for radioactive prep work.

2.26 HPLC Calibration and Analysis - See Section 8.D.

2.27 Calculations of Analyte Concentrations - See Section 9.5.2.

Table 8 Plant Species

PLANT SPECIES	FRESH WEIGHT
Cyperus	5.00g
Aquatics	5.00g
Corn Kernels	10.0g
Corn Silage	10.0g
Tomato	20.0g
Lettuce	20.0g
Radish	20.0g

TITLE: Acid Digestion of Sediments, Sludges, and Soils (SW-846 Method 3050A)

WES 12/.4

SOP NUMBER: M-3050A-00-~~MCX~~-XX

PREPARED BY: _____
Date

REVIEWED BY: _____
Technical Specialist Date

_____
QA Officer Date

_____
Laboratory Director Date

SOP MANUAL CONTROL NO.: _____

1.0 Scope and Application

1.1 This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectroscopy (FLAA and GFAA, respectively) or by inductively coupled argon plasma spectroscopy (ICP).

1.2 Samples prepared by this method may be analyzed by ICP for all the listed metals, or by FLAA or GFAA as indicated below in Table 1.

Table 1. Techniques for Metals Analysis

Analyte	Technique	Symbol	CAS #
Aluminum	ICP/FLAA	Al	7429-90-5
Arsenic	ICP/GFAA	As	7440-38-2
Barium	ICP/FLAA	Ba	7440-39-3
Beryllium	ICP/FLAA/GFAA	Be	7440-41-7
Cadmium	ICP/FLAA/GFAA	Cd	7440-43-9
Calcium	ICP/FLAA	Ca	7440-70-2
Chromium	ICP/FLAA/GFAA	Cr	7440-47-3
Cobalt	ICP/FLAA/GFAA	Co	7440-48-4
Copper	ICP/FLAA	Cu	7440-50-8
Iron	ICP/FLAA/GFAA	Fe	7439-89-6
Lead	ICP/FLAA/GFAA	Pb	7439-92-1
Magnesium	ICP/FLAA	Mg	7439-95-4
Manganese	ICP/FLAA	Mn	7439-96-5
Molybdenum	ICP/FLAA/GFAA	Mo	7439-98-7
Nickel	ICP/FLAA	Ni	7440-02-0
Osmium	ICP/FLAA	Os	
Potassium	ICP/FLAA	K	7440-09-7
Selenium	ICP/GFAA	Se	7782-49-2
Silver	ICP/FLAA	Ag	7440-22-4
Sodium	ICP/FLAA	Na	7440-23-5
Thallium	ICP/FLAA/GFAA	Tl	7440-28-0
Vanadium	ICP/FLAA/GFAA	V	7440-62-2
Zinc	ICP/FLAA	Zn	7440-66-6

2.0 Method Summary

A representative 1 ~~to 2~~ g (~~wet~~ dry weight) sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Hydrochloric acid is used for flame AA and ICP analyses and nitric acid is used for furnace AA work.

2.1 Dilute hydrochloric acid is used as the final reflux acid for the ICP analysis of As and Se, and the flame AA or ICP analysis of Ag, Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Os, Pb, Tl, V, and Zn.

2.2 Dilute nitric acid is employed as the final dilution acid for the furnace AA analysis of As, Be, Cd, Cr, Co, Fe, Pb, Mo, Se, Tl, and V.

2.3 The diluted samples have an approximate acid concentration of 5.0% (v/v).

3.0 Health and Safety

3.1 Use of this procedure requires the handling of reagents and corrosive acids, therefore, protective equipment must be utilized. Minimum personal protection includes the use of laboratory safety glasses, a lab coat or apron, and protective gloves. All digestions must be performed in a fume hood.

3.2 For specific information regarding the toxicity of the acids used in this procedure and other related health and safety issues including the proper storage and handling of reagents and chemicals, the analyst should consult the appropriate Material Safety Data Sheets (MSDS). located in room 69. ~~[Each laboratory should specify location of MSDSs.]~~

3.3 Use of this procedure requires the handling of concentrated acids, nitric and hydrochloric acid. Prior to performing this procedure, the analyst should be familiar with the proper use of corrosive liquid spill kits and containment procedures. Spill kits are located in room 69. ~~[Each laboratory should insert appropriate information on the location, use, and disposal of spill kits. This information should list the specific types of spill kits available and their specific uses i.e., acids, bases, other liquids.]~~

4.0 Sample Preservation, Containers, Handling, and Storage

4.1 Requirements for sample preservation, sample containers, and sample storage are detailed in SOP No. Q-005-XX-MCX-XX, Sample Receipt, Login, and Storage Procedures.

4.2 This method requires the digestion of ~~2~~ 1 g of dry gound sample. It is recommended that a minimum of 50 g be available to allow for QC analyses and possible reanalyses.

4.3 All containers used to store digestates must be pre-washed with detergents, acids, and reagent water. Refer to SOP No. Q-012-XX-MCX-XX, Glassware Cleaning.

4.4 Samples for metals analysis must be digested and analyzed within 6 months of sample collection. Digestates are stored in low-density, polyethylene (LDPE) bottles at room temperature.

5.0 Interferences and Potential Problems

5.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether Method 3050A is applicable to a given waste.

5.2 Refer to the appropriate analytical method SOPs for a discussion of the possible interferences that may be encountered during the analysis of the digestates.

5.3 During the digestion, the samples must be monitored closely so as to prevent the sample from boiling or going to dryness. The temperature of the heating device should be adjusted so that a gentle sample reflux develops and the sample slowly evaporates, but does not boil or bump. If the samples begin to boil, immediately lower the temperature of the heating device.

5.4 Samples must be covered between digestion steps to avoid picking up dust particles.

5.5 The sample digestion area must be kept as clean as possible. This involves regular cleaning of the area and hoods.

6.0 Equipment/Apparatus

6.1 Technicon BD-20 digestion tubes ~~Conical Phillips beakers, or equivalent — [each laboratory should insert type and size of beaker used], (250 mL is recommended).~~

6.2 ~~Watch glasses — Glass, ribbed and non-ribbed watch glasses of sufficient diameter to cover the Phillips beakers. [Each laboratory should insert watch glass make and size.]~~

6.3 Qualitative filter paper, S & S, White ribbon, # 589. ~~Whatman 41 or equivalent [each laboratory shall insert make, size, and type of filter paper used], or centrifugation equipment [if used, laboratory shall list manufacturer, model, and all associated equipment]~~.

6.4 Graduated cylinders — Class A, 100-mL, 500-mL.

6.5 Volumetric flasks — Class A, 100-mL, 1000-mL.

6.6 Automatic pipets or acid-dispensing bottles, accurate to within ± 0.1 mL. Brinkman Dispensette, 2ml to 10mL ~~[Each laboratory should insert type of dispensing bottle used.]~~

6.7 Nalgene polyethylene or equivalent material, squeeze bottles, for dispensing reagent water and for general rinsing purposes.

6.8 Filter funnels,Urbanti,high speed filter funnels, molded TPX, 70mm ~~polyethylene, glass, or equivalent material. Disposable filter funnels may be used. [Each laboratory should insert size, type, and make of filter funnel].~~

6.9 Hotplate or equivalent heating device, ~~with temperature control~~. Tecator Digestion Block 2020 or 1015 with autostep 1012 controller. ~~[Each laboratory should insert type of heating device used and how the temperature will be monitored].~~

6.10 Analytical Balance — Capable of accurately weighing to the nearest 0.01 g.

6.11 Polyethylene bottles for storing digestates, Eagle Picher, 125mL, HDPE, wide mouth nalgene, Level 1, wash C ~~125 mL, with caps [laboratory should specify type, size, and supplier].~~

7.0 Reagents

7.1 Reagent water — As defined in SOP No. Q-008-XX-MCX-XX, Reagent Water Generation and Quality Monitoring.

7.2 Acids must be of sufficient purity for the analytical methods to be employed. Acids must be analyzed to determine levels of impurities. If a method blank with the acid is < MDL, the acid can be used. This should be verified for each new lot of acid.

7.2.1 Concentrated nitric acid, (HNO_3) — ~~for example~~, Fisher TraceMetal grade, Cat.# A-509 or equivalent. ~~[Each laboratory should specify type and vendor.]~~

7.2.2 Concentrated hydrochloric acid, (HCl) — ~~for example~~, Fisher TraceMetal grade Cat.# A-508 or equivalent. ~~[Each laboratory should specify type and vendor.]~~

7.2.3 Nitric acid, (1:1). Using a 500-mL graduated cylinder, measure 250 ± 50 mL of reagent water into a 1-L volumetric flask. Using the same 500-mL graduated cylinder, measure 500 ± 10 mL of concentrated nitric acid and slowly add it to the volumetric flask containing the reagent water. Bring to volume with reagent water, mix. This reagent can be stored in a 1-L plastic bottle at room temperature.

7.3 Hydrogen peroxide (30%), H_2O_2 — ACS reagent grade. This solution is commercially available. H_2O_2 must be stored in a refrigerator away from flammable and combustible materials. Once opened, 30% H_2O_2 should be disposed of after 6 months.

7.4 Metal stock calibration solutions shall be purchased as certified solutions from commercial suppliers (SPEX plasma grade or equivalent). Certificates must be kept on file. Calibration standards are from Alfa Aesar, STK# 35422 ~~[Each laboratory should specify the supplier, catalog number, and concentration of purchased solutions.]~~ All stock standards must be replaced after one year.

7.4.1 Primary source standards shall be used to prepare the initial calibration curve, continuing calibration verification (CCV) standard, laboratory control sample (LCS), and matrix spikes and their duplicates (MS/MSDs).

7.4.2 Secondary source standards shall be used to verify the initial calibration (ICV) curve only. These standards shall be purchased from a different vendor, unless the primary vendor can supply different lot numbers.

7.5 Matrix spike (MS) standard

7.5.1 The matrix spike standard shall be prepared from the calibration stock standard (primary) in Section 7.4.1. by adding 1mL of stock to the matrix spike sample. ~~[Each laboratory should specify how the MS standard is prepared.]~~

7.5.2 The spike should be at a level that would approximately double the concentration of the target analytes present. In the absence of target analytes, the spike would be made at the site action level, assuming that this level did not also correspond to the value of the low standard used. If the action level is the same as the low standard used, then the spiking would occur at a slightly higher level, i.e., at the value of the next calibration standard used. If the action level is not known, the spiking level would then default to a concentration between the low and mid-level of the initial calibration standards.

7.5.3 All method analytes should be contained in the MS spike. Subsets may be used based on project specific requirements.

7.6 Laboratory Control Sample (LCS)

7.6.1 The LCS shall be prepared from the calibration stock standard (primary) in Section 7.3.1. by adding 1mL of stock standard to a blank. ~~[Each laboratory should specify how the LCS standard is prepared.]~~

7.6.2 The LCS is prepared from reagent water and contains all of the method target analytes. A subset of the method target analytes could be used based on the project-specific requirements. The spiking level used would be at the same level as the site-specific action limit. If site-specific action limits are not available, the spiking level shall be at a concentration between the low and mid-level of the initial calibration standards.

8.0 Procedure

All glassware and digestion vessels used to contain a sample must be labelled ~~and rinsed~~. ~~All glassware coming in contact with the sample must also be rinsed [each laboratory should insert specific procedures for labelling and rinsing]~~. The digestion log (see Figure 1) is to be filled out with each step of the procedure.

8.1 Mix the sample thoroughly to achieve homogeneity, (see SOP No. Q-021-XX-MCX-XX, Subsampling of Containers). Dry a representative amount of wet sample at 60 C overnight. When cool using a mortar and pestle, grind sample until it passes through a .40 mesh sieve. For each digestion procedure, weigh 1 ~~2 g~~ of dry gound sample to the nearest 0.01 g and transfer to a ~~conical beaker~~ tube. Record weight on digestion log (see Figure 1). ~~For samples with low percent solids, a larger sample size may be used as long as digestion is completed as described in Section 8.2.~~ Spike QC samples as appropriate.

8.2 ~~A separate determination of percent solids must be performed on a homogeneous aliquot of the sample so that the final result can be reported on a dry weight basis. Refer to SOP No. M-2216-XX-MCX-XX, Determination of Water (Moisture) Content of Soil (ASTM Method 2216).~~

8.3 Using a dispensing bottle, add 10 mL of 1:1 HNO_3, mix the slurry, ~~and cover with a non-ribbed watch glass~~. Program the autostep controller to a temperature of 130°C with a ramp time of 20 minutes and a total run time of 8 hours. When samples are high in organics it may be neccessary to start at a lower temperature. A block temp of 130 will give a sample temp of 90 to 95°C in the sample Heat the sample to 95 ± 5°C and reflux for 10 to 15 minutes without boiling. ~~[Each laboratory should add specific instructions for adjusting the temperature control, i.e., specify control setting.]~~ It is suggested that the temperature of the heating device or representative sample be monitored near the center of the heating device. Record the temperature on the digestion log in Figure 1 at the beginning and end of the digestion process.

8.4 Allow the sample to cool, add 5 mL of concentrated HNO_3, ~~replace the watch glass,~~ and reflux for 30 minutes. Repeat this last step to ensure complete oxidation. Rinse watch glass into beaker. Using a ribbed watch glass, allow the solution to evaporate to 5 mL without boiling, while maintaining a covering of solution over the bottom of the beaker.

8.5 After the sample has cooled, add 2 mL of reagent water and 3 mL of 30%

H_2O_2 using dispensing bottles. ~~Cover the beaker with a non-ribbed watch glass~~ and return the ~~covered beaker~~ sample to the hot plate for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the beaker.

8.6 Continue to add 30% H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

NOTE: Do not add more than a total of 10 mL 30% H_2O_2.

8.7 If the sample is being prepared for the ICP analysis of As and Se, or the flame AA or ICP analysis of Ag, Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Os, Pb, Tl, V, and Zn, then add 5 mL of concentrated HCl and 10 mL of reagent water with dispensing bottles. Return the ~~covered~~ beaker to the hot plate, and reflux for an additional 15 minutes without boiling. After cooling, filter the sample through a ~~[insert type of filter used by laboratory]~~ filter (section 6.3) into a **[volumetric flask ~~or graduated cylinder~~]** ~~as described above~~, or centrifuge. Rinse the filter and solids with ~~an~~ additional ~~10 to 15 mL of~~ reagent water and dilute to a 100 mL volume with reagent water using a **[volumetric flask ~~or graduate cylinder~~]**. Thoroughly mix the sample to ensure the digestate is completely homogenous. ~~Particulates in the digestate that may clog the nebulizer should be removed by filtration through Whatman No. 41 filter paper (or equivalent), or centrifugation~~. The diluted sample has an approximate acid concentration of 5.0% (v/v) HCl and 5.0% (v/v) HNO_3. The sample should be transferred to a clean, acid-rinsed, labelled LDPE bottle.

8.8 If the sample is being prepared for the furnace analysis of As, Be, Cd, Co, Cr, Fe, Mo, Pb, Se, Tl, and V, ~~cover the sample with a ribbed watch glass and~~ continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL. After cooling, filter the sample through a ~~[insert type of filter used by laboratory]~~ filter (section 6.3) into a **[volumetric flask ~~or graduated cylinder~~]** ~~as described above~~, or centrifuge. Rinse the filter and solids with ~~an~~ additional ~~10 to 15 mL of~~ reagent water and dilute to 100 mL with reagent water using a **[volumetric flask ~~or graduated cylinder~~]**. Thoroughly mix the sample to ensure the digestate is completely homogenous. ~~Particulates in the digestate should then be removed by filtration, through Whatman No. 41 filter paper (or equivalent), or centrifugation~~. The diluted digestate solution contains approximately 5% (v/v) HNO_3. The sample should be transferred to a clean, acid-rinsed, labelled LDPE bottle.

8.9 Prior to analysis, digestates are stored at room temperature.

9.0 Calculations

The final metal concentration in the sample should be reported in mg/L or μg/L as

appropriate following analysis by ICP, FLAA or GFAA. All dilution factors or concentration factors used in the digestion must be factored into the final sample concentration. Refer to the appropriate determinative method(s) for sample calculations.

10.0 Quality Assurance/Quality Control

10.1 A preparation batch of samples would be defined as a group of up to field twenty samples of similar matrix type that are extracted at the same time using the same reagents for the same analysis. In addition to the twenty samples, each batch would also contain at a minimum a method blank, a laboratory control sample (LCS), a matrix spike, ~~a matrix spike duplicate~~ (MS/~~MSD~~), and a matrix duplicate (MD).

10.2 A method blank (MB) consisting of consisting of 100 ± 1 mL of reagent water shall be prepared with each batch of samples. Acceptance criteria are presented in the appropriate determinative method.

10.3 A Laboratory Control Sample (LCS) consisting of 100 ± 1 mL of reagent water spiked with all the target metals prior to digestion, is digested and analyzed with each batch of samples. Control charts will be maintained for the LCS for all method target analytes. Acceptance criteria are specified in the appropriate determinative method. The order of preference for spiking levels is as follows:

- If an action level exists, spike at this level. If the action level is at the lowest calibration standard, the concentration of the LCS should be slightly higher.
- If the above condition does not apply, spike at a level between the low and mid-level of the calibration standards.

10.4 The use of the matrix spike and ~~matrix spike duplicate~~ will depend in part on what role the laboratory is playing. When the laboratory serves the role as the primary laboratory, then site-specific documents should be consulted. The sample to be used for the MS/~~MSD~~ may be specified in the field. This previously designated sample would then be spiked with the site-specific target analytes at a concentration equivalent to the site action level. If this information was not specified or unknown, then the laboratory would choose a representative sample from each batch of samples analyzed. If samples from multiple sites were to be analyzed in the same batch, then multiple sets of MS/~~MSD~~s may be required.

When the laboratory serves the role as the QA laboratory, the above scenario may not be practical to implement. If the site-specific requirements are unknown and samples from multiple sites are analyzed in the same batch, then the laboratory should select a single sample for spiking. The order of preference for spiking levels is as follows:

- If the target analyte concentrations are known, spike to increase the background concentration by a factor of approximately two
- If an action level exists, spike at this level
- If neither of the first two conditions apply, spike at a level between the low and mid-level of the calibration standards.

10.5 The use of the matrix duplicate may also depend in part on the role the laboratory is playing. The selection of a matrix duplicate will be performed as described for the MS/MSD in Section 10.4.

10.6 The analyst must demonstrate proficiency in performing this method as outlined in SOP No. Q-016-XX-MCX-XX, Technical Training. Method proficiency must be redemonstrated anytime a major method modification is made.

11.0 Data Validation

11.1 The digestion analyst is responsible for verifying the information recorded on the digestion log (Figure 1) is complete and accurate.

11.2 Additional levels of review are performed as described in SOP No. Q-024-XX-MCX-XX, Data Reduction and Review/Validation (In-House/Contractor Data), using a predesigned form as shown in Figure 2.

12.0 Waste Disposal

This procedure generates corrosive and metallic wastes that must be disposed of in accordance to all federal and local regulations. Refer to the laboratory's Waste Management Plan. **[Each laboratory should describe procedures for the accumulation, storage, and disposal of these wastes.]**

13.0 References

13.1 Test Method for Evaluating Solid Waste, SW-846, Third Edition, Update I, July 1992, Method 3050A.

13.2 SOP No. Q-008-XX-MCX-XX, Reagent Water Generation and Quality Monitoring.

13.3 SOP No. Q-021-XX-MCX-XX, Subsampling of Containers.

13.4 SOP No. Q-005-XX-MCX-XX, Sample Receipt, Login, and Storage.

13.5 SOP No. M-2216-XX-MCX-XX, Determination of Water (Moisture) Content of Soil (ASTM Method 2216).

13.6 SOP No. Q-024-XX-MCX-XX, Data Reduction and Review/Validation (In-House/Contractor Data).

13.7 SOP No. Q-012-XX-MCX-XX, Glassware Cleaning.

13.8 SOP No. Q-003-XX-MCX-XX, Standards Preparation, Traceability, and Storage.

13.9 SOP No. Q-004-XX-MCX-XX, Nonconformances and Corrective Action.

13.10 SOP No. Q-016-XX-MCX-XX, Technical Training.

13.11 **[Identify MSC Laboratory]** Waste Management Plan.

Digestion Log For Metals Analysis
[Identify MSC Laboratory]

Batch No.:	SOP #_____	Matrix: ☐ Solid ☐ Liquid
Start Date:	Project No.:	Analysis Method: ICP, FLAA, GFAA

Type	Sample ID No.	Sample Amount (mL) (g)	Filtration necessary?	Final Volume (mL)	Description/Sample Comments
MB					
LCS					
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
MD					
MS					
MSD					

LCS Spiking Standard ID: _____ Amount Added _____ mL

MS/MSD Spiking Standard ID: _____ Amount Added _____ mL

Witness: _____ Date: _____

Reagent Lot No(s): _____ Temp. of Heating Device: Start: _____ End: _____

_____

_____

Analyst: _____ Reviewed By: _____ Date: _____

Figure 1.

Digestion Log For Metals Analysis
[Identify MSC Laboratory]

Batch No.:	SOP #_____	Matrix: ☐ Solid ☐ Liquid
Start Date:	Project No.:	Analysis Method: ICP, FLAA, GFAA

Type	Sample ID No.	Sample Amount (mL) (g)	Filtration necessary?	Final Volume (mL)	Description/Sample Comments
MB					
LCS					
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
MD					
MS					
MSD					

LCS Spiking Standard ID: _____ Amount Added _____ mL

MS/MSD Spiking Standard ID: _____ Amount Added _____ mL

Witness: _____ Date: _____

Reagent Lot No(s): _____ Temp. of Heating Device: Start: _____ End: _____

_____

_____

Analyst: _____ Reviewed By: _____ Date: _____

Figure 1. Example.

Lab Data Review Check List
Metals Digestion Log
[Identify MSC Laboratory]

Project Number(s):
Batch Number(s):
Method SOP No.:

Review Item	Yes (x)	No (x)	N/A (x)	2nd Level Review (x)
Were the following recorded properly? - batch number - sample identification number(s) - dates				
Were the weight/volume of sample digested and the final digested volume properly recorded?				
Were sample dilutions or concentration factors properly recorded?				
Was a method blank prepared at the required frequency using a blank matrix?				
Was a Laboratory Control Sample (LCS) prepared at the required frequency?				
Were a matrix spike (MS) and matrix spike duplicate (MSD) prepared at the proper frequency?				
Were the matrix duplicates (MD) prepared at the proper frequency?				
Are there any Corrective Action Reports associated with this sample batch?				
Are copies of Corrective Action Reports attached?				
Were the spiking volume, stock source, and spike concentration properly recorded for the MS/MSD and LCS?				

NOTES: _____

_____

_____

Analyst: _____ Date: _____

2nd Level Reviewer: _____ Date: _____

Figure 2.

Lab Data Review Check List
Metals Digestion Log
[Identify MSC Laboratory]

Project Number(s):
Batch Number(s):
Method SOP No.:

Review Item	Yes (x)	No (x)	N/A (x)	2nd Level Review (x)
Were the following recorded properly? - batch number - sample identification number(s) - dates				
Were the weight/volume of sample digested and the final digested volume properly recorded?				
Were sample dilutions or concentration factors properly recorded?				
Was a method blank prepared at the required frequency using a blank matrix?				
Was a Laboratory Control Sample (LCS) prepared at the required frequency?				
Were a matrix spike (MS) and matrix spike duplicate (MSD) prepared at the proper frequency?				
Were the matrix duplicates (MD) prepared at the proper frequency?				
Are there any Corrective Action Reports associated with this sample batch?				
Are copies of Corrective Action Reports attached?				
Were the spiking volume, stock source, and spike concentration properly recorded for the MS/MSD and LCS?				

NOTES: _____

_____

_____

Analyst: _____ Date: _____

2nd Level Reviewer: _____ Date: _____

Figure 2. Example.

TITLE: Microwave Assisted Acid Digestion Of Sediments, Sludges, Soils, And Oils (SW-846 Method 3051)

SOP NUMBER: M-3051-00-WES-X-XX

PREPARED BY: _____
Date

REVIEWED BY: _____
Technical Specialist Date

_____
QA Officer Date

_____
Laboratory Director Date

SOP MANUAL CONTROL NO.: _____

1.0 Scope and Application

1.1 This method is applicable to the microwave assisted acid digestion of sludges, sediments, soils, and oils for the elements listed in Table 1.

Table 1. Techniques for Analyte Analysis

Analyte	Technique	Symbol	CAS #
Aluminum	ICP/FLAA/GFAA	Al	7429-90-5
Antimony	ICP/FLAA/GFAA	Sb	7440-36-0
Arsenic	ICP/GFAA	As	7440-38-2
Boron	ICP	B	
Barium	ICP/FLAA/GFAA	Ba	7440-39-3
Beryllium	ICP/FLAA/GFAA	Be	7440-41-7
Cadmium	ICP/FLAA/GFAA	Cd	7440-43-9
Calcium	ICP/FLAA/GFAA	Ca	7440-70-2
Chromium	ICP/FLAA/GFAA	Cr	7440-47-3
Cobalt	ICP/FLAA/GFAA	Co	7440-48-4
Copper	ICP/FLAA/GFAA	Cu	7440-50-8
Iron	ICP/FLAA/GFAA	Fe	7439-89-6
Lead	ICP/FLAA/GFAA	Pb	7439-92-1
Magnesium	ICP/FLAA/GFAA	Mg	7439-95-4
Manganese	ICP/FLAA/GFAA	Mn	7439-96-5
Molybdenum	ICP/FLAA/GFAA	Mo	7439-98-7
Nickel	ICP/FLAA/GFAA	Ni	7440-02-0
Potassium	ICP/FLAA/GFAA	K	7440-09-7
Selenium	ICP/GFAA	Se	7782-49-2
Silver	ICP/FLAA/GFAA	Ag	7440-22-4
Sodium	ICP/FLAA/GFAA	Na	7440-23-5
Strontium	ICP/FLAA	Sr	
Thallium	ICP/FLAA/GFAA	Tl	7440-28-0
Vanadium	ICP/FLAA/GFAA	V	7440-62-2
Zinc	ICP/FLAA/GFAA	Zn	7440-66-6

1.2 This method provides a rapid multi-element acid leach digestion. If a decomposition including hydrochloric acid is required for certain elements, it is recommended that Method 3050A be used. Digestates produced by the method are suitable for analysis by flame atomic absorption (FLAA), graphite furnace atomic absorption (GFAA), inductively coupled plasma emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS).

2.0 Method Summary

A representative sample of approximately 0.5 g is digested in 10 mL of concentrated nitric acid for 10 minutes in a Teflon digestion vessel. The vessel is capped and heated in the microwave unit. After cooling, the vessel contents are filtered and diluted, or diluted and then centrifuged, or allowed to settle.

3.0 Health and Safety

3.1 Kitchen-type, or modified kitchen-type microwave ovens do not contain sufficient safety devices, and are not acceptable for use with this method. Laboratory microwave ovens have been specifically designed for this procedure, and must be used.

3.2 Acceptable digestion vessels include unlined fluorocarbon (PFA or TFM) containers with pressure relief mechanisms or containers with fluorocarbon liners and pressure relief mechanisms.

3.3 Use of this procedure requires the handling of reagents and corrosive acids, therefore protective equipment must be utilized. Minimum personal protection includes the use of laboratory safety glasses, a lab coat or apron, and protective gloves. During the manual operation of the microwave oven, and particularly in case of vessel failure, acid and nitric oxide fumes will vent. Therefore, the microwave oven must be located next to the fume hood, and vented into it according to manufacturer instructions. Do not leave the microwave unattended during operation. Keep away from the close proximity of the oven as much as possible.

Wait a sufficient amount of time, a minimum of 20 mins, ~~[each laboratory should insert specific procedures here]~~ after the heating cycle for the digestion vessels to cool. **Never open vessels abruptly, and only open vessels in the fume hood.** Try to keep distance between the operator and the vessels they are opening.

3.4 For specific information regarding the toxicity of the acids used in this procedure and other related health and safety issues including the proper storage and handling of reagents and chemicals, the analyst should consult the appropriate Material Safety Data Sheets (MSDSs) located in room 69. ~~[Each laboratory should insert location of MSDSs.]~~

3.5 Use of this procedure requires the handling of concentrated acid, (nitric acid). Prior to performing this procedure, the analyst should be familiar with the proper use of corrosive liquid spill kits and containment procedures. Spill kits are located in room 69. ~~[Each laboratory should insert appropriate information on the location, use, and disposal of spill kits. This information should list the specific types of spill kits available and their specific uses i.e., acids, bases, other liquids.]~~

4.0 Sample Preservation, Containers, Handling, and Storage

4.1 Requirements for sample preservation, sample containers, and sample storage are detailed in SOP No. Q-005-XX-MCX-XX, Sample Receipt, Login, and Storage Procedures.

4.2 All glassware, as well as containers used to store digestates must be prewashed with detergents, acid, and reagent water. Refer to SOP No. Q-012-XX-MCX-XX, Glassware Cleaning.

4.3 Metals digestion and analysis must be completed within 180 days of sample collection.

5.0 Interferences and Potential Problems

5.1 Very reactive or volatile materials that may create high pressures when heated may cause venting of the vessels with potential loss of sample and analytes.

5.2 Samples that contain carbonates or other carbon dioxide generating compounds may cause enough pressure to vent the vessel. Refer to Section 3.0. If this situation is anticipated, the analyst should use a smaller sample volume. If a smaller volume must be used, document on a Corrective Action Report, as described in SOP No. Q-004-XX-MCX-XX, Nonconformances and Corrective Actions.

6.0 Equipment/Apparatus

6.1 Microwave apparatus requirements: CEM MDS-2100 ~~[each laboratory must provide specifics of their equipment here].~~

6.1.1 The microwave unit must provide programmable power with a minimum of 574 W and can be programmed to within ± 10 W of the required power.

6.1.2 The microwave unit cavity must be corrosion resistant and well ventilated.

6.1.3 All electronics must be protected against corrosion for safe operation.

6.1.4 The system requires Teflon PFA digestion vessels (120-mL capacity) capable of withstanding pressures up to 7.5 ± 0.7 at (110 ± 10 psi) and capable of controlled pressure relief at pressures exceeding 7.5 ± 0.7 at (110 ± 10 psi).

6.1.5 A rotating turntable is employed to insure homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm.

6.2 Graduated cylinder, Class A — 50-or 100-mL capacity.

6.3 Quantitative filter paper ~~— Whatman No. 41~~, S&S White label, ~~or equivalent [each laboratory should specify], or centrifugation equipment [if used, laboratory shall list manufacturer, model, and associated equipment].~~

6.4 Analytical balance — 300-g capacity, capable of weighing to nearest 0.001g.

6.5 Filter funnels,Urbanti,high speed filter funnels, molded TPX, 70mm. ~~polyethylene, glass, or equivalent [each laboratory should specify].~~

6.6 Polyethylene bottles for storing digestates, or equivalent — Eagle Picher, 125mL, HDPE, wide mouth nalgene, Level 1, wash C. ~~125-mL, with caps [laboratory should specify type, size, and supplier].~~

6.7 Automatic pipets or acid-dispensing bottle, accurate to within ± 0.1 mL Brinkman Dispensette, 2ml to 10mL ~~[laboratory should insert type of dispensing bottle used].~~

6.8 Volumetric flasks, Class A, 100-mL capacity.

7.0 Reagents

7.1 Reagent Water — As defined in SOP No. Q-008-XX-MCX-XX, Reagent Water Generation and Quality Monitoring.

7.2 Acids must of sufficient purity for the analytical methods to be employed. Acids must be analyzed to determine levels of impurities. If a method blank made with the acid is < MDL, the acid can be used. This should be verified for each new lot of acid.

7.2.1 Nitric acid, concentrated, HNO_3 — ~~for example~~, Fisher TraceMetal grade, Cat# A-509 or equivalent. ~~[Each laboratory should specify type and vendor.]~~

7.2.2 Hydrochloric acid, concentrated, HCl - ~~for example~~, Fisher TraceMetal grade, Cat# A-508 or equivalent. ~~[Each laboratory should specify type and vendor.]~~

7.3 Metal stock calibration solutions shall be purchased as certified solutions from commercial suppliers (SPEX plasma grade or equivalent) Certificates must be kept on file. Calibration standards are from Alfa Aesar, STK# 85422 ~~[Each laboratory should specify the supplier, catalog number, and concentration of purchased solutions.]~~ All stock standards must be replaced after one year.

7.3.1 Primary source standards shall be used to prepare the initial calibration curve, continuing calibration verification (CCV) standard, laboratory control sample (LCS), and matrix spikes and their duplicates (MS/MSDs).

7.3.2 Secondary source standards shall be used to verify the initial calibration (ICV) curve only. These standards shall be purchased from a different vendor, unless the primary vendor can supply different lot numbers.

7.4 Matrix spike (MS) standard

7.4.1 The matrix spike standard shall be prepared from the calibration stock standard (primary) in Section 7.3.1. 0.5 mL of stock standard is added to the matrix spike sample. ~~[Each laboratory should specify how the MS standard is prepared.]~~

7.4.2 The spike should be at a level that would approximately double the concentration of the target analytes present. In the absence of target analytes, the spike would be made at the site action level, assuming that this level did not also correspond to the value of the low standard used. If the action level is the same as the low standard used, then the spiking would occur at a slightly higher level, i.e., at the value of the next calibration standard used. If the action level is not known, the spiking level would then default to a concentration between the low and mid-level of the initial calibration standards.

7.4.3 All method analytes should be contained in the MS spike. Subsets may be used based on project specific requirements.

7.5 Laboratory Control Sample (LCS)

7.5.1 The LCS shall be prepared from the calibration stock standard (primary) in Section 7.3.1. 0.5 mL of stock standard is added to the blank sample. ~~[Each laboratory should specify how the LCS standard is prepared.]~~

7.5.2 The LCS is prepared from reagent water and shall contain all of the method target analytes. A subset of the method target analytes could be used based on the project-specific requirements. The spiking level used would be at the same level as the site-specific action limit. If site-specific action limits are not available, the spiking level shall be at a concentration

between the low and mid-level of the initial calibration standards.

8.0 Procedure

8.1 Calibration of Microwave Equipment

8.1.1 Measurement of the available power for heating is evaluated so that absolute power in watts may be transferred from one microwave unit to another. For cavity type microwave equipment, this is accomplished by measuring the temperature rise in 1 kg of water exposed to microwave radiation for a fixed period of time. The analyst can relate power in watts to the partial power setting of the unit. The calibration format required for laboratory microwave units depends on the type of electronic system used by the manufacturer to provide partial microwave power. Few units have an accurate and precise linear relationship between percent power settings and absorbed power. Where linear circuits have been utilized, the calibration curve can be determined by a three-point calibration method (8.1.3), otherwise, the analyst must use the multiple point calibration method (8.1.2). (Prior to the use of the three-point calibration curve, linearity must be initially verified using the multiple-point calibration procedure.) The MDS-2100 has a microwave power output of 950 watts at 100% power. ~~[Each laboratory should specify the capability of their microwave system~~.]

8.1.2 The multiple point calibration involves the measurement of absorbed power (p) over a large range of power settings. For a 600 W unit, the following power settings are measured; 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40% using the procedure described in Section 8.1.4. These data are clustered about the customary working power ranges. Nonlinearity has been commonly encountered at the upper end of the calibration. If the unit's electronics are known to have nonlinear deviations in any region of proportional power control, it will be necessary to make a set of measurements that bracket the power to be used. The final calibration point must be at the partial power setting that will be used in the test. The power setting (x-axis) is plotted versus the absorbed power (y-axis). This setting should be checked periodically to evaluate the integrity of the calibration. The multiple point calibration must be performed if a significant change in the calculated power setting for this test point is detected (± 10 W). This calibration must also be performed on new units brought into service. **[If appropriate, each laboratory should discuss specific procedures for multiple point calibration.]**

8.1.3 The three-point calibration involves the measurement of absorbed power (p) at three different power settings. Measure the absorbed power at 100% and 50% using the procedure described in Section 8.1.4, and calculate the power setting corresponding to the required test power in watts as determined using the

equation in Section 9.1 from the (2-point) line. Measure the absorbed power (p) at that partial power setting. If the measured absorbed power (p) does not correspond to the specified power within ± 10 W, use the multiple point calibration in Section 8.1.2. **[If appropriate, each laboratory should discuss specific frequencies and procedures for 3-point calibration.]**

8.1.4 Equilibrate a large volume of water to room temperature (23 ± 2 °C). One kg of reagent water is weighed (1000.0 g ± 0.1 g into a Teflon beaker or a beaker made of some other material that does not significantly absorb microwave energy (glass absorbs microwave energy and is not recommended). The initial temperature of the water should be 23 ± 2 °C measured to ±0.05 °C. The covered beaker is circulated continuously (in the normal sample path) through the microwave field for 2 minutes at the desired partial power setting with the unit's exhaust fan on maximum (as it will be during normal operation). The beaker is removed and the water vigorously stirred. Use a magnetic stirring bar inserted immediately after microwave irradiation and record the maximum temperature within the first 30 seconds to ±0.05 °C. Use a new sample for each additional measurement. If the water is reused both the water and the beaker must have returned to 23 ±2 °C. Three measurements at each power setting should be made. The mean of the three power measurements should be calculated.

The absorbed power (p) is determined as described in Section 9.1.

NOTE: Stable line voltage is necessary for accurate and reproducible calibration and operation. The line voltage should be within manufacturer's specification, and during measurement and operation not vary by more than ± 2V. A constant power supply may be necessary for microwave use if the source of the line voltage is unstable.

Electronic components in most microwave units are matched to the unit's function and output. When any part of the high voltage circuit, power source, or control components in the unit have been serviced or replaced, it will be necessary to recheck the units' calibration power. If the power output has changed significantly (±10 W), then the entire calibration should be reevaluated.

8.2 Sample Digestion

All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. When switching between high concentration samples and low concentration samples, all digestion vessels should be

cleanded by leaching with hot (1:1) hydrochloric acid (greater than 80°C, but less than boiling) for a minimum of two hours followed with hot (1:1) nitric acid (greater than 80°C, but less than boiling) for a minimum of two hours and rinsed with reagent water and dried in a clean environment. This cleaning procedure should also be used whenever the prior use of the digestion vessels is unknown or cross contamination from vessels is suspected. Polymeric or glass volumetric ware and storage containers should be cleaned by leaching with more dilute acids (approximately 10% V/V) appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment. To avoid precipitation of silver, ensure that all HCl has been rinsed from the vessels. **[Each laboratory should insert specific procedures for labelling and rinsing].** The digestion log (see Figure 1) is to be filled out with each step of the procedure.

8.2.1 ~~A separate determination of percent solids must be performed on a homogeneous aliquot of the sample so that the final result can be reported on a dry weight basis~~ Dry samples are used in the digestion procedure. Refer to SOP No. M-2216-XX-MCX-XX, Determination of Water (Moisture) Content of Soil (ASTM Method 2216).

8.2.2 Weigh the Teflon PFA digestion vessel, valve and cap assembly to 0.001 g prior to use and record on digestion log (see Figure 1).

[CAUTION: If the sample smells highly organic, additional gasses may develop during digestion. This could result in a dangerous situation. Notify the QA Officer, and determine if a smaller sample volume is possible. Alternatively, a different digestion method can be used.]

8.2.3 Weigh 0.5 g of sample to the nearest 0.001 into the Teflon PFA sample vessel with the number of the vessel recorded on the digestion log following the sample identification. For soils, sediments, and sludges, use no more than 0.500 g. For oils, use no more than 0.250 g.

~~NOTE: Required sample aliquots are on a dry weight basis. For example, for a soil consisting of 80% solids, a sample aliquot of approximately 0.6 g should be used.~~

8.2.4 In a fume hood, using an acid-dispensing bottle, add 10.0 ± 0.1 mL of concentrated (70%) nitric acid to each vessel. Allow any reactions to stop before sealing. Seal each vessel according to manufacturer instructions. Measure the mass of each vessel and record in the digestion log.

8.2.5 Evenly distribute the vessels in the carousel. The carousel can hold 12 samples. ~~**[Each laboratory should specify how many vessels can be microwaved and how even distribution is**~~

~~ensured.]~~ Blanks are treated as samples for the purpose of balancing the power unit. When fewer than 12 vessels are used in the digestion the power setting must be adjusted in accordance with the manufacturers recommendations. ~~When fewer than the recommended number of samples are digested, the remaining vessels should be filled with 10 mL of nitric acid to achieve the full complement of vessels.~~ This provides an energy balance since the microwave power absorbed is proportional to the total mass in the cavity. Alternative power settings for different manufacturers are acceptable as long as they bring the samples to 175°C in less than 5.5 minutes and keeps the temperature between 170 - 180°C during the next 4.5 minutes. This may also be accomplished by the use of temperature feedback, using a monitor vessel.

8.2.6 Place the carousel in the unit; be sure to seat it carefully on the turntable. Program the microwave unit for the first stage of the power program to give the required power calculated as described in Section 9.1. Set power to 100, PSI to 70, time to 10.0, TAP to 4.3 and temp to 175. ~~[Each laboratory should insert appropriate information.]~~ This sequence brings the temperature of samples to 175 °C in less than 5.5 minutes and remain between 170 - 180 °C for the balance of the 10 minute irradiation period. The pressure should peak at less than 6 atm for most soil, sludge, and sediment samples. To prevent catastrophic venting, one may need to start with a lower power setting before applying full power.

NOTE: The pressure will exceed these limits in the case of high concentrations of carbonate or organic compounds. In these cases the pressure will be limited by the relief pressure of the vessel to 7.5 ± 0.7 at (110 ± 10 psi).

Start the turntable motor and be sure the vent fan is running on high and the turntable is turning. Start the microwave generator. ~~[If necessary, each laboratory should revise this section to provide applicable microwave program.]~~

8.2.7 At the end of the microwave program, allow the vessels to cool for a least 5 minutes in the unit before removal to avoid possible injury if a vessel vents immediately after microwave heating. The samples may be cooled outside the unit by removing the carousel and allowing the samples to cool on the bench or in a water bath. When the vessels have cooled to room temperature, weigh and record the weight of each vessel assembly on the digestion log to the nearest 0.001 g. If the weight of the sample plus acid has decreased by more than 10%, discard the sample.

8.2.8 Complete the preparation of the sample by carefully uncapping

and venting each vessel in a fume hood. Transfer the sample to an acid-cleaned 100-mL volumetric flask or another alternative container, if its precision is documented, and dilute to volume with reagent water. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, the sample shall be filtered through acid rinsed qualitative filter paper ~~or centrifugation~~ prior to being transferred to a volumetric flask. The sample is now ready for analyses and can be stored in an acid-cleaned polyethylene bottle. The digestate contains approximately 10% V/V nitric acid.

8.3 Prior to analysis, digestates are stored at room temperature.

9.0 Calculations

The absorbed power (Sec. 8.1.4) is determined as:

$$P = \frac{(K)(C_p)(m)(\Delta T)}{t}$$

where:

P	=	Apparent power absorbed by the sample in watts (W)
K	=	Conversion factor for thermochemical calories·sec^{-1} to watts (=4.184 J/cal)
C_p	=	Heat capacity, thermal capacity, or specific heat of water (cal·g^{-1} °C^{-1})
m	=	Mass of the solid sample in grams (g)
ΔT	=	Final temperature minus the initial temperature (C)
t	=	Time in seconds (s).

Using the experimental conditions of 2 minutes and 1 kg of distilled water (heat capacity at 25 °C is 0.9997 cal·g^{-1} °C^{-1}) the calibration equation simplifies to:

$$P = 34.86\ (\Delta T)$$

10.0 Quality Assurance/Quality Control

10.1 A preparation batch of samples would be defined as a group of up to field twenty samples of similar matrix type that are extracted at the same time using the same reagents for the same analysis. In addition to the twenty samples, each batch would also contain at a minimum a method blank, a laboratory control sample (LCS), a matrix spike, a matrix spike duplicate (MS/~~MSD~~), and a matrix duplicate (MD).

10.2 A method blank (MB) consisting of reagent water and shall be prepared with each batch of samples. Acceptance criteria are presented in the appropriate determinative method.

10.3 A Laboratory Control Sample (LCS) consisting of reagent water spiked with all the target metals prior to digestion, is digested and analyzed with each batch of samples. Control charts will be maintained for the LCS for all method target analytes. Acceptance criteria are specified in the appropriate determinative method. The order of preference for spiking levels is as follows:

- If an action level exists, spike at this level. If the action level is at the lowest calibration standard, the concentration of the LCS should be slightly higher.

- If the above condition does not apply, spike at a level between the low and mid-level of the calibration standards.

10.4 The use of the matrix spike ~~and matrix spike duplicate~~ will depend in part on what role the laboratory is playing. When the laboratory serves the role as the primary laboratory, then site-specific documents should be consulted. The sample to be used for the MS/~~MSD~~ may be specified in the field. This previously designated sample would then be spiked with the site-specific target analytes at a concentration equivalent to the site action level. If this information was not specified or unknown, then the laboratory would choose a representative sample from each batch of samples analyzed. If samples from multiple sites were to be analyzed in the same batch, then multiple sets of MS/~~MSD~~s may be required.

When the laboratory serves the role as the QA laboratory, the above scenario may not be practical to implement. If the site-specific requirements are unknown and samples from multiple sites are analyzed in the same batch, then the laboratory should select a single sample for spiking. The order of preference for spiking levels is as follows:

- If the target analyte concentrations are known, spike to increase the background concentration by a factor of approximately two

- If an action level exists, spike at this level

- If neither of the first two conditions apply, spike at a level between the low and mid-level of the calibration standards.

10.5 The use of the matrix duplicate may also depend in part on the role the laboratory is playing. The selection of a matrix duplicate will be performed as described for the MS/~~MSD~~ in Section 10.4.

10.6 The analyst must demonstrate proficiency in performing this method as outlined in SOP No. Q-016-XX-MCX-XX, Technical Training. Method proficiency must be redemonstrated anytime a major method modification is made.

11.0 Data Validation

11.1 The digestion analyst is responsible for verifying the information recorded on the digestion log (Figure 1) is complete and accurate.

11.2 Additional levels of review are performed as described in SOP No. Q-024-XX-MCX-XX, Data Reduction and Review/Validation (In-House/Contractor Data), using a predesigned form as shown in Figure 2.

12.0 Waste Disposal

This procedure generates corrosive and metallic wastes. All waste disposal must comply with all Federal and local regulations. Refer to the laboratory's Waste Management Plan. **[Each laboratory should describe procedures for the accumulation, storage, and disposal of these wastes.]**

13.0 References

13.1 Test Method for Evaluating Solid Waste, SW-846, Third Edition, Update II, September 1994, Method 3051.

13.2 SOP No. Q-005-XX-MCX-XX, Sample Receipt, Login, and Storage Procedures.

13.3. SOP No. Q-012-XX-MCX-XX, Glassware Cleaning.

13.4 SOP No. Q-008-XX-MCX-XX, Reagent Water Generation and Quality Monitoring.

13.5 Introduction to Microwave Sample Preparation: Theory and Practice. Kingston, H.M., Jassie, L.B., Eds., ACS Professional Reference Book Series, American Chemical Society, Washington, DC, 1988. Chapters 6 and 11.

13.6 SOP No. Q-003-XX-MCX-XX, Standards Preparation, Traceability, and Storage.

13.7 SOP No. Q-021-XX-MCX-XX, Subsampling of Containers.

13.8 SOP No. Q-016-XX-MCX-XX, Technical Training.

13.9 SOP No. Q-004-XX-MCX-XX, Nonconformances and Corrective Action.

13.10 SOP No. Q-024-XX-MCX-XX, Data Reduction and Review/Validation (In-House/Contractor Data).

13.11 SOP No. M-2216-XX-MCX-XX, Determination of Water (Moisture) Content of Soil (ASTM Method 2216).

13.12 **[Identify MSC laboratory]** Waste Management Plan.

Microwave Digestion Log For Metals Analysis
[Identify MSC Laboratory]

Batch No.:	SOP # _____	Matrix: ☐ Solid ☐ Liquid
Start Date:	Project No.:	Analysis Method: ICP, FLAA, GFAA

Type	Sample ID No.	Digestion vessel ID	Sample Amount (mL) (g)	mL Acid Added	Mass of Vessel		Filtration necessary?	Description/ Sample Comments
					before heating	after heating		
MB								
LCS								
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								
11								
12								
13								
14								
15								
16								
17								
18								
19								
20								
Dup								
MS								
MSD								

LCS Spiking Standard ID: _____ Amount Added _____ mL

MS/MSD Spiking Standard ID: _____ Amount Added _____ mL

Witness: _____ Date: _____

Reagent Lot No(s): _____

_____

_____

Analyst: _____ Reviewed By: _____ Date: _____

Figure 1.

Microwave Digestion Log For Metals Analysis
[Identify MSC Laboratory]

Batch No.:	SOP # _____	Matrix: ☐ Solid ☐ Liquid
Start Date:	Project No.:	Analysis Method: ICP, FLAA, GFAA

Type	Sample ID No.	Digestion vessel ID	Sample Amount (mL) (g)	mL Acid Added	Mass of Vessel		Filtration necessary?	Description/ Sample Comments
					before heating	after heating		
MB								
LCS								
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								
11								
12								
13								
14								
15								
16								
17								
18								
19								
20								
Dup								
MS								
MSD								

.CS Spiking Standard ID: _____ Amount Added _____ mL

MS/MSD Spiking Standard ID: _____ Amount Added _____ mL

Vitness: _____ Date: _____

leagent Lot No(s): _____

_____

_____

nalyst: _____ Reviewed By: _____ Date: _____

Figure 1. Example.

Lab Data Review Check List
Metals Digestion Log
[Identify MSC Laboratory]

Batch Number(s):

Method SOP No.:

Review Item	Yes (x)	No (x)	N/A (x)	2nd Level Review (x)
Were the following recorded properly? - batch number - sample identification number(s) - dates				
Were the weight/volume of sample digested and the final digested volume properly recorded?				
Were sample dilutions or concentration factors properly recorded?				
Was a method blank prepared at the required frequency using a blank matrix?				
Was a Laboratory Control Sample (LCS) prepared at the required frequency?				
Were a matrix spike (MS) and matrix spike duplicate (MSD) prepared at the proper frequency?				
Were the matrix duplicates (MD) prepared at the proper frequency?				
Are there any Corrective Action Reports associated with this sample batch?				
Are copies of Corrective Action Reports attached?				
Were the spiking volume, stock source, and spike concentration properly recorded for the MS/MSD and LCS?				

NOTES: _____

_____

_____

nalyst: _____ Date: _____

nd Level Reviewer: _____ Date: _____

Figure 2.

Lab Data Review Check List
Metals Digestion Log
[Identify MSC Laboratory]

Batch Number(s):
Method SOP No.:

Review Item	Yes (x)	No (x)	N/A (x)	2nd Level Review (x)
Were the following recorded properly? - batch number - sample identification number(s) - dates				
Were the weight/volume of sample digested and the final digested volume properly recorded?				
Were sample dilutions or concentration factors properly recorded?				
Was a method blank prepared at the required frequency using a blank matrix?				
Was a Laboratory Control Sample (LCS) prepared at the required frequency?				
[illegible] a matrix spike (MS) and matrix spike duplicate (MSD) prepared at the proper frequency?				
Were the matrix duplicates (MD) prepared at the proper frequency?				
Are there any Corrective Action Reports associated with this sample batch?				
Are copies of Corrective Action Reports attached?				
Were the spiking volume, stock source, and spike concentration properly recorded for the MS/MSD and LCS?				

NOTES: _____

_____

_____

Analyst: _____ Date: _____

2nd Level Reviewer: _____ Date: _____

Figure 2. Example.

TITLE: Inductively Coupled Plasma-Atomic Emission Spectroscopy (SW-846 Method 6010A)

WES 12/14

SOP NUMBER: M-6010A-00-~~MCX~~-XX

PREPARED BY: _____
Date

REVIEWED BY: _____
Technical Specialist Date

_____
QA Officer Date

_____
Laboratory Director Date

SOP MANUAL CONTROL NO.: _____

1.0 Scope and Application

1.1 Inductively coupled plasma-optical emission spectroscopy (ICP-OES) determines trace elements, including metals, in solution. All matrices, including groundwater, aqueous samples, TCLP and EP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis, following SW-846 methods 3005A-3051.

1.2 Elements for which this SOP is applicable are listed in Table 1. This list is a default list to be used in the absence of a project-specific list, which would take preference. Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and model of spectrometer. The data shown in Table 1 provide detection wavelengths and estimated instrument detection limits for analytes in clean aqueous samples. **[Each lab should insert laboratory-generated detection limits as appropriate.]** Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

2.0 Method Summary

2.1 Prior to analysis, samples must be digested using appropriate sample preparation methods (e.g., SW-846 Methods 3005A-3051). When analyzing for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

2.2 This SOP describes the simultaneous or sequential, multi-elemental determination of elements by ICP. The method measures element-emitted light by optical spectrometry.

2.2.1 Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission lines are produced in the r-f inductively coupled plasma. The emission lines are dispersed by a grating spectrometer, and the line intensities are measured by an appropriate detector, such as, photomultiplier tubes or charge-coupled devices. All lines are to be monitored or interferences may be overlooked.

2.2.2 Background correction is required for trace element determination. Background signals must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background photo-multiplier-correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section 5.0 should also be recognized and appropriate corrections made; tests for their presence are described in Step 11.10.

3.0 Health and Safety

3.1 Use of this procedure requires the handling of samples and standards containing corrosive acids and protective equipment must be utilized. Minimum personal protection includes the use of laboratory safety glasses, a lab coat or apron, protective gloves.

CAUTION: Be careful when diluting and mixing acids. ALWAYS pour acid into water when mixing. Gently heat acid mixtures (NEVER HEAT RAPIDLY), to prevent splatter from extremely exothermic reactions typical of acid-water mixtures, etc.

3.2 All digestions must be performed in a laboratory fume hood.

3.3 For specific information regarding the toxicity of the acids used in this procedure and other related health and safety issues including the proper storage and handling of reagents and chemicals, the analyst should consult the appropriate Material Safety Data Sheets (MSDSs). ~~[Lab should insert location of MSDSs.]~~ The location of the MSDSs is in Room 69, Building 6000.

3.4 Use of this procedure requires the handling of samples containing corrosive acid. Prior to performing this procedure, the analyst should be familiar with the proper use of corrosive liquid spill kits and containment procedures. ~~[Lab should insert appropriate information on the location, use, and disposal of spill kits.]~~ The spill kits are located inside the door of Room 69, Building 6000. The use and disposal of the spill kits are by the instructions included with the kits.

4.0 Sample Preservation, Containers, Handling, and Storage

4.1 Requirements for sample preservation, sample containers and sample storage are detailed in SOP No. Q-005-XX-MCX-XX, Sample Receipt, Login, and Storage.

4.2 All glassware must be prewashed with detergents, acid, and reagent water. Refer to SOP No. Q-012-XX-MCX-XX, Glassware Cleaning.

4.3 Metals digestion and analysis must be completed within 180 days of sample collection.

4.4 Digestates are stored in low-density, metal-free polyethylene (LDPE) bottles or equivalent containers 9(e.g., centrifuge tubes) at room temperature.

5.0 Interferences and Potential Problems

5.1 Spectral interferences are caused by

- Overlap of a spectral line from another element at the analytical or background measurement wavelengths.
- Unresolved overlap of molecular band spectra.

- Background contribution from continuous or recombination phenomena.

- Stray light from the line emission of high-concentration elements.

Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternative wavelength. Stray light can usually be compensated for by a background correction adjacent to the analyte line.

Users of all ICP instruments must verify the absence of spectral interference from an element in a sample for which there is no instrument detection channel. Recommended wavelengths are listed in Table 1 and potential spectral interferences for the recommended wavelengths are given in Table 2. The data in Table 2 are intended as rudimentary guides for indicating potential interferences; for this purpose, linear relations between concentration and intensity for the analytes and the interferences can be assumed.

5.1.1 The interference is expressed as analyte concentration equivalents arising from 100 mg/L of the interference element. The interference effects must be evaluated for each individual instrument since the intensities will vary with operating conditions, power, viewing height, argon flow rate, etc. The user should be aware of the possibility of interferences other than those specified. Both positive and negative interferences may occur.

5.1.2 The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

5.1.3 At present, information on the listed silver and potassium wavelengths is not available, but it has been reported that second-order energy from the magnesium 383.231 nm wavelength interferes with the listed potassium line at 766.491 nm.

5.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. Physical interferences are reduced by using a peristaltic pump and/or an internal standard such as Yttrium (Y) or Scandium (Sc). Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, diluting the sample, or using a high solids tolerant nebulizer. Also, it has been reported that better control of the argon flow rate improves instrument performance; this is accomplished with the use of mass flow controllers.

5.3 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique until sodium level reaches between 4 and

500 mg/L in solutions on the standard ICP. The axial ICP can be affected by ionization at lower levels. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), and by procedures such as using ionization modifiers such as Lithium (for DCP analysis) and yttrium for ICP analysis. This is important when running the axial ICP. Chemical interferences are highly dependent on matrix type and the specific analyte element.

6.0 Equipment/Apparatus

6.1 Inductively coupled plasma emission spectrometer ~~[lab must enter specifics of their instrumentation, including all associated options, components, and software].~~ ~~The instrument used is a Perkin Elmer Optima 3000 DV with an autosample, and an ultrasonic nebulizer for clean water samples.~~ The instrument must operate under the following conditions/requirements.

6.1.1 Computer-controlled emission spectrometer with background signal correction.

6.1.2 Radio frequency generator compliant with FCC regulations.

6.1.3 Argon gas supply — Boil-off from liquid argon. ~~[Laboratory shall insert procedure used.]~~ ~~Liquid argon of 99.9996% purity is used to produce the argon gas that is needed.~~

NOTE: Operating conditions for the ICP and related equipment are fully outlined in the instructions provided by the instrument manufacturer. ~~[Laboratory needs to insert specific instructions here.]~~ For operation with organic solvents, use of an auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within the instrument linear range where spectral interference correction factors are valid. The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.

6.2 Pipets — Microliter with disposable tips. Sizes can range from 5 to 1,000 µL, as required. Pipet tips used should be suitable for trace metal analysis (e.g., pyrogen-free, trace metal certified, Fisher Cat # 21-197-8K or equivalent). ~~[Each lab should specify source and type.]~~ ~~Rainin EDP-Plus Electronic Digital pipets with the appropriate liquid ends, (e.g. 25-250 µL, 100-1000 µL, 250-2500 µL, and 0.5-10.0 mL.~~

6.3 Volumetric Flasks — Class A, assorted sizes including 100, 200, 500, and 1000 mL.

6.4 Volumetric pipets — Class A, assorted sizes from 0.5 to 50 mL.

6.5 LDPE storage bottles, 125 and 250 mL.

7.0 Reagents

7.1 Reagent Water — Refer to SOP No. Q-008-XX-MCX-XX, Reagent Water Generation and Quality Monitoring.

7.2 Concentrated nitric acid (HNO_3), Fisher TraceMetal grade, Cat# A-509 or equivalent. ~~[Each lab should specify type and vendor.]~~ Acid must be analyzed to determine levels of impurities. If a method blank made with the acid is < MDL, the acid can be used. This should be verified with each new lot of acid.

7.3 Concentrated hydrochloric acid (HCl), Fisher TraceMetal grade, Cat# 508 or equivalent. ~~[Each lab should specify type and vendor.]~~ Acid must be analyzed to determine levels of impurities. If a method blank made with the acid is < MDL, the acid can be used. This should be verified with each new lot of acid.

AlFa Aesar

7.4 Individual stock solutions or mixed calibration solutions are to be purchased as prepared certified solutions from commercial suppliers (SPEX plasma grade or equivalent). Refer to SOP No. Q-003-XX-MCX-XX, Standards Preparation, Traceability, and Storage for requirements. ~~[Lab shall list name of supplier, desired concentrations.]~~ Purchased stock solutions are stable for one year.

7.4.1 Primary source standards shall be used to prepare the initial calibration curve, continuing calibration verification (CCV) standard, laboratory control sample (LCS), and matrix spikes ~~and their duplicates~~ (MS/~~MSD~~s).

7.4.2 Secondary source standards shall be used to verify the initial calibration (ICV) curve only. These standards shall be purchased from a different vendor, unless the primary vendor can supply different lot numbers.

7.5 If purchasing a certified prepared standard solution is not an option, then the standard stock solutions shall be made from ultrahigh purity grade chemicals/metals material. Prepared stock solutions are stable for one year. ~~[Each laboratory shall insert procedure used in preparation and level of concentration. For example preparations, refer to Method 6010, Section 5.3.]~~ Each stock solution shall be analyzed separately to determine possible spectral interference or the presence of impurities.

7.6 Calibration Standards — Calibration standards are prepared by combining appropriate volumes of the individual stock solutions with reagent water (mixed standards). Calibration standards are to be prepared just before the calibration is performed. Care should be taken when preparing mixed standards to ensure that the elements are compatible and stable together. Standards should be monitored for stability and replaced if change is found. Some typical mixed standards are:

Mixed Standard Solutions

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As and Mo
IV	Al, Ca, Cr, K, Na, Ni, Li and Sr
V	Ag, Mg, Sb and Tl
VI	P

~~[Each laboratory shall specify calibration standards used in lieu of project specific requirements.]~~

7.7 The continuing calibration verification (CCV) standard is prepared from the primary calibration stock standards by the analyst by combining compatible elements at concentrations equivalent to the midpoint of their respective calibration curves.

7.8 The interference check standard (ICS) is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. The interference check standards shall be purchased from a commercial source (e.g., SPEX Plasma Interference Check Standards, Set of 4, or equivalent) ~~[each lab should specify source]~~ ~~Alfa Aesar.~~ Spike the sample with the elements of interest at ~~approximate~~ concentrations ~~of 10 times the instrumental detection limits.~~ comparable to those expected in the sample. In the absence of measurable analyte, over-correction could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

SPEX

7.9 The initial calibration verification (ICV) standard shall be purchased (or prepared) from a second source independent of the initial calibration standards in the same acid matrix as the calibration standards at a concentration near the mid-point of the calibration curve. (When these standards are purchased, flexibility from this criteria may be exercised.) ~~[Each lab should specify source and concentration of ICV sample.]~~ ~~This standard is purchased from Alfa Aesar with most of the elements at 1 mg/L.~~

7.10 Matrix Spike (MS) Standard -

7.10.1 The matrix spike standard shall be prepared from the calibration stock standard (primary) in Section 7.5. ~~[Each lab should specify how the MS standard is prepared.]~~

7.10.2 The spike should be at a level that would approximately double the concentration of the target analytes present. In the absence of target analytes, the spike would be made at the site action level, assuming that this level did not also correspond to the

value of the low standard used. If the action level is the same as the low standard used, then the spiking would occur at a slightly higher level, i.e., at the value of the next calibration standard used. If the action level is not known, the spiking level would then default to a concentration between the low and mid-level calibration standards.

7.10.3 Ideally, all method analytes should be contained in the MS spike. Subsets may be used based on project specific requirements.

7.11 Laboratory Control Sample (LCS)

7.11.1 The LCS shall be prepared from the calibration stock standard (primary) in Section 7.5. ~~[Each lab should specify how the LCS standard is prepared.]~~ A blank is spiked at a concentration between the low and mid-level calibration standards.

7.11.2 The LCS shall be prepared in the appropriate matrix (reagent water); and contains all of the method target analytes. A subset of the method target analytes could be used based on the project specific requirements. The spiking level used would be at the same level as the site-specific action limit. If site-specific action limits are not available or where these levels are very high, the spiking level shall be at a concentration between the low and mid-level calibration standards.

8.0 Procedure

8.1 Sample Preparation — Refer to the appropriate SW-846 digestion method.

8.2 Set up the instrument with proper operating parameters. The instrument must be allowed to become thermally stable before beginning (usually requiring at least ~~30 minutes~~ 1 hour of operation prior to calibration). ~~[Add laboratory-specific requirements here.]~~)

8.3 Initial Calibration — The calibration curve shall consist of a blank and at least three mixed standard concentrations (low, mid, high) for each element. Alternatively, a single standard and a blank may be used for initial calibration as long as verification is performed using both mid and low-level standards. ~~[Each lab shall insert the default standard concentrations and approach to be used in lieu of site-specific requirements.]~~ Flush the system with rinsing solution between each standard. (Use the average intensity of three integrations [minimum of 5 seconds each] for both calibration and sample analysis to reduce random error. The relative standard deviation of these replicate integrations should be less than 3 percent. If not, corrective action must be performed.)

8.4 Reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5%. If they do, troubleshoot the system to correct for this condition. Continue until an acceptable run is made for this highest mixed calibration standard. ~~[Each laboratory shall insert their corrective actions.]~~

8.5 Rinse the system with rinsing solution for at least 1 minute. Analyze the ICV — concentration values must be within 10% of known values. (If single point calibration was performed, both a mid and low-level verification shall be performed.)

8.6 Rinse the system with rinsing solution for at least 50 seconds. Analyze the ICB.

8.7 Rinse the system with rinsing solution for at least 1 minute. Analyze the ICS(s). Concentrations must be within ± 20% of the known values (refer to Section 11.3).

8.8 Sample analysis can now begin. Rinse the system with rinsing solution between samples and QC checks. If data system automates analytical run, program samples into software. If automation is not available, all runs must be recorded using a run log as shown in Figure 2. ~~[Each lab shall insert specific run log used.]~~ The software generates the run log.

[The following is an example analytical sequence and can be changed per each lab.]

Analytical Sequence

Sample	Comment
Reagent Water	Check instrument zero
Calibration Blank	Blank working standard
Standard 1 (S1)	Working standard #1 (low)
Standard 2 (S2)	Working standard #2 (mid)
Standard 3 (S3)	Working standard #3 (high)
Standard 3 (S3)	QC--must be within 5% of known value
ICV	QC check--must be within 10% of known value
ICS	Interference Check Standard(s)
Rinse	To remove any ICS memory
Samples 1-10	
CCB	Acceptance criteria in Section 11
CCV	QC check must be within 10% of known value

Repeat box until samples exhausted; samples include MD, MS/~~MSDs~~, LCS, and method blanks. Then end run with:

CCB

CCV

ICS

8.8 Continue with sample analysis, checking the calibration blank and midpoint standard (CCV) after every 10 samples.

8.9 The analytical sequence must be ended with an acceptable calibration blank,

mid-point standard (CCV) analysis and interference check standard.

8.10 Each sample shall be integrated three times. The RSD between these integrations needs to be evaluated. If RSD of triplicate integrations is consistently >10% and highly variable, this indicates a possible problem with the ICP sample introduction system. Replace tubing or clean nebulizer if necessary.

8.11 If the concentration found is greater than the highest standard, the sample must be diluted with the same concentration of acids used in the standard and in the original sample digestion and reanalyzed.

9.0 Calculations

9.1 The concentration of elements (µg/L) in the samples is read from the calibration curve or directly from the instrument if operating in the direct concentration mode. Samples that required dilution are adjusted according to the following equation:

$$\mu g/L \text{ metal in sample} = \frac{A\,(C + B)}{C}$$

where:

A = sample concentration from calibration curve
B = volume (mL) of calibration blank used to dilute sample
C = volume (mL) of sample used

9.2 The concentration of elements in solid matrices is reported in mg/Kg (dry basis) of waste as follows:

$$mg/Kg \text{ metal in sample} = \frac{A \times V}{W}$$

where:

A = final concentration read from calibration curve (see Section 9.1) in µg/L
V = Final volume of processed sample (L)
W = Weight of sample digested (g) (dry basis)

10.0 Quality Assurance/Quality Control

10.1 A preparation batch of samples is defined as a group of up to twenty field samples of similar matrix type that have been prepared at the same time or time sequence with the same lots of reagents for the same analysis. In addition to the twenty samples, each preparatory batch will contain at a minimum, a method blank, a laboratory control sample, a matrix spike, a matrix spike duplicate and a matrix duplicate. An analytical, or instrumental batch is defined as samples that are analyzed together within the same time period or in continuous sequential time periods. Within the analytical are included individual

QC requirements as defined by the analytical (determinative) method. Preparation batches of samples may be continuously strung together in these run sequences, as long as the analytical batch QC requirements meet the acceptance criteria established within the appropriate SOP. Each analytical sequence must be documented using the run log in Figure 1. ~~[Each lab should insert their own form if necessary.]~~ ~~The run log will be generated by the instrument software.~~

10.2 Run a calibration curve on a daily basis that employs a minimum of a calibration blank and three standard concentrations. Alternatively, a single standard and a blank may be used for initial calibration as long as verification is performed using both mid and low-level standards. Before beginning the sample run, the highest mixed calibration standard shall be analyzed as if it were a sample. Acceptance criteria are presented in Section 11.1.

10.3 After the highest standard, analyze the initial calibration verification (ICV) standard(s) containing all target analytes. Acceptance criteria listed in Section 11.2.

10.4 Check the instrument calibration by analyzing interference check standards (ICS) as follows. Verify the interelement and background correction factors at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Acceptance criteria are presented in Section 11.3.

10.5 Check the calibration by analyzing the continuing calibration blank (CCB) and continuing calibration verification (CCV) standard after every 10 samples and at the end of and analytical run. Acceptance criteria listed are in Section 11.4.

10.6 A method blank shall accompany each sample batch to determine if contamination or any memory effects are occurring. A method blank is a volume of reagent water acidified with the same amounts of acids as were used for preparation of the standards and samples. This sample is carried through the entire digestion and analysis procedure. Acceptance criteria are presented in Section 11.5.

10.7 A laboratory control sample must be prepared and analyzed with each batch of samples. The LCS would be prepared using the primary source standard and would contain all method target analytes. Control charts will be maintained for the LCS for all target analytes. Acceptance criteria are presented in Section 11.6.

10.8 The use of the matrix spike ~~and matrix spike duplicate~~ will depend in part on what role the laboratory is playing. When the laboratory serves the role as the primary laboratory, then site-specific documents should be consulted. The sample to be used for the MS~~/MSD~~ may be specified in the field. This previously designated sample would then be spiked with the site-specific target analytes at a concentration equivalent to the site action level. The MS~~/MSD~~ would be prepared using the primary source standards. If this information was not specified or unknown, then the laboratory would choose a representative sample from each batch of samples analyzed. If samples from multiple sites were to be analyzed in the same batch, then multiple sets of MS~~/MSD~~s may be

required. When the laboratory serves the role as the QA laboratory, the above scenario may not be practical to implement. If the site-specific requirements are unknown and samples from multiple sites are analyzed in the same batch, then the laboratory should select a single sample for spiking. Each batch of samples would then contain at least one MS~~/MSD pair.~~ Refer to the appropriate metals preparation SOP. Acceptance criteria are presented in Section 11.7 for percent recovery ~~and RPD.~~

10.9 The use of the matrix duplicate may also depend in part on the role the laboratory is playing. The selection of a matrix duplicate will be performed as described for the MS~~/MSD~~ in Section 10.7. Acceptance criteria are presented in Section 11.8 for RPD.

10.10 All sample analytical results used for final data reporting must be above the MDL and below the high standard of the calibration curve. Corrective actions are described in Section 11.9.

10.11 Whenever a new or unusual sample matrix is encountered, a series of tests shall be performed prior to reporting concentration data for analyte elements. These tests, as outlined in 11.10.1 and 11.10.2, will ensure the analyst that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

10.12 Data shall be checked to ascertain if it conforms to accepted practices for reporting of results at or near the MDL. The reporting limits which are required are (listed in order of preference); 1) project-specific requirements, or 2) the lowest standard of the standard curve. ~~Results between the MDL and the low standard shall be reported as estimates.~~

10.13 MDLs are determined in reagent water and verified on a project-specific schedule or annually if no project-specific requirements are in place. Refer to SOP No. Q-019-XX-MCX-XX, Method Detection Limits (MDLs), Method Quantitation Limits (MQLs), and Laboratory Reporting Limits (LRLs).

10.14 The analyst must demonstrate proficiency in performing the analysis as outlined in SOP No. Q-016-XX-MCX-XX, Technical Training. Method proficiency must be redemonstrated anytime a major method modification is made, a major software revision is added, or a major instrument modification is made. Demonstration of method proficiency may also be required after major instrument maintenance. This is decided on a case by case basis through discussions with the Section Chief, Laboratory Director, and Laboratory QA Officer.

11.0 Data Validation

11.1 After running the calibration standards, the highest standard is to be analyzed as a sample, prior to actual sample analysis. Concentration values obtained should not deviate from the actual values by more than 5%. If they do, troubleshoot the system to correct for this condition. Continue until an

acceptable run is made for this highest mixed calibration standard.

11.2 The results of the ICV for all analytes are to be within 10% of known values. If this criteria is not met, recalibrate and reanalyze, using the same standards. If acceptance criteria are still not met, recheck standard curve and ICV preparation and/or perform routine instrument maintenance (e.g., replace tubing, clean nebulizer/torch), recalibrate and reanalyze. If still not acceptable, refer to manufacturers's instructions or call service representative.

11.3 The analyst shall verify that the ICS has been analyzed at the required frequency. The prepared ICS is to be run at the beginning and end of each analytical run, or at the beginning and end of an 8 hour shift, whichever occurs more often. Results should be within ± 20% of the true value for all target analytes within the prepared ICS sample. If this criteria is not met, check the background correction protocols (IEC factors) currently in place for appropriateness and recalculate if needed. If this is the initial ICS run after daily calibration, recalibrate and reanalyze. If the ICS did not check at the end of an 8 hour shift, readjust background correction factors, and if needed, reanalyze any samples in the previous run that may have been affected.

11.4 Continuing Calibration

11.4.1 The results of the continuing calibration verification (CCV) check standard shall agree to within 10% of the expected value. If not, correct the problem, and reanalyze the previous ten samples since the last acceptable CCV.

11.4.2 The results of the calibration blank are to agree to within three standard deviations of the mean blank value. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, correct the problem, recalibrate, and reanalyze the samples analyzed since the last acceptable calibration blank.

11.5 Assess the method blanks. The analyst shall confirm that this blank was analyzed at the required frequency.

The method blank should not exhibit any contamination of any analyte above the MDL for any of the method target analytes. Corrective action should be performed any time method target analytes are detected above the MDL to reduce and control contamination. Corrective action will be required if site-specific target analytes are detected at greater than 5% of the regulatory limit for that analyte or if the concentration in the blank is greater than 5% of that in the sample. The first step of corrective action is to assess the effect on the samples. Corrective action would include reanalysis of field and QC samples in the batch if some or all of the samples also contained levels of target analytes that exceeded the above criteria. If none of the field samples had values above the stated criteria, then reanalysis may not be necessary. The source of contamination should still be investigated and reduced/eliminated. Any time contamination is noted in the method blank, the situation and impact

on the data should be discussed in the case narrative.

11.6 Verify that the LCSs were prepared at the required frequency. Plot the target analytes on appropriate control charts. (Refer to SOP No. Q-009-XX-MCX-XX, Control Chart Generation, Maintenance, and Usage.) If all target analytes are not within control limits, reanalyze the LCS digestate. If still unacceptable, redigest and reanalyze a new LCS and all associated samples. If the LCS is still unacceptable, then the entire procedure must be systematically investigated to locate the source of error.

Note: Even though control charts must be maintained for the LCSs, the acceptance criteria derived from these charts may not be appropriate if the charted ranges are too wide. A maximum default range should be used. It is recommended that the maximum default range be set to 80-120%. **[Each lab should specify maximum default ranges.]**

The RPD of interbatch LCSs should fall within the control limits determined from the precision control charts. However, if the RPD is outside these control limits, the batch will not be rejected, as long as the LCS recovery is acceptable. This precision information should be evaluated to see if systematic problems can be identified. If problems are suspected, the method should be fully evaluated.

11.7 Verify that matrix spike/matrix spike duplicates were analyzed at required frequency. The analyst shall also verify that the samples were spiked at the appropriate level. The order of preference for spiking levels is as follows; 1) If the target analyte concentrations are known, spike to increase the background concentration by a factor of approximately two, 2) if an action level exists, spike at this level, or 3) if neither of the first two conditions apply, spike at a level that corresponds between the low and mid-level calibration standards. Acceptance criteria are that all % Recovery and/or RPD results meet project established goals. If no project goals are specified, then results must be within the indicated control limits on the appropriate LCS control charts. If these conditions are not met, perform the following corrective actions as appropriate.

- If both LCS and MS/~~MSD~~ recoveries and/or precision are unacceptable, then the entire batch of field and QC samples must be redigested and reanalyzed.

- If the MS/~~MSD~~ recovery is unacceptable, but the LCS is acceptable, then a potential matrix effect has been identified. Reanalyze the MS/~~MSD~~ digestates to verify a matrix effect. If a matrix effect is still suspected, then the project manager must be contacted to discuss further alternatives and the potential impact on the project. These further alternatives may include redigestion/reanalysis.

11.8 Verify matrix duplicates were analyzed at required frequency (one per digestion unit). Acceptance criteria are that all RPD results meet project established goals. If no project goals are specified, then results must be within the indicated control limits on the appropriate LCS precision control charts. The acceptance criteria derived from these charts may not be appropriate if the

charted ranges are too wide. A maximum default range of 25% RPD should be used. ~~[Each lab should specify maximum default ranges.]~~ If these conditions are not met, perform the following corrective actions as appropriate.

- Reanalyze the sample and duplicate digestates.

- If the duplicate precision is unacceptable, then a potential matrix effect has been identified. The project manager must be contacted to discuss further alternatives and the potential impact on the project. These further alternatives may include redigestion/reanalysis.

11.9 The analyst must verify all reported results are derived from analytical results that are above the MDL or below the highest calibration standard. Verify the results are reported as follows:

- Sample concentrations that have been analyzed using the digestate in its most concentrated form, and are below the laboratory reporting limit (LRL), should report the result as less than the LRL.

- For sample results (again using the digestate in its most concentrated form) that are above the MDL but below the LRL, results need to be flagged as estimates (J values).

- For samples that exceed the calibration curve, dilute and analyze an appropriate sample aliquot.

11.10 For each new matrix, ensure that the following series of tests were performed and meet the listed acceptance criteria. If criteria are not met, the method of standard additions (MSA) should be considered. The project manager should be consulted.

11.10.1 Serial dilution

If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a 1:4 dilution should agree within ± 10% of the original determination. If not, a chemical or physical interference effect should be suspected.

11.10.2 Post-digestion spike addition

An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75% to 125% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected.

CAUTION: If spectral overlap is suspected, use of computerized compensation (interelement correction factors and background correction points evaluation), an alternate wavelength, or comparison with an alternate method is

recommended. ~~[Add laboratory specific operating parameters here.]~~

11.11 Besides the items listed in Sections 11.1 through 11.10, the analyst should also verify the additional items as noted in Figure 1.

11.12 Additional levels of review are performed as described in SOP No. Q-024-XX-MCX-XX, Data Reduction and Review/Validation (In-House/Contractor Data), using a predesigned form as shown in Figure 1.

12.0 Waste Disposal

This procedure generates acidic wastes. All wastes should be disposed of according to local regulatory as well as laboratory established guidelines. Refer to the laboratory's Waste Management Plan. **[Laboratory should include procedure for accumulation, storage, and disposal of these wastes.]**

13.0 References

13.1 Method 6010A, Test Methods for the Analysis of Solid Waste, Physical/Chemical Methods, Update II, Third Edition, July 1992.

13.2 Methods 3005A - 3051, Test Methods for the Analysis of Solid Waste, Physical/Chemical Methods, Update II, Third Edition, July 1992.

13.3 SOP No. Q-005-XX-MCX-XX, Sample Receipt, Login, and Storage.

13.4 SOP No. Q-012-XX-MCX-XX, Glassware Cleaning.

13.5 SOP No. Q-008-XX-MCX-XX, Reagent Water Generation and Quality Monitoring.

13.6 SOP No. Q-009-XX-MCX-XX, Control Chart Generation, Maintenance, and Usage

13.7 SOP No. Q-016-XX-MCX-XX, Technical Training.

13.8 SOP No. Q-019-XX-MCX-XX, Method Detection Limits (MDLs), Method Quantitation Limits (MQLs), and Laboratory Reporting Limits (LRLs).

13.9 SOP No. Q-024-XX-MCX-XX, Data Reduction and Review/Validation (In-House/Contractor Data).

13.10 **[Identify MSC laboratory]** Waste Management Plan.

13.11

Table 1
~~Recommended Wavelengths and Estimated Instrumental Detection Limits.~~

~~Analyte~~	~~CAS #~~	~~Wavelength (nm)[a]~~	~~Estimated Element Detection Limit (µg/L)[b]~~
~~Aluminum~~	~~7429-90-5~~	~~308.215~~	~~55~~
~~Antimony~~	~~7440-36-0~~	~~206.833~~	~~50~~
~~Arsenic~~	~~7440-38-2~~	~~193.696~~	~~50~~
~~Barium~~	~~7440-39-3~~	~~455.403~~	~~2~~
~~Beryllium~~	~~7440-41-7~~	~~313.042~~	~~1~~
~~Cadmium~~	~~7440-43-9~~	~~226.052~~	~~5~~
~~Calcium~~	~~7440-70-2~~	~~317.933~~	~~500~~
~~Chromium~~	~~7440-47-3~~	~~267.716~~	~~2~~
~~Cobalt~~	~~7440-48-4~~	~~228.616~~	~~1~~
~~Copper~~	~~7440-50-8~~	~~324.754~~	~~5~~
~~Iron~~	~~7439-89-6~~	~~259.940~~	~~20~~
~~Lead~~	~~7439-92-1~~	~~220.353~~	~~40~~
~~Lithium~~	~~7439-93-2~~	~~670.784~~	~~5~~
~~Magnesium~~	~~7439-95-4~~	~~279.079~~	~~200~~
~~Manganese~~	~~7439-96-5~~	~~257.610~~	~~1~~
~~Molybdenum~~	~~7439-98-7~~	~~202.030~~	~~1~~
~~Nickel~~	~~7440-02-0~~	~~231.604~~	~~5~~
~~Phosphorous~~	~~7723-14-0~~	~~213.618~~	~~51~~
~~Potassium~~	~~7440-09-7~~	~~766.491~~	~~2000~~
~~Selenium~~	~~7782-49-2~~	~~196.026~~	~~50~~
~~Silver~~	~~7440-22-4~~	~~328.068~~	~~5~~
~~Sodium~~	~~7440-23-5~~	~~588.995~~	~~200~~
~~Strontium~~	~~7440-24-6~~	~~407.771~~	~~1~~
~~Thallium~~	~~7440-28-0~~	~~190.864~~	~~50~~
~~Vanadium~~	~~7440-62-2~~	~~292.402~~	~~1~~
~~Zinc~~	~~7440-66-6~~	~~213.856~~	~~10~~

~~(a) The wavelengths listed are recommended because of their sensitivity and overall acceptance.~~

~~(b) The estimated instrumental detection limits shown are taken from Reference 1 in Section 13. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies. Detection limits using an axial torch will be lower.~~

~~(c) Highly dependent on operating conditions and plasma position.~~

Table 1
Recommended Wavelengths and Estimated Method Detection Limits.

Analyte	CAS #	Wavelength (nm)[a]	Estimated Element Detection Limit (µg/L)[b]	Method Reporting Limits. (ug/L)
Aluminum	7429-90-5	308.215	5	25
Antimony	7440-36-0	206.833	10	50
Arsenic	7440-38-2	188.979	3	20
Barium	7440-39-3	317.933	3	1
Beryllium	7440-41-7	313.042	0.2	1
Cadmium	7440-43-9	226.052	0.2	5
Calcium	7440-70-2	317.933	20	200
Chromium	7440-47-3	267.716	0.3	2
Cobalt	7440-48-4	228.616	0.5	1
Copper	7440-50-8	324.754	0.5	5
Iron	7439-89-6	238.204	0.1	20
Lead	7439-92-1	220.353	10	10
Lithium	7439-93-2	670.784	5	5
Magnesium	7439-95-4	279.079	10	200
Manganese	7439-96-5	257.610	0.5	1
Molybdenum	7439-98-7	202.030	0.6	2
Nickel	7440-02-0	231.604	0.6	5
Phosphorous	7723-14-0	213.618	51	51
Potassium	7440-09-7	766.491	200(c)	200(c)
Selenium	7782-49-2	196.026	2	50
Silver	7440-22-4	328.068	1	5
Sodium	7440-23-5	588.995	20	200
Strontium	7440-24-6	407.771	0.03	0.2
Thallium	7440-28-0	190.864	2	50
Vanadium	7440-62-2	292.402	0.3	1
Zinc	7440-66-6	206.200	1	10

(a) The wavelengths listed are recommended because of their sensitivity and overall acceptance. These wavelengths are also based on Perkin Elmer's recommendations.

(b) The estimated instrumental detection limits shown are taken from Reference 1 in Section 13. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies. Detection limits are based on axial operation.

(c) Highly dependent on operating conditions and plasma position.

Table 2
Analyte Concentration Equivalents Arising From Interference at the 100 mg/L Level.

Analyte	Wavelength (nm)	Interferant (a,b,c)									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Tl	V
Al	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Sb	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
As	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Ba	455.403	--	--	--	--	--	--	--	--	--	--
Be	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Cd	226.052	--	--	--	--	0.03	--	--	0.02	--	--
Ca	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Cr	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Co	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Cu	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Fe	259.940	--	--	--	--	--	--	0.12	--	--	--
Pb	220.353	0.17	--	--	--	--	--	--	--	--	--
Mg	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Mn	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Md	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Ni	231.604	--	--	--	--	--	--	--	--	--	--
Se	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Na	588.995	--	--	--	--	--	--	--	--	0.08	--
Tl	190.864	0.30	--	--	--	--	--	--	--	--	--
V	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zn	213.856	--	--	--	0.14	--	--	--	0.29	--	--

(a) Dashes indicate that no interference was observed in the presence of the following interferants:

Al, Ca, Fe, and Mg at 1000 mg/L, and Cr, Cu, Mn, Tl, and V at 200 mg/L.

(b) The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferant figure.

(c) Other lines can be used if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interferences.

NOTE: Negative concentration equivalents can arise from some interferants.

Data Review Check List
ICP Metals
[Identify MSC Laboratory]

Project Number(s)	
Batch Number(s)	
SOP No.	

Review Item	Yes (x)	No (x)	N/A (x)	2nd Level Review (x)
1. Does the daily standard curve consist of a Calibration Blank and the required minimum number of calibration standards?				
2. Is the low standard near, but above, the MDL?				
3. Is the highest initial calibration standard reanalyzed immediately after calibration and results within QC limits?				
4. Are the CCV standards analyzed at required frequency and at the end of the analytical sequence and all parameters within QC limits?				
5. Are the CCB standards analyzed at required frequency and at the end of the analytical sequence and all parameters within QC limits?				
6. Are all sample holding times met?				
7. Are all samples with concentrations > the highest standard used for initial calibration diluted and reanalyzed?				
8. Is the method blank run at the desired frequency and is its concentration for target analytes less than the LRLs?				
9. Is the ICV from a second source and is its percent recovery within QC limits?				
10. Is the Matrix Spike/Matrix Spike Duplicate run at the desired frequency and is the percent recovery/RPD within QC limits?				
11. Is the Matrix Duplicate run at the desired frequency and is the RPD within QC limits?				
12. Is a Serial Dilution analysis performed at the desired frequency and within QC limits?				
13. Are post-digestion spikes analyzed at the desired frequency and within QC limits?				
14. Are Interference check standards analyzed at the beginning and end of analytical run or at minimum frequencies and within QC limits?				

Figure 1.

Data Review Check List
ICP Metals
[Identify MSC Laboratory]

Review Item	Yes (x)	No (x)	N/A (x)	2nd Level Review (x)
15. Are all nonconformances include and noted?				
16. Is the correct methodology used for sample prep and analysis?				
17. Are all calculations checked at the minimum frequency?				
18. Did analyst sign/date the appropriate printouts and report sheets?				
19. Are all sample ID and units checked for transcription errors?				

Comments on any "No" response:

_____

_____

_____

_____

_____

_____

_____

Analyst: _____ Date: _____

2nd Level Reviewer: _____ Date: _____

Figure 1.(cont.).

Data Review Check List
ICP Metals
[Identify MSC Laboratory]

Project Number(s)	
Batch Number(s)	
SOP No.	

Review Item	Yes (x)	No (x)	N/A (x)	2nd Level Review (x)
1. Does the daily standard curve consist of a Calibration Blank and the required minimum number of calibration standards?				
2. Is the low standard near, but above, the MDL?				
3. Is the highest initial calibration standard reanalyzed immediately after calibration and results within QC limits?				
4. Are the CCV standards analyzed at required frequency and at the end of the analytical sequence and all parameters within QC limits?				
5. Are the CCB standards analyzed at required frequency and at the end of the analytical sequence and all parameters within QC limits?				
6. Are all sample holding times met?				
7. Are all samples with concentrations > the highest standard used for initial calibration diluted and reanalyzed?				
8. Is the method blank run at the desired frequency and is its concentration for target analytes less than the LRLs?				
9. Is the ICV from a second source and is its percent recovery within QC limits?				
10. Is the Matrix Spike/Matrix Spike Duplicate run at the desired frequency and is the percent recovery/RPD within QC limits?				
11. Is the Matrix Duplicate run at the desired frequency and is the RPD within QC limits?				
12. Is a Serial Dilution analysis performed at the desired frequency and within QC limits?				
13. Are post-digestion spikes analyzed at the desired frequency and within QC limits?				
14. Are Interference check standards analyzed at the beginning and end of analytical run or at minimum frequencies and within QC limits?				

Figure 1. Example.

Data Review Check List
ICP Metals
[Identify MSC Laboratory]

Review Item	Yes (x)	No (x)	N/A (x)	2nd Level Review (x)
15. Are all nonconformances include and noted?				
16. Is the correct methodology used for sample prep and analysis?				
17. Are all calculations checked at the minimum frequency?				
18. Did analyst sign/date the appropriate printouts and report sheets?				
19. Are all sample ID and units checked for transcription errors?				

Comments on any "No" response:

_____

_____

_____

_____

_____

_____

_____

Analyst: _____ Date: _____

2nd Level Reviewer: _____ Date: _____

Figure 1. Example.(cont.).

ICP Run Log
[Identify MSC Laboratory]

Instrument ID:		
Date:		SOP No. _____

No.	Lab ID	Dil. Factor	Conc. Factor	Conc. from Instrument	Final Conc.
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					

Notes: _____

_____

_____

Figure 2.

ICP Run Log
[Identify MSC Laboratory]

Instrument ID:		
Date:		SOP No. _____

No.	Lab ID	Dil. Factor	Conc. Factor	Conc. from Instrument	Final Conc.
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					

Notes: _____

_____

_____

Figure 2. Example.

Sample Information Detail Report
Document Name: Untitled

File Description

Parameters Common To All Samples

Batch ID
Analyst Name
Volume Units mL
Weight Units g
OID

Parameters That Vary With All Samples

A/S Location	Sample ID	Aliquot Volume	Diluted To Vol.
001			
002			
003			
004			
005			
006			
007			
008			
009			
010			
011			
012			
013			
014			
015			
016			
017		1	5
018			
019			
020			
021			
022			
023			
024			
025			
026			
027			
028		1	5
029			
030			
031			
032			
033			
034			
035			
036			
037			
038			
039			
040			
041			
042			
043			
044			
045			
046			

Sample Information Detail Report
Document Name: 72115CU

File Description
smith

Parameters Common To All Samples

Batch ID	lab #
Analyst Name	AHW
Volume Units	mL
Weight Units	g
OID	57237160

Parameters That Vary With All Samples

	A/S Location	Sample ID	Aliquot Volume	Diluted To Vol.
001	7	HIGH		
002	10	ICV ICAP19		
003	1	ICB		
004	11	ICSA		
005	12	ICSAB		
006	6	CCV1		
007	13	CCB1		
008	14	PBW		
009	15	LCS BS		
010	16	CLP 431		
011	17	72115		
012	18	72115R		
013	19	72115L	1	5
014	20	72115A		
015	21	ICSA		
016	22	ICSAB		
017	6	CCV2		
018	23	CCB2		
019				
020				
021				
022				
023				
024				
025				
026				
027				
028				
029				
030				
031				
032				
033				
034				
035				
036				
037				
038				
039				
040				
041				
042				

TITLE: Mercury In Solid Or Semisolid Waste (Manual Cold-Vapor Technique) (SW-846 Method 7471A)

SOP NUMBER: M-7471A-00-WES-XX

PREPARED BY: _____
Date

REVIEWED BY: _____
Technical Specialist Date

_____
QA Officer Date

_____
Laboratory Director Date

SOP MANUAL CONTROL NO.: _____

1.0 Scope and Application

1.1 This SOP details a cold-vapor fluorescence ~~atomic absorption procedure (CVAA)~~ for determining the concentration of mercury in soils, sediments, wastes, bottom deposits, and sludge-type materials.

1.2 This procedure is used for the determination of total mercury.

2.0 Method Summary

2.1 Prior to analysis by the mercury cold-vapor technique, all samples must be prepared according to the procedure discussed in Section 8.0 of this SOP.

2.2 This is a cold-vapor fluorescence ~~atomic absorption~~ technique and is based on the emittance ~~absorption~~ of radiation at 253.7 nm by mercury vapor. During the digestion step, inorganic forms of mercury and organo-mercury compounds are oxidized by potassium permanganate and potassium persulfate and converted to mercuric ions. This method has been shown to be effective for measuring a number of organic mercurials including phenyl mercuric acetate and methyl mercuric chloride. The effectiveness of this procedure for other organic mercurials should be evaluated with duplicates and matrix spikes. (Refer to Section 10.0 of this SOP for quality assurance information.)

2.3 After digestion, the mercuric ion is reduced to the elemental state and aerated from the solution in a closed system.

2.4 The mercury vapor passes through a cell positioned in the light path of an fluorescence ~~atomic absorption~~ spectrophotometer.

2.5 The sample fluorescence ~~absorbance~~ (as measured by peak height ~~or peak area~~) is measured and quantified on a calibration curve constructed from known mercury standards.

2.6 The typical detection limit using ~~0.2~~ 0.5 grams of sample is ~~0.1~~ 0.04 mg/Kg. **[Each laboratory shall insert the appropriate laboraotry generated MDL and associated LRL. The LRL should be at the same level of the low standard.]**

3.0 Health and Safety

3.1 Use of this procedure requires the handling of corrosive acids and protective equipment must be utilized.

3.2 All sample handling must be performed in a fume hood.

3.3 For specific information regarding the toxicity of the reagents used in this procedure and other related health and safety issues including the proper storage and handling of reagents and chemicals, the analyst should consult the appropriate Material Safety Data Sheets (MSDSs) which are located in Room

69. ~~[Lab should insert location of MSDSs.]~~

3.4 Use of this procedure requires the handling of concentrated acid (sulfuric acid). Prior to performing this procedure, the analyst should be familiar with the proper use of corrosive liquid spill kits and containment procedures. Minimum personal protection includes the use of laboratory safety glasses, a lab coat or apron, and protective gloves. All digestions must be performed in a laboratory fume hood.

4.0 Sample Preservation, Containers, Handling, and Storage

4.1 Requirements for sample preservation, sample containers, and sample storage are detailed in SOP No. Q-005-XX-WES-XX, Sample Receipt, Login and Storage.

4.2 All samples must be preserved and stored at 4 ± 2 °C until analyzed. The holding time for mercury in solid matrices is 28 days from the date of collection.

5.0 Interferences and Potential Problems

5.1 Potassium permanganate is added to eliminate possible interference from sulfide. Sulfide concentrations as high as 20 mg/Kg have been shown not to interfere with the recovery of added inorganic mercury from reagent water.

5.2 Copper has also been reported to interfere with the analysis of mercury, however, copper concentrations as high as 10 mg/Kg had no effect on recovery of mercury from spiked samples.

5.3 Samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine hydrochloride solution ~~sulfate reagent~~ (25 mL). ~~In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate~~. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique. Excessive amounts of chlorine have not been found to cause interferences with a fluorescence detector.

5.4 ~~Certain volatile organic materials that absorb at this wavelength may also cause interference. If high concentrations of volatile organics are suspected, a preliminary run without reagents may be used to determine if this type of interference is present. If this type of interference is confirmed, the sample should be diluted to eliminate the interference.~~

6.0 Equipment/Apparatus

6.1 ~~Atomic absorption spectrophotometer (AAS), mercury analyzer or equivalent~~

~~instrument~~ P.S. Analytical Merlin Plus with a Merlin Fluorescence Detector - ~~An atomic absorption unit with an open sample presentation area in which to mount the absorption cell is suitable. [Lab should insert the specifics of the instrument used.]~~ A closed atomic presentation area where the sample enters the detector as a gas which is carried through a chimney past a light source and a photomultiplier tube at an angle to each other. The mercury vapor absorbs the light at a wavelength of 253.7.

6.2 ~~Mercury hollow cathode lamp or electrodeless discharge lamp (EDL), [lab should insert type of lamp used].~~ High intensity Mercury lamp developed by Cathodeon which provides the required excitation and emission wavelengths using a fixed 254 nm filter and a Photomultiplier tube which detects fluorescence from the sample.

6.3 ~~Recorder — Any multi-range variable-speed recorder compatible with the instrument may be used to graphically record sample response. Computerized systems capable of recording instrument response may also be used. [Lab should describe the system used.]~~ P.S. Analytical TouchStone Software version 3.4 with a printer. The output from the Merlin Detector is fed to the computer using the Merlin's RS232 port. The software controls the operation of the individual components and collects, calculates, and reprints the results of blanks, samples, and standards.

6.4 ~~Absorption cell — Standard spectrophotometer cells, 10-cm long with quartz end windows, may be used. [Lab should insert the specifics of the cells used.]~~

6.5 ~~Air pump — Any peristaltic pump capable of delivering 1 liter air/min may be used. A Masterflex pump with electronic speed control has been found to be satisfactory. [Lab should specify what is used.]~~ Liquid Argon Tank set at 20 psi is used to deliver flow at 0.5 ±0.07 liters/min.

6.6 Flowmeter — Capable of measuring an air flow of 1 L/min.

6.7 ~~Impinger — A straight glass tube fitted with a frit with a coarse porosity. Impingers are commercially available from a number of glassware supply companies. [Lab should specify type of impinger and supplier.]~~

6.8 ~~Aeration tubing — Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.~~ Gas/liquid separator - strips mercury from the liquid using a flow rate of approximately 0.5 litre/min of argon. This vapor is fed into the central tube of the chimney interface where a further argon stream of approximately 0.2 litre/min is fed to a concentric ring of outlets around the central stream. This effectively constrains the mercury vapour in a laminar flow of argon past the fluorescence head of the monitor.

6.9 Drying tube — ~~A 6 inch x ¾ inch diameter polyethylene or glass tube fitted with serrated tips. The drying tube is filled with approximately 20 g of magnesium perchlorate and is attached to the sample line between the sample and the absorption cell to absorb excess moisture during the analysis. Alternatively, a small reading lamp fitted with 60-W bulb may be positioned directly above the~~

~~absorption cell to prevent the condensation of moisture inside the cell. The lamp should be positioned so that the temperature of the cell is about 10 °C above ambient temperature. {Lab should describe procedure for reducing moisture.}~~ The drier tube is made by Perma Pure and is composed of silicon and nylon tubing. The drier tube has an internal tubular membrane through which the mercury and water vapor from the sample travels. Carrier argon pushes these vapors through. The water vapor permeates through the membrane to the other tube. Dilute argon gas is passed through the outer space to sweep out the water vapor that goes through the membrane. This process dries the mercury vapor which causes noise and matrix effects in detectors.

6.10 The Hydride ~~cold~~-vapor generator is assembled according to the manufacturer's instructions. ~~{Lab should insert specifics here.}~~

6.10.1 Carfully unpack the Hydride/Vapour generator.

6.10.2 Place the generator on the left side of the Merlin.

6.10.3 Ensure that voltage selector is switched to correct voltage selection.

6.10.4 Plug into mains supply and turn on switch at rear. Ensure Hydride motor starts and front LEDS light. Turn Hydride/Vapour Generator off.

6.10.5 Place Gas/liquid separator on right hand side of Hydride unit in spring clips provided and carefully connect up the gas and liquid lines.

6.10.6 Connect drain line to Gas/Liquid Separator U-tube, ensure this is free running.

6.10.7 Connect sample out line from top of separator to rear of Merlin marked SAMPLE IN.

6.10.8 Connect the snap-in connector to inputs of both rotameters and other end to Argon supply. Ensure Argon supply is regulated, a pressure setting of approximately 20 psi is required by the Merlin System.

6.10.9 Connect sheath gas rotameter to Merlin SHEATH GAS Input via suitable gas line.

6.10.10 Connect 15 way 'D' connector supplied to the rear of Hydride Gererator, connect other end of the cable to the 25 way 'D' connector at the rear of the computer.

Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system either to vent the mercury into an exhaust hood or to pass the vapor through a absorbing medium (an activated charcoal filter). Refer to Section 7.0 of this SOP for instructions on the preparation of a mercury absorbing medium.

6.11 ~~Water bath, hot plate, or equivalent heating device — Adjustable and capable of maintaining a temperature of 90-95°C. [Lab should specify equipment used for digesting samples.]~~ Blue M oven - adjustable and capable of maintaining a temperature of 90-95°C.

6.12 Graduated cylinders — Class A, various sizes, 25 to 1000-mL.

6.13 Balance, capable of weighing to the nearest 0.001 g.

6.14 Acid-dispensing bottles, polyethylene, polypropylene or equivalent material, in various dispensing sizes (2.5, 3, 5, 10 and 15-mL).

6.15 ~~300-mL BOD bottles — glass with ground glass stoppers.~~ 250 mL Teflon bottles with caps.

6.16 Volumetric pipets — Class A, various sizes.

6.17 Squeeze bottles — polyethylene or equivalent material, 500-mL size. Used for general rinsing purposes and to dispense reagent water.

6.18 ~~Autoclave (optional).~~

6.19 ~~Aluminum foil.~~

6.20 Thermometer — 0-100 °C, accurate to ± 1 °C.

6.21 Volumetric flasks, Class A, various sizes.

6.22 Electronic pipets - checked daily (acceptable ranges are 99-101%).

7.0 Reagents

7.1 Reagent water — Refer to SOP No. Q-008-XX-MCX-XX, Reagent Water Generation and Quality Monitoring.

7.2 Acids must be analyzed to determine levels of impurities. If a method blank made with the acid is < MDL, the acid can be used. This should be verified with each new lot of acid.

7.2.1 Concentrated sulfuric acid (H_2SO_4, JT Baker TraceMetal grade, Cat# 7664-93-9 or equivalent): ~~[Laboratory shall list name of supplier, catalog number, and specific acid type.]~~

7.2.2 ~~Sulfuric acid, 0.5 N — Using a 25-mL graduated cylinder, transfer 14.0 ± 0.5 mL concentrated sulfuric acid to a 1.0-L volumetric flask containing approximately 200 ± 50 mL reagent water. Mix and bring to volume with reagent water. This solution may be stored at room temperature in a 1-L plastic or glass bottle.~~

7.2.3 Concentrated nitric acid (HNO_3, Fisher TraceMetal grade, Cat# A-509

~~or equivalent). {Laboratory shall list name of supplier, catalog number, and specific acid type.}~~

7.2.4 ~~Concentrated hydrochloric acid (HCl, Fisher TraceMetal grade, Cat# A-508 or equivalent). {Laboratory shall list name of supplier, catalog number, and specific acid type.}~~

7.3 ~~Aqua regia (3:1 v/v HCl:HNO_3) — This reagent is prepared immediately before use. Using a 200-mL graduated cylinder, carefully measure 150 ± 5 mL concentrated HCl into a 1-L beaker or Erlenmeyer flask. Using the same graduated cylinder, measure 50 ± 2 mL of concentrated HNO_3 and carefully add to the flask containing the Hcl.~~

7.4 ~~Stannous sulfate (0.46 M $SnSO_4$) - Weigh 25 ± 0.1 g of stannous sulfate ($SnSO_4$, certified grade) and transfer it to a 250-mL volumetric flask. Using a 100 mL graduated cylinder, add approximately 100 mL of 0.5 N H_2SO_4 (Section 7.2.3) to the flask. Mix to dissolve and bring to final volume with 0.5 N H_2SO_4. This mixture is a suspension and should be stirred continuously during use. This solution may be stored in a glass 1-L bottle at room temperature.~~

Note: A stannous chloride solution may be used in place of stannous sulfate (see below).

7.5 Stannous chloride (0.52 M $SnCL_2$) - Using a 25-mL graduated cylinder, transfer 12.5 ± 0.5 mL of concentrated HCl to a 1-L volumetric flask containing approximately 250 mL of reagent water and mix. Weigh ~~100~~ 20 ± 1 g stannous chloride (certified grade) and transfer it to the volumetric flask. Bring to volume with reagent water and mix. This mixture will form a suspension that must be stirred continuously during use. This solution may be stored in a 1-L glass reagent bottle at room temperature.

7.6 Sodium chloride (NaCl) — ACS Reagent grade.

7.7 Hydroxylamine hydrochloride ~~sulfate $(NH_2OH)_2 \cdot H_2SO_4$~~ — ACS Certified.

7.8 Sodium chloride-hydroxylamine hydrochloride ~~sulfate~~ solution (0.73 M hydroxylamine sulfate) Weigh 120 ± 1 g of sodium chloride (Section 7.6) and 120 ± 1 g of hydroxylamine sulfate (Section 7.7) and transfer to a 1-L volumetric flask containing approximately 500 mL of reagent water. Mix to dissolve and bring to volume with reagent water. This solution may be stored in a 1-L glass reagent bottle at room temperature.

7.9 Potassium permanganate ($KMnO_4$), 5% solution (w/v) — Weigh 50 ± 0.5 g of potassium permanganate and transfer to a 1-L volumetric flask containing approximately 500 mL of reagent water. Mix to dissolve and bring to volume with reagent water. This solution may be stored in a 1-L ~~plastic or~~ glass bottle at room temperature. (Solutions suitable for mercury analysis can be purchased.)

~~7.10 Saturated permanganate ($KMnO_4$) - {This reagent should only be prepared if the~~

~~autoclave method (see Section 8.6) will be used). Saturated $KMnO_4$ is prepared by adding approximate 7 ± 0.1 g of $KMnO_4$ to 100 ± 2 mL of reagent water (at room temperature). Saturation is indicated by the presence of undissolved $KMnO_4$ after the solution is thoroughly mixed.~~

7.10 Potassium Persulfate: Dissolve 5 grams of potassium persulfate ($K_2S_2O_8$) in 100 mL of deionized water.

7.11 Stock Mercury Standard (~~1000~~ 10 mg/L Mercury) — Purchased from Alfa Aesar Stock #36747. Stock calibration solutions shall be purchased as certified solutions from commercial suppliers. Refer to SOP No. Q-003-XX-WES-XX, Standards Preparation, Traceability, and Storage for requirements. Certificates must be kept on file. ~~[Laboratory shall specify the supplier, catalog number, and concentrations.]~~ Purchased stock solutions are stable for one year.

7.11.1 Primary source standards shall be used to prepare the initial 5-point calibration curve, continuing calibration verification (CCV) standard, and matrix spikes ~~and their duplicates~~ (MS/~~MSDs~~).

7.11.2 Secondary source standards shall be used to verify the initial calibration (ICV) curve only. These standards shall be purchased from a different vendor, unless the primary vendor can supply different lot numbers. See Section 7.16 for the preparation and final concentration of these standards. Secondary source is a 10 mg/L mercury standard from Claritas PPT catalog # CL-ICS-2.

~~7.12 Intermediate Mercury working standard (10 mg/L Mercury) — Using a 1-mL volumetric pipet, transfer 1 mL of the mercury stock (Section 7.11) to a 100-mL volumetric flask containing approximately 50 mL reagent water and 1.5 ± 0.1 mL HNO_3. Mix and dilute to volume with reagent water. The final acid concentration will be approximately 0.15%. Prepare fresh each day.~~

7.13 Mercury working standard (~~0.1~~ 0.2 mg/L Mercury) — Using a 1-mL volumetric pipet, transfer 1 mL of the intermediate mercury stock (Section ~~7.12~~ 7.11) to a ~~100~~ 200-mL volumetric flask containing approximately 50 mL reagent water and ~~1.5~~ 2 ± 0.1 mL HNO_3. Mix and dilute to volume with reagent water. The final acid concentration will be approximately 0.15%. Prepare fresh each day.

Note: For convenience, 1.5 mL of HNO_3 may be added to each volumetric flask with a 1.5 mL acid-dispensing bottle prior to the addition of reagent water or stock solution. The final acid concentration will be approximately ~~0.15~~ 0.10%.

7.14 ~~If purchasing a certified prepared standard solution is not an option then the stock solution shall be made from neat materials as follows: [Laboratory shall insert specific procedures.]~~

7.15 Calibration Standards

7.15.1 Prepare a five point calibration curve which includes a calibration blank

using the working standard from Section 7.13. The lowest standard shall be 3 to 5 times MDL. The highest standard shall not exceed the linear range of the instrument.

7.15.2 Transfer 0.0, 0.2, 0.5, 1.0, 2.0, and 4.0-ml aliquots of the mercury working standard (~~0.1~~ 0.2 mg/L) to a series of 200 ~~300~~-ml class A volumetric flasks ~~BOD bottles~~. Add enough reagent water using a micropipetter to bring to a total volume of 200 ml ± 0.5 mL. See Table 1 ~~[This curve is an example and should be replaced with laboratory specific information.]~~ Calibration standards are to be processed at the same time of the sample batch. Refer to Sections 8.1.2, 8.1.3, 8.1.4, 8.1.5, and 8.1.7.

Table 1. Default Calibration Curve

Volume of Working Standard (mL)	Hg per 10 mL of Standard (μg)
4.0	0.4
2.0	0.2
1.0	0.1
0.5	0.05
0.2	0.02
0 (calibration blank)	0 (calibration blank)

7.15.3 Client specific requirements may require a different calibration curve. DQOs should be consulted before sample analysis to ensure the calibration range is appropriate. In the absence of project specific requirements, the following default calibration curve in Table 1 will be used.

7.16 Laboratory Control Sample (LCS)

7.16.1 The LCS ~~shall be~~ is prepared from the ~~intermediate working standard (primary) in Section 7.12.~~ NIST standard soil.

7.16.2 The LCS shall be prepared in the appropriate matrix (purified solid) and is processed at the same time as the sample batch. See Sections 8.1.2, 8.1.3, and 8.1.4.

7.16.2 The spiking level used should be at the same level as the site-specific action limit, with the exception that the concentration can never be lower than the lowest standard used for the initial calibration.

7.16.3 If an action level is not known, the spiking level shall default between the low and mid-level calibration standards. **[Each lab should specify default level and how it is prepared.]**

7.17 Continuing Calibration Verification (CCV) standard

7.17.1 The CCV is prepared the same as the primary mid-level standard (Section 7.15.2) and is run after every 8 ~~10~~ samples (sample includes duplicates and MS/~~MSD~~(s)) and at the end of the analytical sequence.

7.17.2 A sufficient number of CCVs will need to be processed to meet the requirements of the batch size being used. They are processed in the same manner and at the same time of the sample batch. See Section 8.1.2, 8.1.3, and 8.1.4.

7.18 Matrix Spike (MS) Standard

7.18.1 The MS standard shall be prepared from the primary source calibration standard and processed at the same time as the sample batch. See Sections 8.1.2, 8.1.3, and 8.1.4..

7.18.2 The spike should be at the site action level, if applicable, or twice the expected concentration, if known. If an action level is not known, the spiking level would default between the low and mid-level calibration standards. ~~The sample is spiked at either 1 or 2 ppb using the 0.2 mg/L working standard. For the 1 ppb spike use 75 µl of the .2 mg/L then dilute to 1 L and add 10 ml to the sample. For the 2 ppb spike use 150 µl of the .2 mg/L working standard to 1.5 ml with the sample. The 1 ppb spike is usually used for sandy matrices and the 2 ppb spike is used for clay matrices. [Each lab should specify default level and how it is prepared.]~~

7.19 ~~Mercury absorber solution, Potassium permanganate, (0.1 M KMnO4 in 10% H_2SO_4) - Weigh out approximately 16 ± 1 g of $KMnO_4$ and transfer it to a 100-mL volumetric flask containing approximately 50 mL of reagent water and 10 ± 1 mL H_2SO_4. Mix and bring to volume with reagent water.~~

8.0 Procedure

8.1 Sample preparation

8.1.1 Dry sample in oven at 60°C for approximately two hours (or until completely dry). Homogenize sample and seive through a 40 mesh seive. Weigh ~~three~~ two separate aliquots of ~~0.2~~ 0.5 g, ~~or one aliquot of 0.5 to 1.0 g~~ (to the nearest 0.001g). ~~(The laboratory may choose the approach to be used.)~~ Place each aliquot in the bottom of a separate ~~teflon~~ ~~BOD~~ bottle. Using an automatic dispenser ~~pipetter~~, add ~~5~~ 2 ± ~~0.5~~ 0.1 mL of reagent water. Sample weights are to be recorded on the mercury digestion log (see Figure 1).

Note: A separate determination of percent solids must be performed. Refer to SOP No. M-2216-XX-WES-XX, Determination of Water (Moisture) Content of Soil (ASTM Method 2216).

~~8.1.2 Using an automatic pipetter, add 5 ± 0.5 mL of aqua regia (Section~~

~~7.3) to each sample and standard. Place in a heating device and heat from 90-95°C for at least 2 minutes from the time the bath reaches 90°C. Remove from heating device and cool. **[Lab should replace heating device with equipment actually used.]**~~

~~Note: The temperature of the heating device may be monitored with a temperature blank prepared by inserting a thermometer into a BOD bottle fitted with a rubber stopper and containing approximately 120 mL of reagent water. Adjust the temperature control on the heating device until the sample temperature equilibrates at 90-95°C.~~

8.1.2 Add 5 mL sulfuric acid.

8.1.3 Add 2.5 mL nitric acid.

8.1.4 Add 15 mL of the 5% potassium permanganate solution.

8.1.5 Add 10 mL of the 5% potassium persulfate.

8.1.6 Heat at 90-95°C for 90 ± 5 min.

~~8.1.3 Using a automatic pipetter, add 50 ± 2 mL of reagent water to each bottle. Swirl. Using an automatic pipetter, add 15 ± 0.5 mL $KMnO_4$ solution (Section 7.9) to each bottle. Mix thoroughly and return to the heating device. Heat at 90-95°C for 30 ± 5 min.~~

8.1.7 Remove from heating device and allow to cool to room temperature. Using an automatic pipetter, add 6 ± 0.2 mL of sodium chloride-hydroxylamine hydrochloride ~~sulfate~~ (Section 7.8) to each bottle to reduce the excess permanganate. Swirl until all traces of purple color clears. ~~Using a 100-mL graduated cylinder, add 55 ± 2 mL of reagent water to each bottle.~~ The samples are now ready for analysis. See Section 8.2.6 for the next applicable step for samples. Samples should be capped until ready for analysis.

CAUTION: The addition of sodium chloride-hydroxylamine hydrochloride ~~sulfate~~ should be performed in a laboratory fume hood as Cl_2 could be evolved.

8.2 Instrument Calibration and Sample Analysis

8.2.1 Set up or zero mercury analyzer used according to manufacturer's recommended procedures. **[Each lab shall specify procedures.]**

8.2.2 Set up the analytical run as presented in Table 2. If data system automates the analytical run, program samples into software. **[The analytical run sequence listed below is an example and can be modified.]**

Table 2. Analytical Sequence

Sample	Comment
Calibration Blank (CB)	Blank working standard
Standard 1 (S1)	Calibration standard #1
Standard 2 (S2)	Calibration standard #2
Standard 3 (S3)	Calibration standard #3
Standard 4 (S4)	Calibration standard #4
Standard 5 (S5)	Calibration standard #5
ICV	QC check--must be within ±10%
ICB	Instrument calibration blank
MB/Calibration blank	No contamination above the MDL
LCS	QC check--must be within control chart limits
1-8 Samples	Samples include field and QC (MS, MD, etc.)
CCV	QC check must be within 20% of known value
CCB	QC check must not indicate contamination above the MDL
Repeat box until samples are exhausted.	
Then end run with:	
CCV	
CCB	

8.2.3 ~~Immediately before analysis, using an automatic pipetter, add 5 ± 0.5 mL of $SnSO_4$ (Section 7.4) to the standard to be analyzed and immediately insert the aeration device into the solution.~~ ~~The instrument is programmed to automatically mix the proper amount of stannous chloride to reduce the mercury to metallic mercury, which is pumped to the liquid-gas separator where it is separated into the gaseous phase. The program will~~ continue aerating until the absorbance reaches a maximum reading (usually within 30 seconds). ~~The program saves the reading. Record reading on log (Figure 1).~~ The program continues aerating until the absorbance reading falls back to zero or baseline reading.

Note: Between each standard, sample, or QC sample, check the instrument zero with reagent water.

8.2.4 Construct a calibration curve by plotting the absorbances of the standards versus the true mercury concentration (~~micrograms~~ ppb of mercury). The

instrument software is programmed to automatically construct a calibration curve by plotting the fluorescence of the standards versus the true mercury concentration.

8.2.5 The results of the ICV must be within control limits of ± 10% for the curve to be acceptable for sample analysis. Verify the LCS is within control chart, or default limits.

8.2.6 Proceed with sample analysis as in Section 8.2.3. Check the calibration curve with the midpoint standard (CCV) after every 8 ~~10~~ samples and at the end of the analytical sequence.

8.2.7 Determine sample concentrations (in ~~micrograms~~ ppb of mercury). Calculate the concentration in mg/kg as presented in Section 9.1. For sample absorbances that exceed the highest calibration standard, dilute and rerun the sample ~~redigestion and reanalysis must be performed.~~

9.0 Calculations

9.1 Calculate the mercury concentration for each sample on a dry weight basis as follows:

$$Concentration\ (mg/Kg) = \frac{A}{W}$$

where:

A = µg mercury read from standard curve
W = weight in g of sample (dry weight basis)

9.2 If the triplicate approach is used, the average mercury concentration should be reported, along with the three individual results.

9.3 Percent Recovery

9.3.1 For LCS, recovery is calculated using:

$$\%\ Recovery = \frac{A}{B} \times 100$$

where:

A = µg/L mercury measured
B = known true value

9.3.2 For MS/MSDs, recovery is calculated using:

$$\%\ Recovery = \frac{|Sample + Spike\ Result - Sample\ Result|}{Spike\ Added}$$

9.4 Relative percent difference

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

where:

S_1 and S_2 represent sample and duplicate sample results, or matrix spike and matrix spike duplicate results.

10.0 Quality Assurance/Quality Control

10.1 A preparation batch of samples is defined as a group of up to twenty field samples of similar matrix type that have been prepared at the same time or time sequence with the same lots of reagents for the same analysis. In addition to the twenty samples, each preparatory batch will contain at a minimum, a method blank, a laboratory control sample, a matrix spike, ~~a matrix spike duplicate~~ and a matrix duplicate. An analytical, or instrumental batch is defined as samples that are analyzed together within the same time period or in continuous sequential time periods. Within the analytical batch are included individual QC requirements as defined by the analytical (determinative) method. For instance, each analytical batch would begin with the 5 point calibration plus a calibration blank, an ICV, an LCS, followed by the up to ten QC (normally a method blank, MS, MSD, MD, etc.) and field samples, then continuing calibration verification, an instrument blank, and so on. Preparation batches of samples may be continuously strung together in these run sequences, as long as the analytical batch QC requirements meet the acceptance criteria established within the appropriate SOP. At the conclusion of the last sequence, a CCV is required. Each analytical sequence must be documented using the run log in Figure 1. ~~[Each lab should insert their own form if necessary.]~~ See the attached run log in Figure 3, page 20.

10.2 Run a 5-point initial calibration curve plus a calibration blank, using the primary source standards with each sample preparation batch. Acceptance criteria are presented in Section 11.1.

10.3 A method blank must be prepared with each batch of samples. The method blank should be prepared with reagent water. Acceptance criteria for these blanks are listed in Section 11.2.

10.4 Run an ICV standard using second source standards following the 5-point calibration curve Acceptance criteria are presented in Section 11.3.

10.5 A laboratory control sample must be prepared and analyzed with each batch of

samples. The LCS would be prepared using the primary source standard. Control charts will be maintained for the LCS. Acceptance criteria are presented in Section 11.4.

10.6 Run a mid-point Continuing Calibration Verification (CCV) using the primary source standards after every 8 ~~10~~ samples (bottles), and at the end of the analysis. Acceptance criteria are listed in Section 11.5.

10.7 The use of the matrix spike and matrix spike duplicate will depend in part on what role the laboratory is playing. When the laboratory serves the role as the primary laboratory, then site-specific documents should be consulted. The sample to be used for the MS/MSD may be specified in the field. This previously designated sample would then be spiked a concentration equivalent to the site action level. The MS/MSD would be prepared using the primary source standards. If this information was not specified or unknown, then the laboratory would choose a representative sample from each batch of samples analyzed. If samples from multiple sites were to be analyzed in the same batch, then multiple sets of MS/MSDs may be required. When the laboratory serves the role as the QA laboratory, the above scenario may not be practical to implement. If the site-specific requirements are unknown and samples from multiple sites are analyzed in the same batch, then the laboratory should select a single sample for spiking. Each batch of samples would then contain at least one MS/MSD pair. Acceptance criteria are presented in Section 11.6 for percent recovery and RPD.

10.8 The use of the matrix duplicate may also depend in part on the role the laboratory is playing. The selection of a matrix duplicate will be performed as described for the MS/~~MSD~~ in Section 10.7. Acceptance criteria are presented in Section 11.7 for RPD.

10.9 Data shall be checked to ascertain if it conforms to accepted practices for data reporting. All sample analytical results used for final data reporting must be above that of the low standard used during the initial calibration. Results which fall below the low standard are to be reported as estimated values. Corrective actions are described in Section 11.8. Other reporting limits can be used based upon site specific criteria.

10.10 MDLs are determined in reagent water and verified annually. (Project-specific requirements may require that the MDL study be performed in the site-specific matrix.) Refer to SOP No. Q-019-XX-WES-XX, Method Detection Limits (MDLs), Method Quantitation Limits (MQLs), and Laboratory Reporting Limits (LRLs).

10.11 The analyst must demonstrate proficiency in performing the analysis as outlined in SOP No. Q-016-XX-MCX-XX, Technical Training. Method proficiency must be redemonstrated anytime a major method modification is made, a major software revision is added, or a major instrument modification is made. Demonstration of method proficiency may also be required after major instrument maintenance. This is decided on a case by case basis through discussions with the Section Chief, Laboratory Director, and Laboratory QA

Officer.

11.0 Data Validation

Site-specific requirements must be checked and used, if known, for data review. The criteria presented in this section should be used as a default list in the absence of site specific requirements. The items shall be verified and documented using the data review checklist in Figure 2.

11.1 The calibration curve shall be linear. The correlation coefficient of the curve shall be ≥ 0.995.

11.2 Assess the method blanks. The analyst shall confirm that these blanks were analyzed at the required frequency.

The method blank should not exhibit any mercury contamination above the MDL. Corrective action should be performed any time mercury is detected above the MDL to reduce and control contamination. Corrective action will be required if mercury is detected at greater than 5% of the regulatory limit or greater than 5% of the sample result, or if detected above the low standard used during initial calibration. Corrective action would include reanalysis of field and QC samples in the batch if some or all of the samples also contained mercury levels that exceeded the above criteria. If none of the field samples had values above the stated criteria, then reanalysis may not be necessary. The source of contamination should still be investigated and reduced/eliminated. Any time contamination is noted in the method blank, the situation and impact on the data should be discussed in the case narrative.

11.3 After the 5-point initial calibration, verify the initial calibration verification (ICV) was performed. The recovery of the ICV must be within 90 - 110%. If not, reanalyze or prepare a new calibration curve as necessary.

11.4 Assess that LCSs were prepared at the required frequency. Plot on the appropriate control charts. (Refer to SOP No. Q-009-XX-WES-XX, Control Chart Generation, Maintenance, and Usage.) If not, control limits, redigestion and reanalysis of the sample preparation batch is necessary.

Note: Even though control charts must be maintained for the LCSs, the acceptance criteria derived from these charts may not be appropriate if the charted ranges are too wide. A maximum default range should be used. It is recommended that the maximum default range be set to 80-120%. ~~[Each lab should specify maximum default ranges.]~~ The maximum default ranges for the LCS is set at the recommended range of 80-120%.

The RPD of interbatch LCSs should fall within the control limits determined from the precision control charts. However, if the RPD is outside these control limits, the batch will not be rejected, as long as the LCS recovery is acceptable. This precision information should be evaluated to see if systematic problems

can be identified. If problems are suspected, the method should be fully evaluated.

11.5 Verify that the continuing calibration verification (CCV) standard was run at the required frequency (after every 10 samples and at the end of the analytical sequence). The acceptance criteria is that the CCV must be within 20% of the true value.

If a CCV fails during an analytical sequence, the previous ten samples need to be reprocessed from digestion through analysis.

11.6 Assess that matrix spike/matrix spike duplicates were analyzed at required frequency. The analyst shall also verify that the samples were spiked at the appropriate level. The order of preference for spiking levels is as follows; 1) If the target analyte concentrations are known, spike to increase the background concentration by a factor of approximately two, 2) if an action level exists, spike at this level, or 3) if neither of the first two conditions apply, spike at a level that corresponds between the low and mid-level calibration standards. Acceptance criteria are that all % Recovery and/or RPD results meet project established goals. If no project goals are specified, then results must be within the indicated control limits on the appropriate LCS control charts. If these conditions are not met, perform the following corrective actions as appropriate.

- If both LCS and MS/MSD recoveries are unacceptable, then the entire batch of field and QC samples must be redigested and reanalyzed.

- If the MS/MSD is unacceptable, but the LCS is acceptable, then a potential matrix effect has been identified. Redigest and reanalyze the MS/MSD to verify matrix effect. If a matrix effect is still suspected then the project manager must be contacted to discuss further alternatives and the potential impact on the project. Reasonable attempts must be made to address a matrix interference. Reported data should be flagged.

11.7 Assess matrix duplicates were analyzed at required frequency. Acceptance criteria are that all RPD results meet project established goals. If no project goals are specified, then results must be within the indicated control limits on the appropriate LCS precision control charts. If these conditions are not met, perform the following corrective actions as appropriate.

- Reanalyze that sample to verify a matrix effect.

- If the duplicate precision is still unacceptable, then a potential matrix effect has been identified. The project manager must be contacted to discuss further alternatives and the potential impact on the project.

11.8 The analyst must verify all reported results are derived from analytical results that are below the highest standard of the initial calibration curve and above the low standard. Values reported below the low standard are to be reported as estimated values (J values). For samples that exceed the calibration curve,

reanalyze using a smaller sample size.

11.9 Besides the items listed in Sections 11.1 through 11.8, the analyst should also verify the additional items as noted in Figure 2.

11.10 Additional levels of review are performed as described in SOP No. Q-024-XX-WES-XX, Data Reduction and Review/Validation (In-House/Contractor Data).

12.0 Waste Disposal

This procedure generates corrosive and metallic wastes that must be disposed of in accordance to all local regulations. Refer to the laboratory's Waste Management Plan. **[Each lab should describe how these wastes are accumulated, stored, and disposed of.]**

13.0 References

13.1 Test Methods for Evaluating Solid Waste Methods, SW-846, Third Edition, Update II, July 1992, Method 7471A.

13.2 SOP No. Q-003-XX-MCX-XX, Standards Preparation, Traceability, and Storage.

13.3 SOP No. Q-008-XX-MCX-XX, Reagent Water Generation and Quality Monitoring.

13.4 SOP No. Q-005-XX-MCX-XX, Sample Receipt, Login, and Storage.

13.5 SOP No. Q-019-XX-MCX-XX, Method Detection Limits (MDLs), Method Quantitation Limits (MQLs), and Laboratory Reporting Limits (LRLs).

13.6 SOP No. Q-016-XX-MCX-XX, Technical Training.

13.7 SOP No. Q-024-XX-MCX-XX, Data Reduction and Review/Validation (In-House/Contractor Data)

13.8 SOP No. Q-009-XX-MCX-XX, Control Chart Generation, Maintenance, and Usage.

13.9 SOP No. M-2216-XX-MCX-XX, Determination of Water (Moisture) Content of Soil (ASTM Method 2216).

13.10 **[Identify MSC laboratory]** Waste Management Plan.

DIGESTION/ANALYSIS LOG FOR MERCURY
[Identify MSC laboratory]

Batch No.:	Project:	Matrix: ☐ Solid ☐ Liquid
Start Date:	SOP No.:	

BOD bottle #	Lab/Sample ID	Sample Amt.	Absorbance Reading	Final Conc.	Avg. Conc. (solids only)	RSD (solids only)

LCS Std ID: _____ Amt Added: _____

MS Std ID: _____ Amt Added: _____
Reagent lot numbers: _____

Analyst: _____ Reviewed by: _____ Date: _____

Figure 1.

DIGESTION/ANALYSIS LOG FOR MERCURY
[Identify MSC laboratory]

Batch No.:	Project:	Matrix: ☐ Solid ☐ Liquid
Start Date:	SOP No.:	

BOD bottle #	Lab/Sample ID	Sample Amt.	Absorbance Reading	Final Conc.	Avg. Conc. (solids only)	RSD (solids only)

LCS Std ID: _____ Amt Added: _____

MS Std ID: _____ Amt Added: _____
Reagent lot numbers: _____

Analyst: _____ Reviewed by: _____ Date: _____

Figure 1. Example.

Data Review Check List for Mercury
[Identify MSC Laboratory]

Project Number(s)

Batch Number(s)

SOP No.

	Review Item	Yes (x)	No (x)	N/A (x)	2nd Level Review (x)
1.	Does the daily standard curve consist of a Calibration Blank and the required 5 calibration standards?				
2.	Is the low standard near, but above, the MDL?				
3.	Is the LCS from a second source and is its percent recovery within QC limits?				
4.	Are the CCV standards analyzed at required frequency and at the end of the analytical sequence and meet QC limits?				
5.	Is the Matrix Spike/Matrix Spike Duplicate run at the desired frequency and is the percent recovery/RPD within QC limits?				
6.	Is the Matrix Duplicate run at the desired frequency and is the RPD within QC limits?				
7.	Are all samples with concentrations > the highest standard used for initial calibration reprocessed and reanalyzed?				
8.	Are all sample holding times met?				
9.	Are all nonconformances included and noted?				
10.	Is the correct methodology used for sample prep and analysis?				
11.	Are all calculations checked at the minimum frequency?				
12.	Did analyst sign/date the appropriate printouts and report sheets?				
13.	Are all sample ID and units checked for transcription errors?				

Comments on any "No" response:

Analyst: _____ Date: _____
2nd Level Reviewer: _____ Date: _____

Figure 2.

Data Review Check List for Mercury
[Identify MSC Laboratory]

Project Number(s)

Batch Number(s)

SOP No.

	Review Item	Yes (x)	No (x)	N/A (x)	2nd Level Review (x)
1.	Does the daily standard curve consist of a Calibration Blank and the required 5 calibration standards?				
2.	Is the low standard near, but above, the MDL?				
3.	Is the LCS from a second source and is its percent recovery within QC limits?				
4.	Are the CCV standards analyzed at required frequency and at the end of the analytical sequence and meet QC limits?				
5.	Is the Matrix Spike/Matrix Spike Duplicate run at the desired frequency and is the percent recovery/RPD within QC limits?				
6.	Is the Matrix Duplicate run at the desired frequency and is the RPD within QC limits?				
7.	Are all samples with concentrations > the highest standard used for initial calibration reprocessed and reanalyzed?				
8.	Are all sample holding times met?				
9.	Are all nonconformances included and noted?				
10.	Is the correct methodology used for sample prep and analysis?				
11.	Are all calculations checked at the minimum frequency?				
12.	Did analyst sign/date the appropriate printouts and report sheets?				
13.	Are all sample ID and units checked for transcription errors?				

Comments on any "No" response:

_____

_____

_____

_____

Analyst: _____ Date: _____
2nd Level Reviewer: _____ Date: _____

Figure 2. Example.

MERCURY ANALYTICAL LOG
CEWES-EE-C

HGA Inst.:	File Name:
OID No.:	Project:
Parameters Analyzed:	Method:

AZ	
S1	
S2	
S3	
S4	
S5	
RS	

	Sample ID	spike	DILUT
1			
2			
3			
4			
5			
6			
7			
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FIGURE 3

Appendix C

Cricket Study

CRICKET STUDY

1. Initial preparation of crickets.
   - 1.1. Obtain crickets from Armstrong Cricket Farm in Monroe, LA.
   - 1.2. Sacrifice with ethyl acetate.
   - 1.3. Store in freezer until used.

2. The following analytical processes can be halted at any step as data is evaluated and certain extractions or cleanups do not seem to warrant investing additional resources. Mercury has been chosen as an indicator for proceeding with metal pre-extraction preparation processes.

3. Grind thawed cricket with mortar & pestle
   - 3.1. Perform percent solids determination (This is used to convert final concentrations to mg/kg dry weight.)
   - 3.2. Explosives extraction (report final as dry weight)
     - 3.2.1. Extract wet - no clean-up
       - 3.2.1.1. Cricket tissue alone (This will be used to determine baseline interferences.)
       - 3.2.1.2. Cricket tissue spiked with explosives (This will be used to determine spike recovery as well as interferences impacting specific analyte peaks.)
     - 3.2.2. Extract wet - with silica gel clean-up
       - 3.2.2.1. Cricket tissue alone (This will be used to determine baseline interferences.)
       - 3.2.2.2. Cricket tissue spiked with explosives (This will be used to determine spike recovery as well as interferences impacting specific analyte peaks.)
     - 3.2.3. Analysis by SW-846 Method 8330
   - 3.3. Metals digestion (report final as dry weight)
     - 3.3.1. Digest wet by SW-846 Method 7471A (mercury only)
       - 3.3.1.1. Cricket tissue alone (The pair will be used to determine spectral interferences as well as spike recoveries.)
       - 3.3.1.2. Cricket tissue spiked with metals
     - 3.3.2. Digest wet by SW-846 Method 3050A (metals other than mercury)
       - 3.3.2.1. Cricket tissue alone (The pair will be used to determine spectral interferences as well as spike recoveries.)
       - 3.3.2.2. Cricket tissue spiked with metals
     - 3.3.3. Digest wet by SW-846 Method 3051 (metals other than mercury)
       - 3.3.3.1. Cricket tissue alone (The pair will be used to determine spectral interferences as well as spike recoveries.)
       - 3.3.3.2. Cricket tissue spiked with metals

4. Freeze-dry frozen crickets, then grind with mortar & pestle
   - 4.1. Freeze-dry reference materials to evaluate loss of mercury due to freeze-drying process. Compare values to non freeze-dried materials.
     - 4.1.1. NBS Oyster Tissue - 1566a
     - 4.1.2. NIST Buffalo River Sediment - 2704
     - 4.1.3. Fish tissue currently undergoing analysis for mercury
   - 4.2. Freeze dried percent solids will be determined but will not be used in any calculations
   - 4.3. Explosives extraction (report final as dry weight)
     - 4.3.1. Extract dry - no clean-up
       - 4.3.1.1. Cricket tissue alone (This will be used to determine baseline interferences.)

4.3.1.2. Cricket tissue spiked with explosives (This will be used to determine spike recovery as well as interferences impacting specific analyte peaks.)

4.3.2. Extract dry - with silica gel clean-up

4.3.2.1. Cricket tissue alone (This will be used to determine baseline interferences.)

4.3.2.2. Cricket tissue spiked with explosives (This will be used to determine spike recovery as well as interferences impacting specific analyte peaks.)

4.3.3. Analysis by SW-846 Method 8330

4.4. Metals digestion (report final as dry weight)

4.4.1. Digest dry by SW-846 Method 7471A (mercury only)

4.4.1.1. Cricket tissue alone (The pair will be used to determine spectral interferences as well as spike recoveries.)

4.4.1.2. Cricket tissue spiked with metals

4.4.1.3. Freeze-dried NBS Oyster Tissue - 1566a

4.4.1.4. Freeze-dried NIST Buffalo River Sediment - 2704

4.4.1.5. Freeze-dried fish tissue currently undergoing analysis for mercury

4.4.2. Digest dry by SW-846 Method 3050A (metals other than mercury)

4.4.2.1. Cricket tissue alone (The pair will be used to determine spectral interferences as well as spike recoveries.)

4.4.2.2. Cricket tissue spiked with metals

4.4.3. Digest dry by SW-846 Method 3051 (metals other than mercury)

4.4.3.1. Cricket tissue alone (The pair will be used to determine spectral interferences as well as spike recoveries.)

4.4.3.2. Cricket tissue spiked with metals

5. Freeze thawed cricket with liquid nitrogen and grind with mortar & pestle. Separate sample into two portions: explosives analysis and metals analysis

5.1. Freeze with liquid nitrogen reference materials to evaluate loss of mercury due to freezing process. Compare values to non - treated materials.

5.1.1. NBS Oyster Tissue - 1566a

5.1.2. NIST Buffalo River Sediment - 2704

5.1.3. Fish tissue currently undergoing analysis for mercury

5.2. Explosives extraction - (report final as dry weight)

5.2.1. Freeze-dry sample

5.2.2. Freeze-dried percent moisture will be determined but will not be used in any calculations.

5.2.3. Extract dry - no clean-up

5.2.3.1. Cricket tissue alone (This will be used to determine baseline interferences.)

5.2.3.2. Cricket tissue spiked with explosives (This will be used to determine spike recovery as well as interferences impacting specific analyte peaks.)

5.2.4. Extract dry - with silica gel clean-up

5.2.4.1. Cricket tissue alone (This will be used to determine baseline interferences.)

5.2.4.2. Cricket tissue spiked with explosives (This will be used to determine spike recovery as well as interferences impacting specific analyte peaks.)

5.2.5. Analysis by SW-846 Method 8330

5.3. Metals digestion (report final as dry weight)

5.3.1. Perform percent solids determination (This is used to convert final concentrations to mg/kg dry weight.)

5.3.2. Digest wet by SW-846 Method 7471A (mercury only)

5.3.2.1. Cricket tissue alone (The pair will be used to determine spectral interferences as well as spike recoveries.)

5.3.2.2. Cricket tissue spiked with metals

5.3.2.3. Freeze-dried NBS Oyster Tissue - 1566a

5.3.2.4. Freeze-dried NIST Buffalo River Sediment - 2704

5.3.2.5. Freeze-dried fish tissue currently undergoing analysis for mercury

5.3.3. Digest wet by SW-846 Method 3050A (metals other than mercury)

5.3.3.1. Cricket tissue alone (The pair will be used to determine spectral interferences as well as spike recoveries.)

5.3.3.2. Cricket tissue spiked with metals

5.3.4. Digest wet by SW-846 Method 3051 (metals other than mercury)

5.3.4.1. Cricket tissue alone (The pair will be used to determine spectral interferences as well as spike recoveries.)

5.3.4.2. Cricket tissue spiked with metals

6. Surrogate study for detection limits

6.1. Explosives

6.1.1. MDL will be calculated using selected method

6.1.2. Minimum sample amounts will be estimated to achieve MDL

6.2. Metals

6.2.1. MDL will be calculated using selected method

6.2.2. Minimum sample amounts will be estimated to achieve MDL

Cricket Study

In order to prepare for analysis of insects from Crane Naval Surface Warfare Center, the ECB at WES performed a preliminary study utilizing crickets (*Acheta domestica*) to determine the most appropriate methods for sample preparation and extraction/digestion of explosives and metals. Crickets obtained from Armstrong Cricket Farm in Monroe, LA, were placed in a closed container and sacrificed with ethyl acetate after which they were stored in the freezer until needed. Crickets used in the study ranged between 0.25 and 0.60 grams in weight and measured between 1.5 and 2.5 cm in length. Percent solids for the crickets were 31%.

Initially, the cricket tissue was prepared for additional processing in three ways: 1) the thawed tissue was ground with a ceramic mortar and pestle and analyzed "wet"; 2) the frozen tissue was freeze-dried, then ground with a mortar and pestle; and 3) the thawed tissue was refrozen with liquid nitrogen, ground with a mortar and pestle, and separated into a portion to be freeze-dried for explosives and a second portion to be analyzed "wet" for metals.

Freeze-drying procedure:

Like sized aliquots of whole crickets or diced tissue are placed in freeze drying flasks, covered with parafilm and placed into a freezer. When completely frozen the flasks are placed on a Labconco 4.5 liter freeze drying system. Samples are dried overnight or until the flask reaches room temperature. The dried tissue is emptied into a ceramic mortar and ground to a powder with a ceramic pestle. The tissue is stored in the freezer until needed for extraction/digestion in preparation for analysis.

Explosives:

For explosives (Method 8330), the freeze-dried sample was found to have fewer chromatographic interferences than did the sample obtained from the "wet" extraction. As a result, freeze-drying was selected as the pre-extraction method for explosives.

Explosives extraction will follow SOP M-8330-00-WES-XX . 0.25 g of freeze-dried tissue will be extracted with 10 mL of acetonitrile, sonicated for 18 hours, cut with calcium chloride solution and filtered. The cricket tissue did not require further clean-up prior to analysis.

Using the above procedure, the following detection and reporting limits were obtained:

Explosives	MDL (mg/kg)	LRL (mg/kg)
HMX	1.0	3.2
RDX	0.3	0.8
TNB	0.4	1.2
DNB	0.3	1.0
Tetryl *		
NB	0.8	1.7
TNT	0.4	1.3
4-A-DNT	0.8	2.5
2-A-DNT	0.4	1.2
2,4-DNT	0.2	0.7
2,6-DNT	0.4	1.3
2-NT	0.6	1.9
3-NT	0.5	1.6
4-NT	0.6	2.1

Tetryl recoveries were low. The analysis will be repeated before Crane tissue is analyzed.

Mercury was selected as the indicator metal because of its volatility. Portions of NIST reference material as well as fish tissue previously analyzed for mercury in our lab were subjected to freeze drying prior to analysis for mercury. Additional sample was also prepared by grinding frozen tissue made brittle by the addition of liquid nitrogen to the mortar during the grinding process. This process took less than 30 minutes. After the liquid nitrogen evaporated, the tissue quickly thawed. This thawed tissue was prepared for mercury analysis along side the freeze-dried material. A comparison of recoveries indicated that the freeze-drying did not affect mercury recovery. Freeze-drying was, therefore selected as the best pre-preparative method for the insect tissue. Analysis will follow SOP M-7471-00-WES-XX using 0.5 grams of freeze-dried material.

EPA method 3051, microwave digestion, was chosen to prepare the cricket tissue for analysis by ICP/MS. The microwave program is listed below:

Program Variables
File Name = Insects
Inorganic Sample Digestion

Stage	1	2	3	4	5
Power	60 %	60 %	60 %	60 %	60 %
Pressure	0020	0040	0085	0135	0175
Run Time	05:00	05:00	05:00	05:00	05:00
Time @ P	05:00	05:00	05:00	05:00	05:00
Temperature	120 C	140 C	160 C	170 C	180 C
Fan Speed	100 %	100 %	100 %	100 %	100 %

Number of Vessels: 12
Volume per Vessel: 10 mL
Sample Wt.: 0.5 g
Acid: HNO3

Cricket tissue prepared by method 3051 was scanned using an ICP/MS. The digest will need to be diluted 1 to 10 prior to analysis. This dilution is also performed on soil and salt water matrices analyzed by ICP/MS in our lab.

Using the above methods for metals, the following detection limits should be achievable:

Analyte	Target MDL (mg/L)	Est MDL (mg/L) *
Silver	-	0.026
Aluminum	5	0.078
Arsenic	0.5	0.073
Barium	1	0.009
Cadmium	0.1	0.005
Chromium	0.5	0.065
Copper	0.5	0.05
Magnesium	5	0.13
Manganese	1	0.01
Nickel	0.5	0.032
Lead	0.5	0.007
Antimony	-	0.014
Zinc	1	0.19
Mercury	0.20	0.20

* The MDL s were estimated from MDL s developed for water samples.

The method detection limits (MDLs) listed above are clearly below the target detection limits. We believe, barring unexpected interferences not observed in the crickets, we will be able to achieve the reporting limits necessary to fulfill the objectives of this project. We did not evaluate P by ICP/MS, but have obtained a standard. We do not know if we will have interferences for the P analysis using this analytical method.

Sample Size:

Initial results from the sorting indicate that the total insect mass per box will be around 16 to 18 grams maximum. This should produce about 5 to 6 grams of dry mass per box. To obtain the required QC analyses (field dup, MS & MSD), we will need to use a different sample as a QC sample for each analytical procedure (Hg, metals, and explosives). I have estimated the minimum sample size using the required weights.

Procudure	Sample (g)	Field Dup (g)	MS (g)	MSD (g)	Total/Procedure
Metals	1	1	1	1	4
Mercury	1	1	1	1	4
Explosives	.5	.5	.5	.5	2
T Phos **	5	5	5	5	20

** analysis by nutrient method

Procedure	Min sample required for all (g)	Min sample without T Phos (g)
Metals	10.5	5.5
Mercury	10.5	5.5
Explosives	9	4
T Phos	22.5	-

Please note that some of these weights do not allow for any re-extractions.