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Environmental Technology Verification Program

Verification Test Plan

Evaluation of Field Portable Measurement Technologies for Lead in Dust Wipes

Oak Ridge National Laboratory

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Evaluation of Field Portable Measurement Technologies for Lead in Dust Wipes

By

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and

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APPROVAL SIGNATURES

This document is intended to ensure that all aspects of the verification are documented, scientifically sound, and that operational procedures are conducted within quality assurance/quality control specifications and health and safety regulations.

The signatures of the individuals below indicate concurrence with, and agreement to operate compliance with, procedures specified in this document.

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TABLE OF CONTENTS

EXECUTIVE SUMMARY v

ABBREVIATIONS AND ACRONYMS vi

1 INTRODUCTION 1
1.1 Verification Objectives 1
1.2 What is the Environmental Technology Verification Program? 1
1.3 Technology Verification Process 2
1.3.1 Needs Identification and Technology Selection 2
1.3.2 Verification Planning and Implementation 2
1.3.3 Report Preparation 3
1.3.4 Information Distribution 3
1.4 Purpose of this Verification Test Plan 3

2 VERIFICATION RESPONSIBILITIES AND COMMUNICATION 3
2.1 Verification Organization and Participants 3
2.2 Organization 4
2.3 Responsibilities 5

3 TECHNOLOGY DESCRIPTIONS 6
3.1 Monitoring Technologies International (MTI) 6
3.1.1 General Description 6
3.1.2 Sample Analysis 6
3.1.3 Quantification 7
3.2 Niton Corporation 8
3.2.1 Field Portable X-ray Fluorescence Analyzer I ("BASP" Detector) 8
3.2.2 Field Portable X-ray Fluorescence Analyzer II (Dual Detector) 9
3.3 Palintest 10
3.3.1 General Technology Description 10
3.3.2 Analytical Procedure 10
3.3.3 Sample Disposal 11

4 VERIFICATION TEST DESIGN 11
4.1 Drivers and Objectives of the Verification Test 11
4.2 Summary of the Experimental Design 11
4.2.1 ELPAT and Blank Sample Description 11
4.2.2 University of Cincinnati Sample Description 12
4.3.3 Distribution and Number of Samples 13
4.3 Comparison of Field Technology Results to an NLLAP-Recognized Laboratory's Results 13
4.3.1 Laboratory Selection 13

5 EXECUTION OF THE VERIFICATION TEST 14
5.1 Summary of Verification Activities 14
5.1.1 Test Location 14

5.2 Sample Distribution 15
5.3 Submission of Results 15
5.4 Verification Performance Factors 15

6 QUALITY ASSURANCE PROJECT PLAN (QAPP) 15
6.1 Purpose and Scope 15
6.2 Quality Assurance Responsibilities 15
6.3 Field Operations 16
6.3.1 Site Training 16
6.3.2 Communication and Documentation 16
6.4 Performance and System Audits 16
6.4.1 Technical Systems Audit 16
6.4.2 Data quality audit of the laboratory 16
6.4.3 Surveillance of Technology Performance 16
6.5 Quality Assurance Reports 17
6.5.1. QC Reports of Sample Preparation 17
6.5.2 QAS Remote Surveillance Report 17
6.5.3 Status Reports 17
6.5.4 Audit Reports 17
6.6 Corrective Actions 17
6.7 Laboratory Quality Control Checks 17
6.8 Data Management 17
6.9 Data Reporting, Validation, and Analysis 18
6.9.1 Data Reporting 18
6.9.2 Data Validation 18
6.9.3 Data Analysis for Verification Factors 19

7 HEALTH AND SAFETY PLAN 21
7.1 Contact Information 21
7.2 Health and Safety Plan Enforcement 22
7.3 Site Access 22
7.4 Waste Generation 22
7.5 Hazard Evaluation 22
7.6 Personal Protection 22
7.7 Physical Hazards 22
7.8 Fire 23
7.9 Mechanical, Electrical, Noise Hazards 23
7.10 Medical Support 23
7.11 Environmental Surveillance 23
7.12 Safe Work Practices 23
7.13 Complaints 23

REFERENCES 24

EXECUTIVE SUMMARY

EPA created the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative technologies through performance verification and information dissemination. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. The ETV Program is intended to assist and inform those involved in the design, distribution, permitting, and purchase of environmental technologies. The verification study described in this test plan will be conducted by the Advanced Monitoring Technology Center (AMT), one of six Centers of the ETV program. The AMT Center is administered by the EPA's National Exposure Research Laboratory. The Oak Ridge National Laboratory (ORNL) will serve as the verification organization for the test.

The verification test will consist of vendors of commercially available portable technologies, capable of measuring lead in dust wipe samples, operating their equipment in a field setting. The types of technologies participating include two x-ray fluorescence instruments (XRF) and two anodic stripping voltammetry systems (ASV). The vendors will blindly analyze 160 dust wipe samples containing known amounts of lead, ranging in concentration from ≤ 2 to 1,500 μg/wipe. The experimental design is particularly mindful of germane clearance levels, such as those identified in the Code of Federal Regulations of 40, 250, and 400 $\mu g/ft^2$. The samples will include wipes newly-prepared and archived from the Environmental Lead Proficiency Analytical Testing Program (ELPAT). These samples have been/will be prepared from dust collected in households in North Carolina and Wisconsin. Also, newly-prepared samples will be acquired from the University of Cincinnati. These dust wipe samples will be prepared from National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs).

ABBREVIATIONS AND ACRONYMS

AIHA	American Industrial Hygiene Association
AMT	Advanced Monitoring Technology Center, ETV
ASTM	American Society for Testing and Materials
ASV	Anodic Stripping Voltammetry
CDC	Centers for Disease Control and Prevention
EDXRF	energy dispersive x-ray fluorescence
ELPAT	Environmental Lead Proficiency Analytical Testing program
EPA	U. S. Environmental Protection Agency
ESD-LV	Environmental Science Division-Las Vegas
ESH&Q	Environmental Safety, Health, and Quality
ETV	Environmental Technology Verification Program
ETVR	Environmental Technology Verification Report
fn	false negative result
fp	false positive result
HASP	Health and Safety Plan
ICP-AES	Inductively coupled plasma-atomic emission spectrometry
MTI	Monitoring Technologies International
NIST	National Institute of Standards & Technology
NLLAP	National Lead Laboratory Accreditation Program, U.S. EPA
OPPT	Office of Pollution Prevention and Toxics, U.S. EPA
ORNL	Oak Ridge National Laboratory
PPE	personal protective equipment
QA	quality assurance
QAPP	Quality Assurance Project Plan
QAS	ORNL Quality Assurance Specialist
QC	quality control
RSD	relative standard deviation
RTI	Research Triangle Institute
SRM	Standard Reference Material
UC	University of Cincinnati
XRF	x-ray fluorescence instrument

1 INTRODUCTION

This chapter discusses the purpose of the verification and the verification test plan, describes the elements of the verification test plan, and provides an overview of the Environmental Technology Verification (ETV) Program and the technology verification process.

1.1 Verification Objectives

The purpose of this verification test is to evaluate the performance of commercially available field analytical technologies for analyzing dust wipe samples for lead. Specifically, this plan defines the following elements of the verification test:

- Roles and responsibilities of verification test participants;
- Procedures governing verification test activities such as sample collection, preparation, analysis, data collection, and interpretation;
- Experimental design of the verification test;
- Quality assurance (QA) and quality control (QC) procedures for conducting the verification and for assessing the quality of the data generated from the verification; and,
- Health and safety requirements for performing the verification test.

1.2 What is the Environmental Technology Verification Program?

The U.S. Environmental Protection Agency (EPA) created the Environmental Technology Verification Program (ETV) to facilitate the deployment of innovative or improved environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized standards and testing organizations and stakeholder groups consisting of regulators, buyers, and vendor organizations, with the full participation of individual technology vendors. The program evaluates the performance of innovative technologies by developing verification test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance (QA) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

ETV is a voluntary program that seeks to provide objective performance information to all of the participants in the environmental marketplace and to assist them in making informed technology decisions. ETV does not rank technologies or compare their performance, label or list technologies as acceptable or unacceptable, seek to determine “best available technology,” or approve or disapprove technologies. The program does not evaluate technologies at the bench or pilot scale and does not conduct or support research. Rather, it conducts and reports on testing designed to describe the performance of technologies under a range of environmental conditions and matrices.

The program now operates six Centers covering a broad range of environmental areas. ETV began with a 5-year pilot phase (1995–2000) to test a wide range of partner and procedural alternatives in various pilot areas, as well as the true market demand for and response to such a program. In the Centers, EPA utilizes the expertise of partner “verification organizations” to design efficient processes for conducting performance tests of innovative technologies. These expert partners are both public and private organizations, including federal laboratories, states, industry consortia, and private sector entities. Verification organizations oversee and report verification activities based on testing and QA protocols developed with input from all major stakeholder/customer groups associated with the technology area. The verification test described in this plan will be administered by the Advanced Monitoring Technology (AMT) Center, with Oak Ridge National Laboratory (ORNL) serving as the verification organization. (To learn more about ETV,

visit ETV's Web site at www.epa.gov/etv and ORNL's web site at www.ornl.gov/etv). The AMT Center is administered by EPA's National Exposure Research Laboratory (NERL).

1.3 Technology Verification Process

The technology verification process is intended to serve as a template for conducting technology verifications that will generate high quality data which can be used to verify technology performance. Four key steps are inherent in the process:

- Needs identification and technology selection;
- Verification test planning and implementation;
- Report preparation;
- Information distribution.

1.3.1 Needs Identification and Technology Selection

The first step in the technology verification process is to determine technology needs of the user-community (typically state and Federal regulators and the regulated community). Each Center utilizes stakeholder groups. Members of the stakeholder groups come from EPA, the Departments of Energy and Defense, industry, and state regulatory agencies. The stakeholders are invited to identify technology needs and to assist in finding technology vendors with commercially available technologies that meet the needs. Once a technology need is established, a search is conducted to identify suitable technologies. The technology search and identification process consists of reviewing responses to *Commerce Business Daily* announcements, searches of industry and trade publications, attendance at related conferences, and leads from technology vendors. The following criteria are used to determine whether a technology is a good candidate for the verification:

- Meets user needs
- May be used in the field or in a mobile laboratory
- Applicable to a variety of environmentally impacted sites
- High potential for resolving problems for which current methods are unsatisfactory
- Costs are competitive with current methods
- Performance is better than current methods in areas such as data quality, sample preparation, or analytical turnaround
- Uses techniques that are easier and safer than current methods
- Is commercially available and field-ready.

For this verification test of lead measurement technologies, ORNL has assembled a technical panel of the nation's experts in this field. The technical panel includes representation from the U.S. Department of Housing and Urban Development, the National Institute for Occupational Safety and Health, the National Institute of Standards and Technology, Research Triangle Institute, the American Industrial Hygiene Association, the Massachusetts Childhood Lead Poisoning and Prevention Program, and several EPA offices, including the Office of Pollution Prevention and Toxics (OPPT).

1.3.2 Verification Planning and Implementation

After a vendor agrees to participate, EPA, the Verification Organization, and the vendor meet to discuss each participants responsibilities in the verification process. In addition, the following issues are addressed:

- Site selection. Identifying sites that will provide the appropriate physical or chemical environment, including contaminated media
- Determining logistical and support requirements (for example, field equipment, power and water sources, mobile laboratory, communications network)
- Arranging analytical and sampling support

- Preparing and implementing a verification test plan that addresses the experimental design, sampling design, QA/QC, health and safety considerations, scheduling of field and laboratory operations, data analysis procedures, and reporting requirements

1.3.3 Report Preparation

Innovative technologies are evaluated independently and, when possible, against conventional technologies. The technologies being verified are operated by the vendors in the presence of independent observers. The observers are EPA staff, technical panel staff and from a independent third-party organization. The data generated during the verification test are used to evaluate the capabilities, limitations, and field applications of each technology. A data summary and detailed evaluation of each technology are published in an Environmental Technology Verification Report (ETVR). The original complete data set is available upon request.

An important component of the ETVR is the Verification Statement, which consists of three to five pages, using the performance data contained in the report, are issued by EPA and appear on the ETV Internet Web page. The Verification Statement is signed by representatives of EPA and ORNL.

1.3.4 Information Distribution

Producing the ETVR and the Verification Statement represents a first step in the ETV outreach efforts. ETV gets involved in many activities to showcase the technologies that have gone through the verification process. The Program is represented at many environmentally-related technical conferences and exhibitions. ETV representatives also participate in panel sessions at major technical conferences. ETV maintains a traveling exhibit that describes the program, displays the names of the companies that have had technologies verified, and provides literature and reports.

We have been taking advantage of the Web by making the ETVRs available for downloading to anyone interested. The ETVRs and the Verification Statements are available in Portable Document Format (.pdf) on the ETV Web site (http://www.epa.gov/etv).

1.4 Purpose of this Verification Test Plan

The purpose of the verification test plan is to describe the procedures that will be used to verify the performance goals of the technologies participating in this verification. This document incorporates the QA/QC elements needed to provide data of appropriate quality sufficient to reach a credible position regarding performance. This is not a method validation study, nor does it represent every environmental situation which may be appropriate for these technologies. But it will provide data of sufficient quality to make a judgement about the application of the technology under conditions similar to those encountered in the field under normal conditions.

2 VERIFICATION RESPONSIBILITIES AND COMMUNICATION

This section identifies the organizations involved in this verification test and describes the primary responsibilities of each organization. It also describes the methods and frequency of communication that will be used in coordinating the verification activities.

2.1 Verification Organization and Participants

Participants in this verification are listed in Table 2-1. The specific responsibilities of each verification participant are discussed in Section 2.3 This verification test is being coordinated by the Oak Ridge National Laboratory (ORNL) under the direction of the U.S. Environmental Protection Agency's (EPA) Office of Research and Development, National Exposure Research Laboratory, Environmental Sciences Division - Las Vegas, Nevada (ESD-LV). ESD-LV's role is to administer the verification program. ORNL's role is to provide technical and administrative leadership and support in conducting the verification.

Table 2-1. Verification Participants in the Lead in Dust Field Analytical Technology Verification Test

Organization	Point(s) of Contact	Role
Oak Ridge National Laboratory P.O. Box 2008 Bethel Valley Road Bldg. 4500S, MS-6120 Oak Ridge, TN 37831-6120	**Project Manager:** Roger Jenkins phone: (865) 576-8594 fax: (865) 576-7956 jenkinsra@ornl.gov **Technical Lead:** Amy Dindal phone: (865) 574-4863 fax: (865) 576-7956 dindalab@ornl.gov	verification organization
U. S. EPA National Exposure Research Laboratory Environmental Science Division P.O. Box 93478 Las Vegas, NV 89193-3478	**Project Officer:** Eric Koglin phone: (702) 798-2432 fax: (702) 798-2291 koglin.eric@epa.gov	EPA project management
U. S. DOE ORNL Site Office P.O. Box 2008 Bldg. 4500N, MS-6269 Oak Ridge, TN 37831-6269	**Program Coordinator:** Regina Chung phone: (865) 576-9902 fax: (865) 574-9275 chungr@ornl.gov	DOE/ORO project management
Monitoring Technologies International (MTI) 29 Chinthurst Park Shalford Surrey GU48JH United Kingdom	**Contact:** Colin Green phone: 441-483-564183 cgreen@colingreen.idps.co.uk	technology vendor
Niton Corporation 900 Middlesex Turnpike, Bldg 8 Billerica, MA 01821-3926	**Contact:** Jon Shein phone: (978) 670-7460 fax: (978) 670-7430 jjshein@niton.com	technology vendor
Palintest USA 21 Kenton Lands Road Erlanger, KY 41018	**Contact:** Dave Miller phone: (859) 341-7423 fax: (859) 341-2106 info@palintestusa.com	technology vendor
DataChem 4388 Glendale-Milford Road Cincinnati, Ohio 45242	**Contact:** Chris Gibson phone: (513) 733-5336, x304 fax: (513) 733-5347	NLLAP-recognized laboratory

2.2 Organization

In Figure 2-1 is presented an organizational chart depicting the lines of communication for the verification.

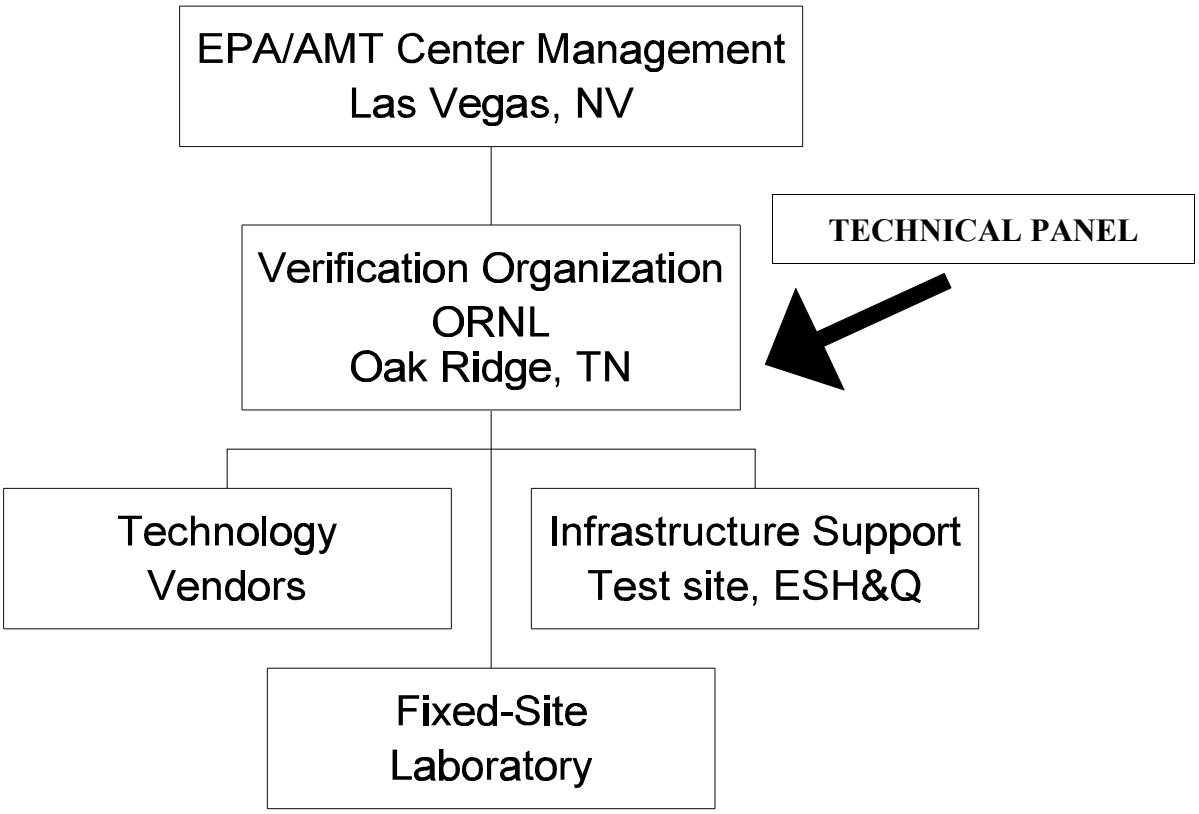

Figure 2-1. Organizational Chart for the verification test.

2.3 Responsibilities

The following is a delineation of each participant's responsibilities for the verification test. In this section, the term "vendor" applies to Monitoring Technologies International (MTI), Niton, and Palintest.

The Vendor, in consultation with ORNL and EPA, is responsible for the following elements of this verification test:

- Contribute to the design and preparation of the verification test plan;
- Provide detailed procedures for using the technology;
- Prepare field-ready technology for verification;
- Operating the technology during the verification test;
- Documenting the methodology and operation of the technology during the verification;
- Furnish data in a format that can be compared to laboratory values;
- Logistical, and other support, as required.

ORNL has responsibilities for:

- Preparing the verification test plan;
- Developing a quality assurance project plan (QAPP) (Section 6 of the verification test plan);
- Preparing a health and safety plan (HASP) (Section 7 of the verification test plan) for the verification activities;
- Developing a test plan for the verification;
- Acquiring the necessary laboratory analysis data;
- Performing sample preparation activities (including purchasing, labeling, and distributing).

ORNL and EPA have coordination and oversight responsibilities for:

- Providing needed logistical support, establishing a communication network, and scheduling and coordinating the activities of all verification participants, including the technical panel;
- Auditing the on-site sampling activities;
- Managing, evaluating, interpreting, and reporting on data generated by the verification;
- Evaluating and reporting on the performance of the technologies;
- Other logistical information and support needed to coordinate access to the site for the field portion of the verification, such as waste disposal.

3 TECHNOLOGY DESCRIPTIONS

This section provides descriptions of the technologies participating in the verification test. These descriptions were provided by the technology vendors, with minimal editing by ORNL.

3.1 Monitoring Technologies International (MTI)

3.1.1 General Description

Monitoring Technologies International's PDV5000 is a self-contained anodic stripping analyzer. Modifications in electrode design and software has allowed a miniaturization of the instrument, yielding a truly portable instrument. The new PDV 5000 is a handheld analyzer that can detect heavy metals in liquid samples at a concentration as low as 10 ppb. ASV (Anodic Stripping Voltammetry) works by electroplating metals in solution onto an electrode. This concentrates the metal. The metals on the electrode are then sequentially stripped off, which generates a current that can be measured. The current (milliamps) is proportional to the amount of metal being stripped off. The potential (voltage in millivolts) at which the metal is stripped off is characteristic for each metal. This means the metal can be identified as well as quantified. The method has found widespread acceptance, particularly in specialist laboratories that need to analyze metals in the low part per trillion (nanogram per litre) range, without needing to concentrate the sample.

The PDV 5000 system is a new type of 3 electrode device. Instead of liquid mercury as the electrode, this device uses a glassy carbon electrode that is plated with a very thin film of Mercury. (Mercury Thin Film Electrode, MTFE) This is carried out at the beginning of an analytical run and lasts for between 10 and 30 subsequent analyses. The Mercury is contained as a salt in the supporting buffer used. This means only a very small amount of Mercury is used and ensures the operator never comes into contact with liquid Mercury. The amount of Mercury used per analysis is measured in parts per billion. If however the analysis is for Arsenic, Selenium or Mercury, the glassy carbon electrode is given a Gold film. Ease of use has been the primary objective in the design. A simple, menu driven software allows the user to select the metal and concentration range of interest. Analysis time is dependant on the metal concentration, but ranges from a few minutes to 20 minutes for an ultra low concentration. The initial calibration can be used for many subsequent 'unknown' analyses without the need for recalibration.

Figure 3-1. MTI's PDV 5000 system

The PDV 5000 is a practical and economical device for real time heavy metal analysis in environmental, industrial, geological, agricultural and process applications. It is simple to use, reliable and accurate and is more than sensitive enough for the common heavy metals of concern.

3.1.2 Sample Analysis

The liquid sample is added to the supporting electrolyte (buffer) to ensure the oxidation states of the metal ions are optimized for electrochemistry. This also dilutes the sample, which removes many of the

potentially interfering compounds. Another component of the buffer removes any dissolved oxygen in the sample that would interfere with the analysis.

The analysis proceeds by initially plating the working electrode with Mercury or Gold. Several quick runs with a standard are performed to stabilize the Mercury or Gold film and to confirm the analyzer is working correctly. Each film lasts between 10 and 30 subsequent analyses. The diluted sample is then added to the cell and the working electrode is given a negative potential relative to the reference electrode. The value can be varied depending on which metals are to be analyzed. The negative potential attracts the positive metal ions to it, where electrons combine with the metal ions to produce the metal. The use of the Mercury film enhances the process as when the metal ion is reduced to the metallic state, it forms an amalgam with the Mercury, which stabilizes it during the stripping phase. Mercury on glassy carbon also has a high over potential relative to Hydrogen. This means the potential can be set that allows metals such as Zinc to be plated onto the electrode, without producing hydrogen gas. Hydrogen is very reducing and will interfere with the subsequent stripping. The potential is then held for around 60 seconds (up to 300 in some applications) while the metal ions accumulate on the electrode, effectively concentrating the sample.

During the plating process, the sample is mixed at high speed. This ensures that the metal ion concentration at the electrode/sample interface is the same as the concentration in the bulk sample. By mixing the sample, the major factor that pulls the ions to the working electrode is the negative potential and not diffusion, convection or other random movement in the sample. This also helps prevent a capacitive build up on the electrode where a layer of positive ions shield the negative electrode from other ions in the sample. By ensuring the negative potential is the dominant factor during the analysis, the reproducibility of the analysis is dramatically improved. An added bonus is the complex mathematical formula used to calculate the amount of metal deposited for a given time at a given potential is simplified.

The potential is then allowed to become less negative and the metals re-oxidize (or are stripped from the electrode), which generates electrons (2 for each Cu atom, 3 for As etc). Each metal will strip from the electrode at a specific potential, which allows for identification of a metal. The rate at which the potential is changed is called the sweep rate and is another variable that can be altered to optimize an analysis. The faster the sweep rate, (mV/sec) the better the resolution, however with lower sensitivity. This is because at high sweep rates, the metals on the electrode have a much shorter time to strip off giving, less chance for the peaks to overlap. A slow sweep rate allows more metal to strip off, giving a larger signal, but conversely increases the noise on the baseline, potentially masking the metal of interest. By applying different waveforms to the sweep, stripping potentials can be shifted, which is useful when 2 metals of interest strip at a similar potential.

The generation of electrons is measured by the counter electrode as a current produced in the cell. The current in micro or nano amps is proportional to the metal concentration on the electrode. As each metal strips from the electrode, a graph is produced showing a series of peaks corresponding to current (metal concentration) at specific potentials. By selecting a potential “window” where a specific metal is expected to appear, ASV can be used to identify and quantify the metal concentration in the sample.

3.1.3 Quantification

The calibration curves for individual metals are linear over 3 orders of magnitude. Most ASV instruments can therefore use a single concentration of standard to analyze samples from 10 ppb and 30,000 ppb. The calibration curve also has a characteristic gradient which is useful for initial QC of the instrument performance. This method is called ***calibration curve comparison*.**

As with all analytical methods there can be interferences. The matrix and presence of other metals or substances can change the potential at which a metal strips from the electrode. Certain metals have similar stripping potentials so a slight shift in stripping potential can cause peak overlap (similar to gas chromatography). For this reason the analysis is always run with a standard of the metal of interest to identify the exact stripping potential.

To minimize the effects of interference, methods have been developed that use specific buffers that are best suited to various matrixes and metals together with a procedure known as ***standard addition***. The instrument is first calibrated using a known concentration of the metal of interest in specific buffer. The concentration selected should be in the same order of magnitude as the expected concentration of metal in the

sample. The current produced should match the expected value for that instrument. If it does the system passes the initial QC check.

The sample is then analyzed and an initial metal concentration calculated. A small volume of a known concentration of the standard is then added to the sample and it is re-analyzed. A second, small volume of the same standard is then added to this sample and it is analyzed again. The three results are compared. As ASV produces a linear calibration curve over 3 orders of magnitude, the results should also produce a linear curve with a gradient similar to that expected for the target metal. For simple shifts in the line such as a slight curve, parallel line or slight divergence, a simple calculation can take the analytical result and convert it to a compensated result. The software supplied with the more sophisticated instrumentation can compensate for more complex shifts in the calibration curve.

3.2 Niton Corporation

Niton will have the performances of two instruments verified. The major difference between the two instruments is the detector system. Both instruments resemble the photograph in Figure 3-2.

3.2.1 Field Portable X-ray Fluorescence Analyzer I ("BASP" Detector)

The sample analyzer is an energy dispersive x-ray fluorescence (EDXRF) spectrometer that uses a sealed, cadmium-109 radioisotope source (<50 mCi) to excite characteristic x-rays of a test sample's constituent elements. These characteristic x-rays are continuously detected, identified and quantified by the spectrometer during sample analysis. Stated simply, the energy of each x-ray detected identifies a particular element present in the sample, and the rate at which x-rays of a given energy are counted provides a determination of the quantity of that element that is present in the sample.

Detection of the characteristic lead x-rays is achieved using a highly efficient, thermo-electrically cooled, solid-state detector, the Big-Area Silicon PIN-diode (BASP). Signals from the BASP detector are amplified, digitized and then quantified via integral multichannel analysis and data processing units. Sample test results are displayed in total micrograms of lead per dust-wipe.

Figure 3-2. Niton portable XRF system.

3.2.1.1 Calibration

The instrument is factory calibrated. Verify instrument performance as follows: place the response verification samples (RSV) in the metal dust wipe holder and follow steps one through five inclusive of the Sample Analysis procedure. Confirm the obtained reading is within the allowed limits printed on the sample bag before proceeding with an unknown analysis.

3.2.1.2 Sample Preparation

1. For samples from ELPAT and U. Cincinnati, unfold and distribute the sample across the surface of the wipe. This is only required for prepared samples where the lead loading is clumped in discrete areas.
2. Fold the sample five times, as specified in the attached schematic, such that it is neatly folded to the proper size (1 x 1.5 inches).
3. Dry the sample prior to testing: dry for 20 minutes at 250 °F. in a toaster oven, or expose the sample overnight to ambient temperature and humidity. After oven drying, allow the dried sample to sit in ambient air for 5 minutes.
4. Bag the wipe sample in a 2 x 2 inch plastic bag (NITON part number 187-471 or equivalent) and label. To eliminate the potential for cross-contamination of samples, never reuse plastic bags.
5. Position the wipe sample in its plastic bag within the frame of the metal dust wipe holder (NITON part number 180-407 or equivalent).

3.2.4.3 Sample Analysis

1. Position the metal dust wipe holder at the number-one position on the thin sample test stand and take the first of four measurements (minimum of 60 nominal seconds). Note that the following procedure using four sample measurements has been designed to insure that the entire area of the folded dust-wipe sample is properly measured by the spectrometer.
2. Place the metal dust wipe holder at the number-two position on the test stand and take the second measurement (minimum 60 nominal seconds).
3. Rotate the dust wipe holder 180 degrees (without turning the sample holder upside-down).
4. Place the metal dust wipe holder at the number-one position on the test stand and take the third measurement (minimum 60 nominal seconds).
5. Place the metal dust wipe holder at the number-two position on the test stand and take the fourth measurement (minimum 60 nominal seconds).

3.2.2 Field Portable X-ray Fluorescence Analyzer II (Dual Detector)

The sample analyzer is an energy dispersive x-ray fluorescence (EDXRF) spectrometer that uses a sealed, cadmium-109 radioisotope source (<50 mCi) to excite characteristic x-rays of a test sample's constituent elements. These characteristic x-rays are continuously detected, identified and quantified by the spectrometer during sample analysis. Stated simply, the energy of each x-ray detected identifies a particular element present in the sample, and the rate at which x-rays of a given energy are counted provides a determination of the quantity of that element that is present in the sample.

Detection of the characteristic lead x-rays is achieved using a highly efficient, thermo-electrically cooled, solid-state, silicon PIN-diode detector, a part of the Dual Detector system. Signals from the Dual Detector are amplified, digitized and then quantified via integral multichannel analysis and data processing units. Sample test results are displayed in total micrograms of lead per dust-wipe.

3.2.2.1 Sample Preparation

1. For samples from ELPAT and U. Cincinnati, unfold and distribute the sample across the surface of the wipe. This is only required for prepared samples where the lead loading is clumped in discrete areas.
2. Fold the sample five times, as specified in the attached schematic, such that it is neatly folded to the proper size (1 x 1.5 inches).
3. Dry the sample prior to testing: dry for 20 minutes at 250 ° F. in a toaster oven, or expose the sample overnight to ambient temperature and humidity. After oven drying, allow the dried sample to sit in ambient air for 5 minutes.
4. Bag the wipe sample in a 2 x 2 inch plastic bag (NITON part number 187-471 or equivalent) and label. To eliminate the potential for cross-contamination of samples, never reuse plastic bags.
5. Position the wipe sample in its plastic bag within the frame of the metal dust wipe holder (NITON part number 180-407 or equivalent).

3.2.2.2 Sample Analysis

1. Position the metal dust wipe holder at the number-one position on the thin sample test stand and take the first of four measurements (minimum of 60 nominal seconds). Note that the following procedure using four sample measurements has been designed to insure that the entire area of the folded dust-wipe sample is properly measured by the spectrometer.
2. Place the metal dust wipe holder at the number-two position on the test stand and take the second measurement (minimum 60 nominal seconds).
3. Rotate the dust wipe holder 180 degrees (without turning the sample holder upside-down).
4. Place the metal dust wipe holder at the number-one position on the test stand and take the

third measurement (minimum 60 nominal seconds).

5. Place the metal dust wipe holder at the number-two position on the test stand and take the fourth measurement (minimum 60 nominal seconds).

3.3 Palintest

3.3.1 General Technology Description

Palintest's Scanning Analyzer SA-5000 system consists of an instrument and unique pre-calibrated disposable electrodes that offer a method of analyzing lead in paint, surface and airborne dust, soil, wastes and water.

The Scanning Analyzer SA-5000 system uses the electrochemical technique of Stripping Analysis to specifically determine the concentration of lead in a solution. Stripping analysis is a two step process. The first step is called the deposition step and involves the electro-deposition of lead into a disposable mercury-film electrode. The deposition is achieved by cathodic deposition at a fixed potential and time. Following the fixed deposition time the system enters the second step, the stripping or measurement step. The stripping step involves scanning the potential anodically using a potential-time waveform. During this anodic scan the deposited lead is reoxidized and stripped out of the electrode. The current and potential are measured during the anodic scan and the resulting voltammogram contains a peak whose potential is specific to lead and whose height is proportional to the concentration of lead in the solution. The peak height is converted from a current to a concentration using one of many calibration curves stored in the instrument. No user calibration is required because each batch of electrodes is checked during manufacture and assigned an eight figure calibration code. The calibration code is used to select the calibration curve which matches the electrode batch.

3.3.2 Analytical Procedure

1. Place the dust wipe into a 50 mL sonicator tube. Using a pipettor add 15 ml (3 x 5 ml) of 25% nitric acid to the sonicator tube. Use a new crushing rod to push the wipe down into the tube ensuring it is covered by the acid. Continue to push the wipe into the acid solution until trapped air bubbles in the wipe have been released.

2. Place the tube in the ultrasonicator. Fill the ultrasonicator with warm water (45 - 50 °C) so that the level of water in the sonicator is at least 1cm above the level of liquid in the tube.

3. Sonicate the tube for 30 minutes then remove the tube and place in a rack.

4. Take the same crushing rod as previously used and repeat the mixing of the wipe in the tube. Replace the tube in the ultrasonicator and sonicate for an additional 15 minutes.

5. Remove the cap and carefully add deionized or distilled water to the 50 mL mark. Using the same crushing rod as previously used mix the wipe and solution to ensure complete distribution of the extract. Replace the cap and mix well by shaking.

6. Take a 5 mL scew capped test tube and pour a portion of the solution into the tube filling to the 5 mL mark.

7. Add one SoluPrep SP-B tablet, crush and mix until completely dissolved.

8. Test the sample with the scanning analyzer. Switch on the instrument. Select Dust from the menu. Key in the correct calibration code shown on the electrode pack. Open the foil strip containing an electrode and insert into the connector. Insert the electrode into the sample. The instrument automatically starts the test and the result is displayed after 45s.

3.3.3 Sample Disposal

There will be 50mL of 7.5% nitric acid containing lead extracted from the dust sample for each dust wipe tested. Samples containing nitric acid are normally consisdered hazardous because of their acid content. Samples which contain lead at 250mg/sample or higher are classified as toxic. For non-toxic samples the acidity can be neutralised by diluting the sample with water in a container and then adding sodium bicarbonate.

4 VERIFICATION TEST DESIGN

This section discusses the objectives and design of the verification test, factors that must be considered to meet the performance objectives, and the information that ORNL and EPA will use to evaluate the results of the verification.

4.1 Drivers and Objectives of the Verification Test

The purpose of this test is to evaluate the performance of field analytical technologies that are capable of analyzing dust wipe samples for lead contamination. This test will provide information on the potential applicability of field technologies for clearance testing, as the experimental design is built around the three clearance levels of 40 $\mu g/ft^2$ for floors, 250 $\mu g/ft^2$ for window sills, and 400 $\mu g/ft^2$ for window troughs which are outlined in a recent rule amendment to the Code of Federal Regulations [1].

The primary objectives of this verification are to evaluate the field analytical technologies in the following areas: (1) how well each performs relative to a conventional, fixed-site, analytical method for the analysis of dust wipe samples for lead; (2) how well each performs relative to results generated in previously rounds of ELPAT testing, and (3) the logistical and economic resources necessary to operate the technology. Secondary objectives for this verification are to evaluate the field analytical technology in terms of its reliability, ruggedness, cost, range of usefulness, sample throughput, data quality, and ease of use. The planning for this verification test follows the guidelines established in the data quality objectives process.

4.2 Summary of the Experimental Design

All of the samples analyzed in this verification test will be prepared gravimetrically and will be of known quantity. All of the wipes utilized in this test (PaceWipe, Aramsco Lead Wipe, and Palintest Dust Wipe) will meet the specifications of the American Society for Testing and Materials requirements [2]. Initial consideration was given to conducting the test in a real-world situation, where the technologies would have been deployed in a housing unit that had been evacuated due to high levels lead contamination. In addition to the safety concern of subjecting participants to lead exposure, the spatial variability of adjacent samples would have been so great that it would be much larger than the expected variability of these types of technologies, therefore making it difficult to separate instrument/method variability and sampling variability. Also, for the destructive technologies such as ASV, it would be nearly impossible to verify the results of the field method with a standard laboratory analysis, because a replicate sample could not be obtained. The availability of well-characterized samples derived from “real-world” situations made the use of proficiency testing samples (so-called “ELPAT” samples) and other prepared samples an attractive alternative.

4.2.1 ELPAT and Blank Sample Description

In 1992, the American Industrial Hygiene Association (AIHA) established the Environmental Lead Proficiency Analytical Testing (ELPAT) program. The ELPAT Program is a cooperative effort of the American Industrial Hygiene Association (AIHA), and researchers at the Centers for Disease Control and Prevention (CDC), National Institute for Occupational Safety and Health (NIOSH), and the EPA Office of Pollution Prevention and Toxics (OPPT). Participation and proficiency in ELPAT are AIHA requirements for laboratories who wish to seek accreditation and recognition by EPA’s National Lead Laboratory Accreditation Program (NLLAP). The ELPAT program is designed to assist laboratories in improving their analytical performance, and therefore does not specify use of a particular analytical method. Participating laboratories are blindly sent samples to analyze on a quarterly basis. The reported values must fall within a

range of acceptable values in order for the laboratory to be deemed proficient for that quarter.

Research Triangle Institute (RTI) in Research Triangle Park, NC, is contracted to prepare and distribute the lead-containing paint, soil, and dust wipe ELPAT samples. For the rounds of testing which have occurred since 1992, archived samples are available for purchase. These are the samples that will be used in this verification test. Because the samples have already been tested by hundreds of laboratories, a certified concentration value is supplied with the sample. This certified value represents a pooled measurement of all of the results submitted, with outliers excluded from the calculation.

The following description, taken from an internal RTI report, briefly outlines how the samples are prepared RTI developed a repository of real-world housedust, collected from multiple homes in the Raleigh/Durham/Chapel Hill area, as well as from an intervention project in Wisconsin. After collection, the dust was sterilized by gamma irradiation and sieved to 150 μm. A PaceWipe™ was prepared for receiving the dust by opening the foil pouch, removing the wet folded wipe and squeezing the excess moisture out by hand over a trash can. The wipe was then unfolded and briefly set on a Kimwipe to soak up excess moisture. The PaceWipe™ was then transferred to a flat plastic board to await the dust. The weighing paper containing the pre-weighed dust was then removed from the balance, and 0.1000 ± 0.0005 g portions of dust were gently tapped out onto the PaceWipe™. The wipe was then folded and placed in a plastic vial, which was then capped. All vials containing the spiked wipes were stored in a cold room as a secondary means of retarding mold growth until shipment.

Before use in the ELPAT program, RTI performs a series of analyses to confirm that the samples were prepared within the quality guidelines established for the program. Ten samples are analyzed by RTI and nine samples are sent off-site to an independent laboratory for confirmatory analysis. The relative standard deviation of the 10 samples analyzed by RTI must be 10% of less, indicating that the samples were prepared in a homogeneous fashion. The measured concentrations must be within 20% of the target value that RTI was intending to prepare. Additionally, the off-site analysis must be within ± 20% of the RTI results in order for the samples to be acceptable.

RTI will prepare the blank samples using the same preparation method as the ELPAT samples, but the concentration of lead in the dust on the wipe will be below reporting limits of the participants (≤ 2 μg/wipe).

4.2.2 University of Cincinnati Sample Description

As described above, the ELPAT samples consist of dust mounded in the center of a Pacewipe. The University of Cincinnati (UC) prepares “field QC samples” where the dust is spread over the wipe, similar to how a wipe would look when a dust wipe sample is collected in the field. The sample is prepared gravimetrically, so the concentrations can be estimated. In a typical scenario, these control samples would be sent to a laboratory along with actual field-collected samples as a quality check of the laboratory operations. Because the samples are visually indistinguishable from the actual field sample and are prepared on the same wipe and are shipped in the same packaging, the laboratory blindly analyzes the control samples, providing the user with an independent assessment of the quality of the laboratory’s data.

A cluster of twenty UC-prepared samples at the key clearance levels were added to the experimental design to augment the robustness of the test. The UC wipe samples will be prepared from National Institute of Standards & Technology (NIST) Standard Reference Materials (SRMs). For all vendors except Palintest, the UC samples will be prepared on Aramsco Lead Wipes™ (Lakeland, FL), while Palintest’s samples will be prepared on Palintest wipes.[1] To document the variability of the preparation process, UC will analyze approximately 5% of the total number ordered and the results will be provided to ORNL. Additionally, randomly-selected samples will be analyzed by independent organizations as a quality control check of the accuracy and precision of UC’s sample preparation procedure.

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[1] PaceWipes would have been used to prepare the UC samples, but the PaceWipes were unavailable at the time of the study due to a problem with the manufacturer. Based on a NIOSH publication [3], it is recommended to the ASVvendors that the extracts from Aramsco and Palintest wipes be filtered prior to analysis. It will be noted in the verification report if the vendor(s) followed this advice.

4.3.3 Distribution and Number of Samples

Figure 4-1 is a plot containing the distribution of the sample concentrations to be analyzed in this study. A total of 160 samples will be analyzed in the verification test. For the ELPAT samples, four samples will be analyzed at each of 20 test levels (20 test levels x 4 samples each = 80 samples total). While the set of four samples have/will be prepared using homogeneous source materials and an identical preparation procedure, they cannot be considered true "replicates" because each sample will be prepared individually. However, these samples will represent four samples prepared similarly at a specified target concentration. Twenty samples will be prepared near each of the three clearance levels (3 test levels x 20 samples = 60 samples total) by the University of Cincinnati. Twenty blanks, prepared by Research Triangle Institute at lead concentrations ≤ 2 µg, will also be analyzed. In Figure 4-1, the clearance levels are denoted as a horizontal lines.

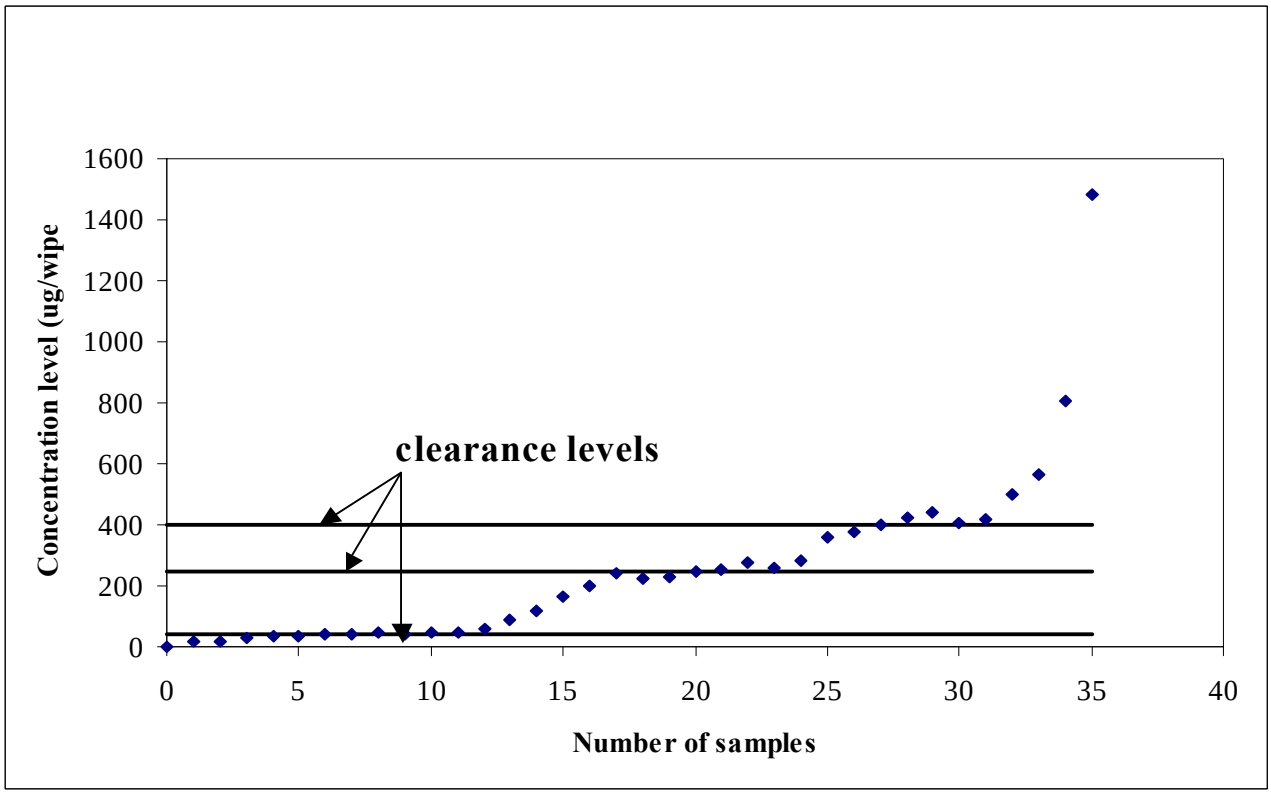

Figure 4-1. Summary of concentration levels in experimental design. Four samples will be analyzed at each concentration level.

4.3 Comparison of Field Technology Results to an NLLAP-Recognized Laboratory's Results

Current EPA regulations for clearance testing of facilities that have been abated for lead contamination stipulate that the laboratory performing the testing must been recognized under NLLAP [4]. Currently, only fixed-site analytical laboratories are recognized under NLLAP. Mobile laboratories and testing firms using field portable equipment may be recognized under NLLAP, even if no such laboratories or firms are on the current NLLAP list. In order to assess whether the field portable technologies participating in this verification test produce results that are comparable to NLLAP-recognized data, an NLLAP-recognized laboratory was selected to analyze samples concurrently with the field testing.

4.3.1 Laboratory Selection

NLLAP was established by the EPA OPPT under the legislative directive of Title X, the Lead-Based Paint Hazard Reduction Act of 1992. In order for laboratories to be recognized under the NLLAP they must successfully participate in the ELPAT Program and undergo a systems audit.

The acceptable range for the ELPAT test samples is based upon consensus values from participating laboratories. A laboratory's performance for each matrix is rated as proficient if their ELPAT results are within three standard deviations of the determined acceptable range for 75 percent of the ELPAT test samples.

The NLLAP required systems audit must include an on-site evaluation by a private or public laboratory accreditation organization recognized by NLLAP. Some of the areas evaluated in the systems audit include laboratory personnel qualifications and training, analytical instrumentation, analytical methods, quality assurance procedures and record keeping procedures.

The list of recognized laboratories is updated monthly. ORNL obtained the list of accredited laboratories in July 2001. The list consisted of approximately 130 laboratories. Those laboratories which did not accept commercial samples and those located on the west coast were automatically eliminated as potential candidates. ORNL interviewed at random approximately ten laboratories and solicited information regarding cost, typical turnaround time, and data packaging. Based on these interviews and discussions with technical panel members who had personal experience with the potential laboratories, ORNL selected DataChem (Cincinnati, OH) as the fixed-site laboratory. As a final qualifying step, DataChem analyzed 16 samples (8 ELPAT and 8 prepared by UC) in a pre-test study, which demonstrated that the laboratory was proficient in analyzing these types of samples.

Because the UC samples will be prepared on two different types of wipes, DataChem will analyze UC samples for both Aramsco and Palintest wipes so that all technology results can be directly compared to an NLLAP-recognized laboratory's results.

4.3.1 Description of Method

The laboratory method used in this study was hot plate/nitric acid digestion, followed by Inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis. The preparation and analytical procedures, as supplied by DataChem, can be found in Appendix A. DataChem's procedures are modification of Methods 3050B and 6010B of EPA SW-846 Method Compendium for the preparation and analysis of metals in environmental matrices [5,6]. Other specific references for the preparation and analysis of dust wipes are available from the American Society for Testing and Materials (ASTM) [7].

5 EXECUTION OF THE VERIFICATION TEST

5.1 Summary of Verification Activities

The verification test will be conducted in Hartford, CT, from November 5 through 9, 2001. The vendors, who will operate their own equipment, must analyze all 160 samples on-site and submit results prior to departure in order to complete the verification test. The samples evaluated during the verification will consist of (1) archived ELPAT samples prepared from housedust collected from multiple homes in North Carolina and Wisconsin, ranging in concentration from 15 to 1,500 μg/wipe, (2) UC-prepared samples from NIST SRMs on Armasco Lead Wipes (or Palintest wipes for Palintest USA), at the three clearance levels of 40, 250, and 400 μg/wipe, and (3) low level samples called "detectable blanks", with concentrations (≤ 2 μg lead/wipe) below typical detection levels for field technologies, prepared by RTI using the same procedure as the ELPAT samples..

On the morning of November 9, the ETV program will invite attendees of a nearby conference on lead-safe housing to visit the test site and participate in a User Session. The attendees with an interest in field portable technologies will be particularly encouraged to attend. The participants will be able to interact with the vendors, gather product literature, and observe demonstrations of the technologies. During the User Session, the ETV program will encourage interested participants to perform vendor-assisted hands-on work by analyzing samples themselves. This will give the participants an opportunity to use an instrument they might be interested in purchasing, as well as give the ETV program some feedback on ease of use and user-friendliness of the technologies.

5.1.1 Test Location

The test will be conducted in a user facility on the campus of Capitol Community Technical College, 401 Flatbush Ave, Hartford, CT. The facility was selected because it is a site routinely used to train

abatement contractors in field portable lead measurement techniques, and it is near the lead-safe housing conference location.

5.2 Sample Distribution

ORNL will be responsible for sample distribution. The samples will be packaged in 20-mL plastic scintillation vials and labeled with a sample identifier. Each participant will received the same suite of samples, but in a randomized order. All samples will be prepared for distribution at the start of the verification. The vendors will go to a sample distribution table to pick-up the samples. The samples will be distributed in batches of 12. Completion of chains-of-custody forms will document sample transfer.

5.3 Submission of Results

The vendor will provide the results to ORNL**.** The vendor will be responsible for reducing the raw data into a presentation format consistent with the evaluation requirements. At the end of the verification test, the vendor will submit all final results and raw data to ORNL. After the conclusion of the field activities, the vendors will have one week to review their data and make revisions to their results. These revisions will not involve re-analysis of any sample. The revisions will be limited to correcting for calculation and transcription errors.

5.4 Verification Performance Factors

The following are the logistical and technical performance verification factors that will be verified for each technology.

- Accuracy: closeness of technology result to an estimated known value (i.e., ELPAT certificate value);
- Precision: reproducibility of technology's results for set of four samples prepared at a specific concentration level;
- Comparability: performance relative to the NLLAP-recognized laboratory;
- Detectable blanks: number of samples where lead is reported above reporting limits for samples which are prepared at low levels ($\leq$ 2 μg/wipe);
- Probability of false positive results: relative to all three clearance levels of 40, 250, and 400 $\mu g/ft^2$. For example, number of samples where the field technology reports a result as $\geq$ 40 μg and the concentration is actually less than 40 μg.
- Probability of false negative results: relative to all three clearance levels of 40, 250, and 400 $\mu g/ft^2$. For example, number of samples where the field technology reports a result as < 40 μg and the concentration is actually $\geq$ 40 μg.
- Sample throughput: number of samples/hour/number of analysts
- Ease of use: user friendliness of the technology; amount of training required to operate independently.

These factors and the anticipated statistical analyses are further discussed in Section 6.

6 QUALITY ASSURANCE PROJECT PLAN (QAPP)

The QAPP for this verification test specifies procedures that will be used to ensure data quality and integrity. Careful adherence to these procedures will ensure that data generated from the verification will meet the desired performance objectives and will provide sound analytical results.

6.1 Purpose and Scope

The primary purpose of this section is to outline steps that will be taken to ensure that data resulting from this verification is of known quality and that a sufficient number of critical measurements are taken. This section is written in compliance with ORNL's ETV Quality Management Plan [8].

6.2 Quality Assurance Responsibilities

The implementation of the verification test plan must be consistent with the requirements of the study and routine operation of the technology. The ORNL technical lead is responsible for coordinating the

preparation of the QAPP for this verification and for its approval by EPA and ORNL. The ORNL project manager will ensure that the QAPP is implemented during all verification activities. ORNL's QA specialist (QAS) will review and approve the QAPP and will provide QA oversight of the verification activities. The ORNL technical lead will be responsible for the laboratory data validation. The ORNL statistician will primarily be responsible for the reduction of the vendor and laboratory data. The EPA project manager and EPA QA manager will review and approve this plan.

6.3 Field Operations

6.3.1 Site Training

Preliminary site training will be provided to all vendors on the first day of testing. This will be required before initiation of the field study. This training will be conducted by the ORNL project manager or his designee. It will entail an overview of the test site, safety information, emergency procedures, and logistical information regarding the verification test.

6.3.2 Communication and Documentation

Successful field operations require detailed planning and extensive communication. ORNL will communicate regularly with the verification participants to coordinate all field activities associated with this verification and to resolve any logistical, technical, or QA issues that may arise as the verification progresses. Pertinent vendor and ORNL field activities will be thoroughly documented. Field documentation will include field logbooks, photographs, field data sheets, and chain-of-custody forms.

The ORNL technical lead will be responsible for maintaining all field documentation. Field notes will be kept in a bound logbook. Each page will be sequentially numbered and labeled with the project name and number. Completed pages will be signed and dated by the individual responsible for the entries. Errors will have one line drawn through them and this line will be initialed and dated. Any deviations from the approved final verification test plan will be thoroughly documented in the field logbook and provided to the ORNL. Photographs will be taken with a digital camera.

6.4 Performance and System Audits

The following audits will be performed during this verification.

6.4.1 Technical Systems Audit

Because the verification test will be conducted in Hartford, CT, the ORNL QAS will not be able to perform an on-site surveillance during the test. However, the ORNL QAS will remotely provide oversight of the verification activities through four mechanisms: a management assessment checklist (to be completed by the ORNL project manager); email interviews with the technical lead and the project statistician that must be completed with 24 hours of receipt; survey for vendors to complete; and review of digital pictures of the verification activities that will be posted in near real-time on the ORNL ETV web site (www.ornl.gov/etv). This plan for remotely assessing the verification activities allows for inputs for multiple sources, so that the QAS will have an unbiased picture of how the study was conducted. The use of email will allow for spontaneous responses and follow-up questions.

6.4.2 Data quality audit of the laboratory

One of the requirements to become an NLLAP-recognized laboratory is routine quality audits. ORNL will not audit the laboratory unless a data quality issue is identified during the analyses of the samples.

6.4.3 Surveillance of Technology Performance

During verification testing, ORNL staff will observe the operation of the field technology, such as observing the vendor operations, photo-documenting the test site activities, surveying calibration procedures, and reviewing sample data. The observations will be documented in a laboratory notebook. The verification report will contain the exact protocols used by the vendors during testing.

6.5 Quality Assurance Reports

QA reports provide the necessary information to monitor data quality effectively. It is anticipated that the following types of QA reports will be prepared as part of this verification.

6.5.1 QC Reports of Sample Preparation

As described in Sections 4.2.1 and 4.2.2, both RTI and UC analyze a portion of the prepared samples to confirm the accuracy and precision of the sample preparation. These data will be made available to ORNL as soon as it is available, preferably prior to the start of verification testing. Additionally, ORNL will distribute 5% of the UC samples to an independent laboratory (EPA Region 1) for confirmation analyses. The concentrations of the samples prepared by RTI have already been through independent confirmation through the ELPAT proficiency testing process.

6.5.2 QAS Remote Surveillance Report

From the information gathered during the Technical Systems Audit (section 6.4.1), the ORNL QAS will prepare a report of the findings. Because information will be gathered from multiple sources, the QAS will be able to provide an independent assessment of performance, even though the test will be conducted off-site. The Technical Systems Audit Report will be distributed to the project staff, the EPA Project manager, and the EPA QA Manager.

6.5.3 Status Reports

ORNL will regularly inform the EPA project manager of the status of the verification. Project progress, problems and associated corrective actions, and future scheduled activities associated with the verification test will be discussed. When problems occur, the vendor and ORNL will discuss them, estimate the type and degree of impact, describe the corrective actions taken to mitigate the impact and to prevent a recurrence of the problems, and discuss with EPA, as necessary. Major problems will be documented in the field logbook.

6.5.4 Audit Reports

Any additional QA audits or inspections, such as those conducted by technical panel members, that take place in the field while the verification test is being conducted will be formally reported by the auditors to the ORNL technical lead, who will forward them to the EPA project manager. Informal reporting of audit results will be reported immediately to EPA through a phone call, personal communication, or email.

6.6 Corrective Actions

Routine corrective action may result from common monitoring activities, such as:

- Performance evaluation audits
- Technical systems audits
- Calibration procedures

If the problem identified is technical in nature, the individual vendors will be responsible for seeing that the problem is resolved. If the issue is one that is identified by ORNL or EPA, the identifying party will be responsible for seeing that the issue is properly resolved. All corrective actions will be documented. Any occurrence that causes discrepancies from the verification test plan will be noted in the technology verification report.

6.7 Laboratory Quality Control Checks

Internal quality control (QC) samples will be analyzed by DataChem to indicate whether or not the samples were analyzed properly. A summary of QC samples include: initial calibration, continuing calibration verification, and analysis of known samples. This data will be reviewed by ORNL as part of the data validation process. Discrepancies will be noted in the data validation records.

6.8 Data Management

The vendor, ORNL, and EPA each have distinct responsibilities for managing and analyzing

verification data. The vendor is responsible for obtaining, reducing, interpreting, validating, and reporting the data associated with their technology's performance. These data should be reported on the chain-of-custody. Vendor results will be due to ORNL at the conclusion of a day's field activities. The vendor's final report will be due to ORNL one week after the verification. Any discrepancies between the originally reported result and the final result must be described. ORNL is responsible for managing all the data and information generated during the verification test. EPA and ORNL are responsible for analysis and verification of the data.

6.9 Data Reporting, Validation, and Analysis

To maintain good data quality, specific procedures will be followed during data reduction, review, and reporting. These procedures are detailed below.

6.9.1 Data Reporting

Data reduction refers to the process of converting the raw results into a concentration which will be used for evaluation of performance. The procedures to be used will be technology dependent, but the following is required for data reporting:

- The concentration unit will be µg of lead/wipe.
- If no lead is detected, the concentration will be reported as less than the reporting limits of the technology, with the reporting limits stated (e.g., < 20 µg/wipe). A result reported as "0" will not be accepted.

6.9.2 Data Validation

Validation determines the quality of the results relative to the end use of the data. ORNL will be responsible for validating the laboratory data. (Note that the vendor is responsible for validating its own data prior to final submission.) Several aspects of the data (listed below) will be reviewed. The findings of the review will be documented in the validation records. As appropriate, the ETVR will describe instances of failure to meet quality objectives and the potential impact on data quality.

6.9.2.1 Completeness of Laboratory Records

This qualitative review ensures that all of the samples that were sent to the laboratory were analyzed, and that all of the applicable records and relevant results are included in the data package.

6.9.2.2 Holding Times

The dust wipe samples will not require refrigeration or other preservation techniques. The method requirement is that the samples be prepared within 6 months of collection.

6.9.2.3 Correctness of Data

So as not to bias the assessment of the technology's performance, errors in the laboratory data will be corrected as necessary. Corrections may be made to data that has transcription errors, calculation errors, and interpretation errors. These changes will be made conservatively, and will be based on the guidelines provided in the method used. The changes will be justified and documented in the validation records.

6.9.2.4 Correlation Between Samples within a Concentration Set

Normally, one would not know if a single sample result was "suspect" unless (a) the sample was a spiked sample, where the concentration is known or (b) a result was reported and flagged by the laboratory as suspect for some obvious reason (e.g., no quantitative result was determined). The experimental design implemented in this verification study will provide an additional indication of the abnormality of data through the inspection of the set of four results for samples prepared at a specific concentration. Criteria has been established to determine if data is suspect. Data sets will be considered suspect if the percent relative standard deviation for a set of four similarly-prepared samples was greater than 50%, because this criteria would indicate imprecision. These data would be flagged so as not to bias the assessment of the technology's performance. Precision and accuracy evaluations may be made with and without these suspect

values to represent the best and worst case scenarios. If both the laboratory and the vendor(s) report erratic results, the data may be discarded if it is suspected that the erratic results are due to a sample preparation error.

6.9.2.5 Evaluation of QC Results

QC samples will be analyzed by the NLLAP-laboratory with every batch of samples to indicate whether or not the samples were analyzed properly. Performance on these samples will be reviewed and major findings will be noted in the validation records.

6.9.2.6 Evaluation of Spiked Sample Data

Spiked samples are samples containing known concentrations of analyte(s). For this verification test, all of the samples are considered spiked samples.

6.9.3 Data Analysis for Verification Factors

This section contains a list of the six primary performance verification factors to be evaluated for both the field technology and the NLLAP-recognized laboratory.

6.9.3.1 Precision

Precision, in general, refers to the degree of mutual agreement among measurements of the same materials and contaminants. Environmental applications often involve situations where "measurements of the same materials" can take on a number of interpretations. In environmental applications, precision is often best specified as a percentage of contaminant concentration. The following lists several possible interpretations of precision for environmental applications.

1) The precision involved in repeated measurements of the same sample without adjusting the test equipment.

2) The precision involved in repeated measurements of the same sample after reset, repositioning, or re-calibration of the test equipment or when using different equipment of the same technology.

3) The precision of measurements due to spatial variability of dust samples from adjacent locations.

4) The precision characteristics of a specific technology in determining contamination at a specific site or at an arbitrary site.

In general, users of the technology will want to be assured that measurement variability in 1) and 2) is small. Measurement variability due to spatial variability described in 3) is likely to be site specific and is minimized in this verification by using samples prepared under homogeneous conditions. The measurement variability discussed in 4) is perhaps of most interest as it includes measurement variability resulting from possible differences in the design activities and effects of environmental conditions such as temperature that would vary from one site characterization to another as well as site and technology specific sources.

The strength of this verification's experimental design is that since an equal number of similar samples will be selected from a homogeneous population at every concentration level, an equal number of precision comparisons can be made.

Precision for this verification will be estimated by the variance, or standard deviation from the measured data. If "n" lead concentration measurements are represented by Y_1, Y_2, ..., Y_n, the estimated variance about their average value "$\overline{Y}$" is calculated by:

$$S^2 = \frac{1}{n-1} \sum_{k=1}^{n} (Y_k - \overline{Y})^2 \quad .$$

The standard deviation is the square root of S^2 and will be analyzed to see if the precision values are a function of lead concentration levels. The estimated S^2 values will also be compared by F-tests to those values reported on the ELPAT certificate and by UC. To express the reproducibility relative to the average lead concentration, percent relative standard deviation (RSD) is used to quantify precision, according to the following equation:

RSD = (standard deviation / average concentration) x 100%

Standard deviations estimated at each concentration level can be used to establish the relationship between the uncertainty and the average lead concentration.

6.9.3.2 Accuracy

Accuracy is a measure of how close the measured lead concentrations are to estimated values of the true concentration. The estimated values for the ELPAT samples will be the certificate values that are reported on the certificate of analysis sheet (see Appendix B for an example sheet). The ELPAT certificate values represent an average concentration determinated by hundreds of laboratories that participated in previous rounds of ELPAT testing. The UC concentration values will be reported by UC for individual samples, calculated by the amount of NIST-traceable material loaded on the dust wipes. The accuracy and precision of the UC value will be assessed through three independent laboratories analyzing randomly selected QC samples. Each of the three labs will analyze 5% of the total number of samples prepared by UC at each of the three concentration levels and confirm that the process used to prepare the samples was in control.

Accuracy of the vendor measurements will be statistically tested using t-tests or non-parametric tests and will also be quantified by computing the percent recovery for four similar samples or a single sample using the equation:

percent recovery = [measured amount(s)/estimated value] × 100%

The optimum percent recovery value is 100%. Percent recovery values greater than 100% indicate results that are biased high, and values less than 100% indicate results that are biased low.

Inaccuracies or biases are the result of systematic differences between measured and known values. These biases may be due to limited calibration range, systematic errors, or standards preparation. Consequently every effort will be made by ORNL, the technology vendors and the laboratory to identify specific sources of inaccuracies. The verification includes blanks, replicates, and spiked samples that should provide substantiating evidence to support this partitioning of sources of bias when results become available.

6.9.3.3 Detectable Blanks

Twenty samples in the study will be prepared at ≤2 μg/wipe, below the anticipated reporting limits of both the field technologies and the laboratory. Any reported lead for these samples will be considered a "detectable blank".

6.9.3.4 False Positive/False Negative Results

A false positive (fp) result is one in which the technology detects lead in the sample above a clearance level when the sample actually contains lead below the clearance level [9]. A false negative (fn) result is one in which the technology indicates that lead concentrations are less than the clearance level when the sample actually contains lead above the clearance level [9]. For example, if the technology reports

the sample concentration to be 35 µg/wipe, and the true concentration of the sample is 45 µg/wipe, the technology's result would be considered a fn. Accordingly, if the technology reports the result as 45 µg/wipe and the true concentration is 35 µg/wipe, the technology's result would be a fp.

A primary objective for this verification test is to assess the performance of the technology at each of the three clearance levels of 40, 250, and 400 µg/wipe, and estimate the probability of the field technology reporting a fp or fn result. Measurement uncertainty (that is, method bias and variability) causes the technology to report fp and fn results. Recall from the experimental design that 20 UC samples (at concentrations +/- 10% of each clearance level) and 16 ELPAT samples (at concentrations +/- 25% of each clearance level) will be analyzed. The data generated for these samples will be used to model the technology's uncertainty. These uncertainties will be used in a normal probability distribution model to calculate probabilities of fp and fn results. Additionally, the required number of samples for specified false acceptance and false rejection rates on decisions about remediation of lead contamination will be examined.

6.9.3.5 Comparability

Comparability refers to how well the field technology and the NLLAP-recognized laboratory data agree. The difference between accuracy and comparability is that accuracy is judged relative to a known value, comparability is judged relative to the results of a laboratory procedure, which may or may not report the results accurately. Comparing averages from similar samples measured by the technology with corresponding averages measured by the laboratory will be performed for all target concentration levels.

A correlation coefficient quantifies the linear relationship between two measurements [10]. The correlation coefficient is denoted by the letter r; its value ranges from –1 to +1, where 0 indicates the absence of any linear relationship. The value $r = -1$ indicates a perfect negative linear relation (one measurement decreases as the second measurement increases); the value $r = +1$ indicates a perfect positive linear relation (one measurement increases as the second measurement increases). The slope of the linear regression line, denoted by the letter m, is related to r. Whereas r represents the linear association between the vendor and laboratory concentrations, m quantifies the amount of change in the vendor's measurements relative to the laboratory's measurements. A value of +1 for the slope indicates perfect agreement. Values greater than 1 indicate that the vendor results are generally higher than the laboratory, while values less than 1 indicate that the vendor results are usually lower than the laboratory.

6.9.3.6 Completeness

Completeness refers to the amount of data collected from a measurement process expressed as a percentage of the data that would be obtained using an ideal process under ideal conditions. The completeness objective for data generated during this verification is 95% or better.

There are many instances which might cause the sample analysis to be incomplete. Some of these are:

- Instrument failure;
- Calibration requirements not being met;
- Elevated analyte levels in the method blank.

7 HEALTH AND SAFETY PLAN

This section describes the specific health and safety procedures that will be used during the field work at the Capitol Community Technical College, in Hartford, CT.

7.1 Contact Information

The ORNL project manager will be Roger Jenkins, (865) 574-4871.
The ORNL technical lead will be Amy Dindal, (865) 574-4863.
The ORNL project statistician will be Chuck Bayne, (865) 574-3134.
The ES&H Coordinator will be Fred Smith, (865) 574-4945.
The ORNL QAS will be Janet Wagner, (865) 576-8335.
The Environmental Protection Officer will be Kim Jeskie, (865) 574-4947.

Emergency phone numbers will be posted at the test site.

7.2 Health and Safety Plan Enforcement

ORNL project manager, ORNL technical lead, the ES&H Coordinator, and the EPO were responsible for developing the health and safety plan. ORNL project manager will ultimately be responsible for ensuring that all verification participants understand and abide by the requirements of this HASP. ORNL technical lead will oversee and direct field activities and is also responsible for ensuring compliance with this HASP.

7.3 Site Access

Site training will be provided to the vendors prior to testing. The training will include a review of this health and safety plan. Because the test will be conducted on a community college campus, there will be public access to the facility. Visitors will follow standard safety and health practices (e.g., wearing safety glasses, as necessary).

7.4 Waste Generation

The EPO will be responsible for ensuring that the chemical waste generated during the test is handled properly. All hazardous waste generated will be properly disposed of by a contract organization (Tri-S Environmental Services, Ellington, CT). The EPO and other ORNL safety personnel interviewed Tri-S prior to the verification test and are comfortable with their ability to perform this task. The technology vendors will assist with this process by providing accurate records of the waste contents and approximate concentrations.

7.5 Hazard Evaluation

The technology vendors must provide their own personal protective equipment (PPE), based on the hazards associated with the operation of their technology. Although unlikely to be necessary, visitors will be provided with PPE if warranted. The hazard information provided below was gathered from the ORNL Material Safety Data Sheet (MSDS) web page and serves as a general guideline for the hazards likely to be encountered during this field test.

Lead will be the most prevalent chemical hazard at the verification test. Exposure to lead can cause eye, skin, and gastrointestinal irritation. If inhaled, it may cause a respiratory tract irritation. The highest concentration of lead in the dust samples will be 1,500 μg, and most of the sample concentrations will be well below that level.

The second most prevalent chemical hazard at the test site will be dilute acid solutions, which are classified as corrosive. Signs/symptoms of exposure include coughing, choking, and inflammation of the upper and lower respiratory tract. Control measures include chemical safety goggles and gloves. Emergency first aid in the case of severe exposure would include moving to fresh air and flushing the exposed area with large amounts of water.

7.6 Personal Protection

PPE is appropriate to protect against known and potential health hazards encountered during routine operation of the technology systems. For this verification, Level D PPE is required. Level D provides minimal protection against chemical hazards. Level D PPE will be supplied by the individual technology vendor. It consists only as a work uniform, with gloves worn, where necessary. The only requirement for this verification test is appropriate work clothes, with no shorts or open-toed shoes. ORNL will provide visitors with PPE if necessary. If site conditions indicate that additional hazards are present, ORNL may recommend different or additional PPE to the vendors.

7.7 Physical Hazards

Physical hazards associated with field activities present a potential threat to on-site personnel. Dangers are posed by unseen obstacles, noise, and poor illumination. Injuries may result from the following:

- Accidents due to slipping, tripping, or falling
- Improper lifting techniques
- Moving or rotating equipment
- Improperly maintained equipment

Injuries resulting from physical hazards can be avoided by adopting safe work practices and by using caution when working with machinery.

7.8 Fire

The following specific actions will be taken to reduce the potential for fire during site activities:

- No smoking in the building.
- Fire extinguishers will be maintained on-site.
- All personnel will be trained on the location and operation of the portable fire extinguishers.
- All personnel will be trained on the location of the phones and the number to call the fire department.

7.9 Mechanical, Electrical, Noise Hazards

Some technology-specific hazards may be identified once the vendors set-up their equipment. Proper hazards controls (i.e., guarding or markings) or PPE (i.e., ear plugs for noise hazards) will be implemented as necessary.

Electrical cables represent a potential tripping hazards. When practical, cables will be placed in areas of low pedestrian travel. If necessary, in high pedestrian travel areas, covers will be installed over cables.

7.10 Medical Support

The community college is located in downtown Hartford. Medical help will be readily available. Prior to the test, ORNL will locate medical facilities and inform the participants of the location during the on-site training. The closest hospital appears to be less than 2 miles away (Hartford Hospital, 80 Seymour St, Hartford, CT 06115-2700, 860-545-5000).

7.11 Environmental Surveillance

The ORNL project manager and ORNL technical lead will be responsible for surveying the site before, during, and after the verification test. Appropriate personnel (e.g., ES&H Coordinator, EPO, etc.) will be contacted to assist with any health or safety concerns.

7.12 Safe Work Practices

Each vendor will provide the required training and equipment for their personnel to meet safe operating practice and procedures. The individual technology vendor and their company are ultimately responsible for the safety of their workers.

The following safe work practices will be implemented at the site for worker safety:

- Eating, drinking, chewing tobacco, and smoking will be permitted only in designated areas;
- Wash facilities will be utilized by all personnel before eating, drinking, or toilet facility use;
- PPE requirements (See Section 7.6) will be followed.

7.13 Complaints

All complaints should be filed with the ORNL technical lead. All complaints will be treated on an individual basis and investigated accordingly.

REFERENCES

[1] Code of Federal Regulations. 2001. "*Identification of Dangerous Levels of Lead*", Final Rule, 40 CFR 745.65. January.

[2] American Society for Testing and Materials. 1996. "Specification E1792-96a: Standard Specification for Wipe Sampling Materials for Lead in Surface Dust" in *ASTM Standards on Lead Hazards Associated with Buildings.* West Conshohocken, PA.

[3] Ashley, K., T.J. Wise, W. Mercado, and D.B. Parry. 2001. "Ultrasonic Extraction and Field-Portable Anodic Stripping Voltammetric Measurement of Lead in Dust Wipe Samples." *Journal of Hazardous Materials.* 83, p 41-50.

[4] Title X, the Lead-Based Paint Hazard Reduction Act of 1992.

[5] EPA (U.S. Environmental Protection Agency). 1996. "Method 3050B-1: Acid Digestion of Sediment, Sludge, and Soils." In *Test Methods for Evaluating Solid Waste: Physical/ Chemical Methods, Update II.* SW-846. U.S. Environmental Protection Agency, Washington, D.C., December.

[6] EPA (U.S. Environmental Protection Agency). 1996. "Method 6010B-1: Inductively Coupled Plasma-Atomic Emission Spectrometry." In *Test Methods for Evaluating Solid Waste: Physical/ Chemical Methods, Update II.* SW-846. U.S. Environmental Protection Agency, Washington, D.C., December.

[7] American Society for Testing and Materials. 1998. "Practice E1644: Standard Practice for Hot Plate Digestion of Dust Wipe Samples for the Determination of Lead" in *ASTM Standards on Lead Hazards Associated with Buildings.* West Conshohocken, PA.

[8] ORNL (Oak Ridge National Laboratory). 1998. *Quality Management Plan for the Environmental Technology Verification Program's Site Characterization and Monitoring Technologies Pilot.* QMP-X-98-CASD-001, Rev. 0. Oak Ridge National Laboratory, Oak Ridge, Tenn., November.

[9] Keith, L.H., G. L. Patton, D.L. Lewis and P.G. Edwards. 1996. *Chapter 1: Determining What Kinds of Samples and How Many Samples to Analyze*, pp. 19. In Principles of Environmental Sampling, Second Edition, Edited by L. H. Keith, ACS Professional Reference Book, American Chemical Society, Washington, DC.

[10] Draper, N. R., and H. Smith. 1981. *Applied Regression Analysis.* 2nd ed. John Wiley & Sons, New York.

APPENDIX A

LABORATORY STANDARD OPERATING PROCEDURES

Supplied by: DataChem (Cincinnati, Ohio)

STANDARD OPERATING PROCEDURE

FOR THE ACID DIGESTION OF SEDIMENT, SLUDGE, AND SOIL FOR ANALYSIS BY AA OR ICP SPECTROSCOPY BY EPA METHOD 3050B

1.0 SCOPE AND APPLICATION

1.1 The EPA method as written provides two separate digestion procedures, one for the preparation of sediments, sludge, and soil samples for analysis by flame atomic absorption spectrometry (FLAA) or inductively coupled plasma atomic emission spectrometry (ICP-AES) and one for the preparation of sediments, sludge, and soil samples for analysis by Graphite Furnace AA (GFAA) or inductively coupled plasma mass spectrometry (ICP-MS). The extracts from these two procedures are not interchangeable and should only be used with the analytical determinations outlined in this section. Samples prepared by using this procedure may be analyzed by ICP-AES or GFAA for all the listed metals as long as the detection limits are adequate for the required end-use of the data. Alternative determinative techniques may be used if they are scientifically valid and the QC criteria of the method, including those dealing with interferences, can be achieved. Other elements and matrices may be analyzed by this method if performance is demonstrated for the analytes of interest, in the matrices of interest, at the concentration levels of interest. The recommended determinative techniques for each element are listed below:

FLAA or ICP-AES		GFAA or ICP-MS
Aluminum	Magnesium	Arsenic
Antimony	Manganese	Beryllium
Barium	Molybdenum	Cadmium
Beryllium	Nickel	Chromium
Cadmium	Potassium	Cobalt
Calcium	Silver	Iron
Chromium	Sodium	Lead
Cobalt	Thallium	Molybdenum
Copper	Vanadium	Selenium
Iron	Zinc	Thallium
Lead		

1.2 This method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become "environmentally available." By design, elements bound in silicate structures are not normally dissolved by this procedure, as they are not usually mobile in the environment.

2.0 SUMMARY OF METHOD

2.1 For the digestion of samples, a representative sample is digested with repeated additions of nitric acid (HNO_3) and hydrogen peroxide (H_2O_2).

2.2 For ICP-AES or FLAA analyses, hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed. In an optional step to increase the solubility of some metals, this digestate is filtered and the filter paper and residues are rinsed, first with hot HCl and then hot reagent water. Filter paper and residue are returned to the digestion flask, refluxed with additional HCl and then filtered again. The digestate is then diluted to a final volume of 100 mL.

2.3 If required, a separate sample aliquot shall be dried for a total percent solids determination.

3.0 SAFETY PRECAUTIONS

3.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data-handling sheets should also be made available to all personnel involved in the chemical analysis.

3.2 Proper precautions such as the use of safety glasses and lab coats are mandatory when dealing with these samples.

3.2.2 Additional protection given by gloves may also be indicated.

NOTE: Any gloves used must undergo prior testing to insure that no method target compounds can be leached from the gloves when contacted by acid in liquid or vapor form.

4.0 SAMPLE HANDLING AND PRESERVATION

4.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of "Test Methods for Evaluating Solid Waste Physical/Chemical Methods," SW-846 current revision. DataChem Laboratories does not participate in sample collection activities.

4.2 All glassware is washed with a non-phosphate detergent in hot water and rinsed with tap water. The glassware is then soaked in a 1:1 nitric acid bath and rinsed with tap water. Finally, the glassware is soaked in a 1:1 hydrochloric acid bath, rinsed with tap water and distilled water then hung upside down to dry on a peg board. After air-drying, all glassware is stored in cabinets to minimize contamination due to airborne particulate. Immediately prior to use, the glassware is rinsed with deionized water.

4.3 Non-aqueous samples shall be maintained at 4°C ± 2°C from immediately after sampling until just prior to digestion. Samples for this procedure have a holding time of 6 months after sampling.

4.4 Plastic or glass containers may be used to store the samples. In the determination of trace metals, sample containers have the potential of introducing positive or negative errors in the measurement by (a) contributing contaminants through leaching or surface desorption, and (b) depleting analyte concentrations through adsorption. Consequently, the collection and treatment of the samples prior to analysis requires particular attention. The following cleaning treatment sequence has been determined to be adequate in minimizing contamination in sample bottles, whether borosilicate glass, linear polyethylene,

polypropylene, or Teflon: detergent, tap water, 2% nitric acid, tap water, and Type II water.

Note: **Chromic acid should not be used to clean glassware**, especially if chromium is one of the analytes. Commercial, no-chromate products (e.g., Nochromix) may be used in place of chromic acid if a more rigorous cleaning procedure is required. (Chromic acid should also not be used with plastic bottles.)

5.0 DETECTION LIMITS

5.1 Detection limits are discussed in the appropriate analytical method.

6.0 INTERFERENCES

6.1 Sludge samples can contain diverse matrix types, each of which may present it's own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether this method is applicable to a given waste.

7.0 APPARATUS

7.1 Digestion Vessels - 250 mL.

7.2 Watch glasses.

7.3 Drying oven – able to maintain 105°C±4°C.

7.4 Thermometer – capable of measuring the range of 0-200°C.

7.5 Filter paper - Whatman No. 41 or equivalent.

7.6 Heating source – Adjustable and able to maintain a temperature of 90-95°C.

7.7 Variable pipetters (1-10 mL capacity)

7.8 50-mL screw top plastic sample containers.

7.9 Balance capable of weighing to 0.01g.

7.10 Funnel, or equivalent.

8.0 REAGENTS

8.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 ASTM Type II Water [ASTM D1193-77 (1983)]. All references to water in the method refer to ASTM Type II unless otherwise specified.

8.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine levels of impurities. If method blank is < MDL, the acid can be used.

8.4 Hydrochloric acid (concentrated), HCl. Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

8.5 Hydrogen peroxide (30%), H_2O_2. Oxidant should be analyzed to determine level of impurities.

9.0 CALIBRATIONS

9.1 Calibrations are discussed in the appropriate analytical method.

10.0 SAMPLE PREPARATION

10.1 See Section 12.0 Procedure

11.0 DIAGRAMS OR TABLES

11.1 LCS AND MS SPIKING INFORMATION

Method	Analyte	*Concentration (mg/mL)	**Soil Amount Spiked (mL)
6010A	Ag	100	0.5 mL
	Al	100	
	As	100	
	B	100	
	Ba	100	
	Be	100	
	Ca	100	
	Cd	100	
	Co	100	
	Cr	100	
	Cu	100	
	Fe	100	
	K	1000	
	Mg	100	
	Mn	100	
	Mo	100	
	Na	100	
	Ni	100	
	Pb	100	
	Sb	100	
	Se	100	
	Si	50	
	Tl	100	
	Ti	100	
	V	100	
	Zn	100	

*Spiking solution is purchased at above listed concentration from vendor.

**Target concentrations and analytes may be altered to better satisfy client project requirements.

12.0 PROCEDURE

12.1 Mix the sample thoroughly to achieve homogeneity. Weigh 0.5 to 2.0 grams ± 0.05 grams and transfer to a digestion vessel.

12.1.1 Quality control samples for each batch of up to 20 samples of the same matrix is prepared as follows:

12.1.1 Prepare a preparation blank by following all steps and reagent additions as used for the samples.

12.1.2 Weigh 0.50 grams of the solid blank material for the preparation of the LCS sample. Spike the solid blank with 0.5 mL of the appropriate spiking solution. (Some analytes may require blank correction for LCS concentration).

12.1.3 Prepare 2 replicates of a client submitted sample for a matrix spike/matrix spike duplicate pair. Spike the matrix spike pair with 0.5 mL of the appropriate spiking solution prior to the addition of any acid.

12.1.4 These samples are digested and analyzed using the same procedure as client submitted samples.

Note: All steps requiring the use of acids should be conducted under a fume hood by properly trained personnel using appropriate laboratory safety equipment.

12.2 Add 10 mL of 1:1 HNO_3, mix the slurry, and cover with a watch glass. Heat the sample to 95°C ± 5°C and reflux for 10 to 15 minutes without boiling. 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 as many times as necessary until no brown fumes are given off by the sample upon the addition of acid indicating complete oxidation. Using a ribbed watch glass, allow the solution to evaporate to 5 mL (or heat for two hours) without boiling, while maintaining a covering of solution over the bottom of the vessel.

12.3 After Step 12.2 has been completed and the sample has cooled, add 2 mL of water and 3 mL of 30% H_20_2. Cover the digestion vessel with a watch glass and return the covered beaker to the heating source 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 vessel.

12.4 Continue to add 30% H_20_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_20_2.

12.5 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 or heat at 95°C ± 5°C without boiling for two hours. Maintain a covering of solution over the bottom of the vessel at all times.

12.6 After cooling, dilute to 100 mL with water. Particulates in the digestate that may clog the nebulizer should be removed by filtration, by centrifugation, or by allowing the sample to settle.

12.6.1 Filtration - Filter through Whatman No. 41 filter paper (or equivalent) and dilute to 100 mL with water.

12.6.2 The diluted sample has an approximate acid concentration of 5.0% (v/v) HCl and 5.0% (v/v) HNO_3.

12.7 For the analysis of samples for FLAA or ICP-AES, add 10 mL concentrated HCl to the sample and cover with a watch glass. Place the sample on the heating source and reflux at 95°C ± 5°C for 15 minutes.

12.8 Filter the digestate through Whatman No. 41 filter paper (or equivalent) and collect filtrate in a 100-mL volumetric flask. Adjust to final volume if needed with ASTM Type II water. The sample is now ready for analysis by FLAA or ICP-AES.

12.9 Make a record of the sample preparation in the analyst laboratory notebook. Include the client identification, preparation procedure, determinative procedure, set and sample IDs, quality control preparations, analyst's name, and the date of preparation. Any special circumstances or notations regarding the preparation or the samples should be included if the analyst deems them necessary for the analysis.

12.10 To improve the solubility and recoveries of antimony, barium, lead, and silver the following procedure may be necessary. These steps are optional and not required on a routine basis.

12.10.1 Add 2.5 mL conc. HNO_3 and 2.5 mL conc. HCl to a 0.5 gram sample and cover with a watch glass. Place the sample on the heating source and reflux for 15 minutes.

12.10.2 Filter the digestate through Whatman No. 41 filter paper, or equivalent, and collect the filtrate in a 50-mL volumetric flask. Wash the filter paper, while still in the funnel, with no more than 5 mL of hot (≈95°C) HCl, then with 20 mL of hot (≈95°C) reagent water. Collect the washings in the same 50-mL volumetric flask.

12.10.3 Remove the filter and residue from the funnel, and place them back in the vessel. Add 5 mL of conc. HCl, place the vessel back on the heating source and heat at 95°C ± 5°C until the filter paper dissolves. Remove the vessel from the heating source and wash the cover and sides with reagent water. Filter the residue and collect the filtrate in the same 50-mL volumetric flask. Allow the filtrate to cool then dilute to volume with reagent water.

Note: High concentrations of metal salts with temperature-sensitive solubility can result in the formation of precipitates upon cooling of primary and/or secondary filtrates. If precipitation occurs in the flask upon cooling, do not dilute to volume. Add up to 10 mL of conc. HCl to dissolve the precipitate. After the precipitate dissolves, dilute to volume with reagent water and the extract is ready for analysis.

12.11 Hotblock digestion procedure.

12.11.1 Mix the sample thoroughly to achieve homogeneity. For the digestion procedure, weigh to the nearest 0.01 g and transfer to a disposable Hotblock digestion vessel.

12.11.2 Quality control samples for each batch of up to 20 samples of the same matrix is prepared as in Sections 12.1.1 through 12.1.4.

12.11.3 To each digestion vessel prepared, add 1 mL Type II water followed by 1 mL concentrated HNO_3. Cap with screw-top caps and place in Hotblock for 15 minutes at 95°C ± 5°C.

12.11.4 Carefully remove the vessels from the Hotblock and allow to cool. Add an additional 1.5 mL HNO_3, reseal with screw caps, and return to the Hotblock for 30 minutes at 95°C ± 5°C.

12.11.5 Remove the samples from the Hotblock and allow to cool. Add 2.5 mL concentrated HCl and reseal with screw caps. Return to the Hotblock and heat at 95°C ± 5°C for 30 minutes.

12.11.6 Remove the digestion vessels and allow digestates to cool. Adjust final volume to 50 mL. Tighten screw caps and gently shake samples. Filtration may be completed prior to analysis, unless Thallium is a requested analyte. (Note: Filtering samples for Thallium analysis reduces analyte concentration present in the samples and QC.) Samples may be filtered using an Acrodisk filter attached to a disposable syringe just prior to analysis.

12.11.7 Acid concentrations and sample size may be adjusted to better suit project requirements.

12.11.8 For accurate analysis and quantitation, it is important that sample acid concentrations match the acid concentration of the analytical standards. The final acid concentration of the digestates using this procedure is 5% HNO_3 and 5% HCl by volume.

13.0 CALCULATIONS

13.1 The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided.

13.2 If a percent solid is desired, a separate determination of percent solids must be performed on a homogeneous aliquot of the sample.

13.3 Additional calculations are discussed in the appropriate analytical method.

14.0 QUALITY ASSURANCE PROVISIONS

14.1 All specific quality control samples described in the analytical procedure should be followed. Refer to the appropriate SOP of the analytical procedure for detailed instructions.

14.2 For each analytical batch of samples processed, reagent blanks should be carried throughout the entire sample-preparation and analytical process at a frequency of one per analytical batch or every 20 samples, whichever is greater. These blanks will be useful in determining if samples are contaminated during the preparation process.

14.3 A matrix spike/matrix spike duplicate (MS/MSD) pair should be processed on a routine basis and whenever a new sample matrix is being processed. An MS/MSD pair is duplicate aliquots of one of the samples, spiked with known amounts of analytes (see Section 11.1), and brought through the entire sample preparation and analytical process. MS/MSD pairs should be processed with each analytical batch or every 20 samples, whichever is greater. MS/MSD samples will be used to determine precision.

14.4 A laboratory control sample (LCS) is a spiked blank sample or standard reference material of a known concentration processed on a routine basis and whenever a new sample matrix is being prepared. An LCS should be processed with each analytical batch or every 20 samples, whichever is greater. The results of the LCS should be employed to

determine the effects of the sample matrix and to determine preparation and analytical accuracy.

14.5 Limitations for the FLAA and ICP-AES optional digestion procedure. Analysts should be aware that the upper linear range for silver, barium, lead and antimony may be exceeded with some samples. If there is a reasonable possibility that this range may be exceeded, or if a sample's analytical result exceeds this upper limit, a smaller sample size should be taken through the entire procedure and re-analyzed to determine if the linear range has been exceeded. The approximate linear ranges for a 0.5-gram sample size are:

Optional Digestion Procedure Linear Range Limitation
mg/Kg

Ag	200,000		Mo	1,000,000
As	1,000,000		Ni	1,000,000
Ba	2,500		Pb	200,000
Be	1,000,000		Sb	200,000
Cd	1,000,000		Se	1,000,000
Co	1,000,000		Tl	1,000,000
Cr	1,000,000		V	1,000,000
Cu	1,000,000		Zn	1,000,000

These ranges will vary with sample matrix, molecular form, and size.

14.6 Responsibility for Inspection

14.6.1 The Section Manager, or designee, is responsible for inspecting the work performed by the analysts to verify completeness and data quality.

14.6.2 The analysts performing this procedure shall have the responsibility to inspect notebooks and worksheets for accuracy and completeness, samples for proper volume/size, labels, forms, and tags for accuracy, and equipment for proper maintenance and operation.

15.0 REPORTING RESULTS

15.1 The process of reporting results is discussed in the appropriate analytical method.

16.0 PREVENTIVE MAINTENANCE

16.1 Preventative maintenance should be performed according to equipment manufacturer's recommendations. All service and maintenance performed is to be recorded in the appropriate equipment service logbook.

17.0 REFERENCES

17.1 Rohrbough, W.G.; et al. Reagent Chemicals, American Society Specifications, 7th Ed.; American Chemical Society: Washington, D.C., 1986.

17.2 1985 Annual Book of ASTM Standard, Vol. 11.01; "Standard Specification for Reagent Water," ASTM: Philadelphia, PA, 1985; D1193-77.

17.3 "Test Methods for Evaluating Solid Waste Physical/Chemical Methods," Version 2, USEPA SW-846, December 1997.

Addendum: Preparation procedure for wipes for 6010B lead analysis

1. Place the wipe in a hotblock digestion vessel.

2. Acid addition

    2.1 Ghost wipe or equivalent.

        2.1.1 Add 2 mL of concentrated HNO_3 to the digestion vessel containing the wipe sample.

        2.1.2 Allow the reaction to subside.

        2.1.3 Loosely attach the screw cap onto the vessel.

    2.2 Other wipes, including gauze, baby wipes, etc.

        2.2.1 Add the appropriate volume of concentrated HNO_3 to the sample. (Note: Wipes larger than Ghost wipes typically require 5 mL of concentrated HNO_3 for digestion. The acid concentration may be adjusted to adequately digest the wipe material used.)

3. Heat on the hotblock for 1 hour at 95 °C.

4. Remove from the hotblock apparatus and allow to cool.

5. Adjust to the required final volume with Type II DI water.

    5.1 The final volume must allow a nitric acid concentration of 10%. (i.e., 2 mL nitric acid used for ghost wipe digestion requires a final volume adjustment to 20 mL with Type II DI water.)

STANDARD OPERATING PROCEDURE

FOR THE DETERMINATION OF TRACE METALS IN SOLUTION BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY BY EPA METHOD 6010B

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-atomic emission spectrometry (ICP-AES) determines trace elements, including metals, in solution. This method is applicable to all of the elements listed in Table 2. All matrices, excluding filtered groundwater samples, but including ground water, aqueous samples, TCLP and EP extracts, industrial and organic wastes, soil, sludge, sediment, and other solid wastes, require digestion prior to analysis. Groundwater samples that have been pre-filtered and acidified will not require acid digestion. Samples, which are not digested, must either use an internal standard or be matrix-matched with the standards.

1.2 Table 2 lists the elements for which this method is applicable. Detection limits, sensitivity, and the optimum and linear concentration ranges of the elements can vary with the wavelength, spectrometer, matrix and operating conditions. Table 2 also lists the recommended analytical wavelengths and estimated instrumental detection limits for the elements in clean aqueous matrices. The instrument detection limit data may be used to estimate instrument and method performance for other samples matrices. Elements and matrices other than those listed in Table 2 may be analyzed by this method if performance at the concentration levels of interest is demonstrated.

1.3 Users of the method should state the data quality objectives prior to analysis and must document and have on file the required initial demonstration performance data described in the following sections prior to using the method for analysis.

1.4 Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical and physical interferences described in this method.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples must be solubilized or digested using appropriate sample preparation methods. When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acidified prior to analysis.

2.2 This method describes multielemental determinations by ICP-AES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer and the intensities of the emission lines are monitored by photosensitive devices. Backgound correction is required for trace element determination. Background 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. In one mode of analysis, the position used should be as free as possible from spectral interference and should reflect the same change in background

intensity as occurs at the analyte wavelength measured. Background 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 7.0 should also be recognized and appropriate correction made; tests for their presence are described in Section 13.9. Alternatively, users may choose multivariate calibration methods. In this case, point selections for background correction are superfluous since whole spectral regions are processed.

3.0 SAFETY PRECAUTIONS

3.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data-handling sheets is also available to all laboratory personnel. The MSDS file is kept in the top drawer of the Health and Safety Officer's filing cabinet. Additional references to laboratory safety are available. They are:

1. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, revised January 1976.

2. "Prudent Practices for Handling Hazardous Chemicals in Laboratories." Committee on Hazardous Substances in the Laboratory. Assembly of Mathematical and Physical Sciences. National Research Counsel, 1987.

3.2 Proper precautions such as the use of safety glasses and lab coats are mandatory when dealing with these samples.

3.2.2 Additional protection given by gloves may also be indicated.

NOTE: Any gloves used must undergo prior testing to insure that no method target compounds can be leached from the gloves when contacted by acid in liquid or vapor form.

4.0 SAMPLE HANDLING AND PRESERVATION

4.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of "Test Methods for Evaluating Solid Waste Physical/Chemical Methods," SW-846 current revision. DataChem Laboratories does not participate in sample collection activities.

4.2 All glassware is washed with a non-phosphate detergent in hot water and rinsed with tap water. The glassware is then soaked in a 1:1 nitric acid bath and rinsed with tap water. Finally, the glassware is soaked in a 1:1 hydrochloric acid bath, rinsed with tap water and then distilled water. After air-drying, all glassware is stored in cabinets to minimize contamination due to airborne particulate. Immediately prior to use, the glassware is rinsed with deionized water.

4.3 Aqueous samples should be acidified to a pH of < 2 with HNO_4.

4.4 Nonaqueous samples shall be maintained at 4°C ± 2°C from immediately after sampling until just prior to digestion.

4.5 Sample holding times, preservation requirements, and suggested collection volumes are listed in Table 1. The volumes listed in Table 1 are adequate for ICP analysis. If the performance of any additional methods is required, a larger sample volume may be necessary. Also, if the other test methods are to be performed requiring different sample preservation, separate aliquots of the same sample must be collected and preserved appropriately.

TABLE 1

RECOMMENDED COLLECTION VOLUMES FOR METAL DETERMINATIONS

Measurement	Digestion Vol. Req.[a] (mL)	Collection Volume (mL)[b]	Preservative	Holding Time
Metals (except hexavalent chromium and mercury):				
Total Recoverable	45	250	HNO_3 to pH <2	6 months
Dissolved	45	250	Filter on site; HNO_3 to pH <2	6 months
Suspended	45	250	Filter on site	6 months
Total	45	250	HNO_3 to pH <2	6 months

[a]Solid samples must be at least 50 g and usually require no preservation other than storing at 4°C ± 2°C until digested.

[b]Either plastic or glass containers may be used.

4.6 In the determination of trace metals, sample containers have the potential of introducing positive or negative errors in the measurement by (a) contributing contaminants through leaching or surface desorption, and (b) depleting analyte concentrations through adsorption. Consequently, the collection and treatment of the samples prior to analysis requires particular attention. The following cleaning treatment sequence has been determined to be adequate in minimizing contamination in sample bottles, whether borosilicate glass, linear polyethylene, polypropylene, or Teflon: detergent, tap water, 2% nitric acid, tap water, and Type II water.

Note: **Chromic acid should not be used to clean glassware**, especially if chromium is one of the analytes. Commercial, no-chromate products (e.g., Nochromix) may be used in place of chromic acid if a more rigorous cleaning procedure is required. (Chromic acid should also not be used with plastic bottles.)

5.0 SAMPLE PREPARATION

5.1 Prior to analysis, samples must be digested using appropriate sample preparation methods. A summary of ICP sample preparation methods is listed below. Refer to the applicable SOP for complete sample preparation information.

5.1.1 **3015**: (or current revision) Describes the microwave induced digestion of aqueous samples for total recoverable or dissolved metals. This method is applicable to ground water, surface water, drinking water, and EP and TCLP extracts.

5.1.2 **3051**: (or current revision) Describes the microwave induced digestion of solid samples. This method is applicable to soils, sludges, and solid waste samples.

5.1.3 **3050B**: Describes the hotplate assisted acid digestion of solid samples. This method is applicable to soils, sludges, and solid waste samples.

5.1.4 **3010A**: Describes the hotplate assisted acid digestion of aqueous samples for total recoverable or dissolved metals. This method is applicable to ground water, surface water, drinking water, and EP and TCLP extracts.

5.1.5 **ENV-3005A**: Describes the hotplate assisted acid digestion of aqueous samples for total recoverable or dissolved metals. This method is applicable to ground water, surface water, drinking water, and EP and TCLP extracts.

6.0 DETECTION LIMITS

6.1 Method detection limits must be determined annually for the actual instrument to be used as detailed in the laboratory Standard Operating Procedure GEN-012, "Method Detection Limits". Table 2 lists the estimated method detection limits.

6.2 Instrument detection limits will be determined by the laboratory semi-annually using the procedure found in Section 13.12.

6.3 Linear dynamic range verification will be conducted semi-annually using the procedure found in Section 13.13.

TABLE 2

RECOMMENDED WAVELENGTHS AND ESTIMATED METHOD DETECTION LIMITS

Element	Wavelength[a] (nm)	Method Detection Limit[b] (µg/L)
Aluminum	308.215	7.0
Antimony	206.833	5.5
Arsenic	188.979	6.1
Barium	233.527	0.0
Beryllium	313.042	0.
Boron	182.527	20.
Cadmium	214.438	0.5
Calcium	315.887	11.2
Chromium	205.552	1.2
Cobalt	228.616	0.3
Copper	324.754	2.7
Iron	273.955	12.8
Lead	220.353	4.0
Lithium	610.364	3.4
Magnesium	279.079	21.9
Manganese	257.610	1.0
Molybdenum	202.030	1.0
Nickel	232.003	0.9
Phosphorus	177.428	30.8
Potassium	766.491	7.3
Selenium	203.985	5.4
Silicon	221.667	2.2
Silver	328.068	0.0
Sodium	589.592	17.5
Strontium	460.733	1.5
Thallium	190.800	5.3
Tin	189.933	54.0
Titanium	368.520	2.8
Vanadium	292.402	0.5
Zinc	213.856	3.4

[a]The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and can be properly corrected for any spectral interferences (see Step 6.1). In time, other elements may be added to this list.

[b]Highly dependent on operating conditions and plasma position.

7.0 INTERFERENCES

7.1 Spectral interferences are caused by: (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) stray light from the line emission of high-concentration elements.

7.1.1 Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate when alternate wavelengths are desirable due to severe spectral interference. These scans will also show whether the most appropriate estimate of background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by measured emission on only one side. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak. For multivariate methods using whole spectral regions, background scans should be included in the correction algorithm. Off-line spectral interferences are handled by including spectra on interfering species in the algorithm.

7.1.2 To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the analyst must determine and document both the overlapping and nearby spectral interference effects from all method analytes and common elements and provide for their automatic correction on all analyses. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 100 mg/L single element solutions are sufficient; however, for analytes such as iron that may be found at high concentration, a more appropriate test would be to use a concentration near the upper analytical range limit.

7.1.3 Spectral overlaps may be avoided by using an alternate wavelength or can be compensated by equations that correct for interelement contributions. Instruments that use equations for interelement correction require the interfering elements be analyzed at the same time as the element of interest. When operative and uncorrected, interferences will produce false positive determinations and be reported as analyte concentrations. More extensive information on interferant effects at various wavelengths and resolutions is available in reference wavelength tables and books. Users may apply interelement correction equations determined on their instruments with tested concentration ranges to compensate (off line or on line) for the effects of interfering elements. Some potential spectral interferences observed for the recommended wavelengths are given in Table 3. For multivariate methods using

whole spectral regions, spectral interferences are handled by including spectra of the interfering elements in the algorithm. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature are listed. The overlaps were observed with a single instrument having a working resolution of 0.035nm.

7.1.4 When using interelement correction equations, the interference may be expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/L of Al. According to Table 3, 100 mg/L of Al would yield a false signal of As equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for As equivalent to approximately 0.13mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 3. The interference effects must be evaluated for each individual instrument since the intensities will vary.

7.1.5 Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating, the entrance and exit slit widths, and by the order of dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear should be avoided when practical. Interelement correction, that constitutes a major portion of an emission signal, may not yield accurate data. Users should not forget that some samples may contain uncommon elements that could contribute spectral interferences.

7.1.6 The interference effects must be evaluated for each individual instrument whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths, the analyst is required to determine and document for each wavelength the effect from referenced interferences (Table 3) as well as any other suspected interferences that may be specific to the instrument or matrix. The analyst is encouraged to utilize a computer routine for automatic correction on all analyses.

7.1.7 Users of sequential instruments must verify the absence of spectral interferences by scanning over a range of 0.5nm centered on the wavelength of interest for several samples. The range for lead, for example, would be 220.6 to 220.1nm. This procedure must be repeated whenever a new matrix is analyzed and when a new calibration curve using different instrumental conditions is to be prepared. Samples that show an elevated background emission across the range may be background corrected by applying a correction factor equal to the emission adjacent to the line or at two points on either side of the line and interpolating between them. An alternate wavelength that does not exhibit a background shift or spectral overlap may also be used.

7.1.8 If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. The concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and divided by 10. If after the

subtraction of the calibration blank the apparent analyte concentration falls outside of this range in either a positive or negative direction, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor updated. The interference check solutions should be analyzed more than once to confirm a change has occurred. Adequate rinse time between solutions and before analysis of the calibration blank will assist in the confirmation.

7.1.9 When interelement corrections are applied, their accuracy should be verified daily, by analyzing spectral interference check solutions. If the correction factors or multivariate correction matrices tested on a daily basis are found to be within the 20% criteria for 5 consecutive days, the required verification frequency of those factors in compliance may be extended to a weekly basis. Also, if the nature of the samples analyzed is such that they do not contain concentrations of the interfering elements at ± one reporting limit from zero, daily verification is not required. All interelement spectral correction factors or multivariate correction matrices must be verified and updated every six months or when a change in instrumentation, such as in the torch, nebulizer, injector, or plasma conditions occurs. Standards solution should be inspected to ensure that there is no contamination that may be perceived as a spectral interference.

7.1.10 When interelement corrections are <u>not</u> used, verification of absence of interferences is required.

7.1.10.1 One method is to use a computer software routine for comparing the determinative data to limits files for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration, (i.e. greater than) the analyte instrument detection limit, or false negative analyte concentration, (i.e. less than the lower control limit of the calibration blank defined for a 99% confidence interval).

7.1.10.2 Another method is to analyze an Interference Check Solution(s) which contains similar concentrations of the major components of the samples (>10mg/L) on a continuing basis to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the check solution confirms an operative interference that is ≥20% of the analyte concentration, the analyte must be determined using (1) analytical and background correction wavelengths (or spectral regions) free of the interference, (2) by an alternative wavelength, or (3) by another documented test procedure.

7.2 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. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump, by using an internal standard or by using a high solids nebulizer. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, affecting aerosol flow rate and causing instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, using a high solids nebulizer or diluting the sample. Also, it has been reported that better control of the argon flow rate, especially to the nebulizer, improves instrument performance. This

may be accomplished with the use of mass flow controllers. The test in Section 13.9 will help determine if a physical interference is present.

7.3 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique, but if observed, can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte.

7.4 Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements at a concentration ten times the usual amount or at the top of the linear dynamic range. The aspiration time for this sample should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of two of the method detection limit should be noted. Until the required rinse time is established, this method suggests a rinse period of at least 60 seconds between samples and standards. If memory interference is suspected, the sample must be re-analyzed after a rinse period of sufficient length. Alternate rinse times may be established by the analyst, based upon their data quality objectives.

7.5 Users are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests. If the instrument does not display negative values, fortify the interference check solution with the elements of interest at 0.5 to 1 ml/L and measure the added standard concentration accordingly. Concentrations should be within 20% of the true spiked concentration or dilution of the samples will be necessary. In the absence of measurable analyte, over-correction could go undetected if a negative value is reported as zero.

7.6 The dashes in Table 3 indicate that no measurable interferences were observed even at higher interferent 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.

TABLE 3
EXAMPLE OF POTENTIAL INTERFERENCES
ANALYTE CONCENTRATION EQUIVALENTS ARISING FROM INTERFERENTS AT THE 100 mg/L LEVEL

Analyte	Wavelength (nm)	Interferent										
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Tl	V	Zn
Aluminum	396.153	--	--	--	--	--	--	--	--	--	--	--
Antimony	206.833	--	--	1.6	--	--	--	--	--	--	--	--
Arsenic	188.979	--	--	0.44	--	--	--	.002	--	--	--	.003
Barium	233.527	--	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	--	.24	--
Cadmium	214.438	--	--	--	--	--	--	--	--	--	--	--
Calcium	315.887	--	--	--	--	--	--	--	--	--	.001	--
Chromium	205.552	--	--	--	--	--	--	--	--	--	--	--
Cobalt	228.616	--	--	.009	--	--	--	--	.008	--	--	--
Copper	324.754	--	--	--	--	--	--	--	--	--	--	--
Iron	273.955	--	--	--	--	--	.009	.02	.008	--	1.7	--
Lead	220.353	--	--	--	--	--	--	.006	--	--	--	--
Magnesium	279.079	--	--	--	--	--	--	--	--	--	--	--
Manganese	257.610	--	--	--	--	--	--	--	--	--	--	--
Molybdenum	202.030	--	--	--	--	--	--	--	--	--	--	--
Nickel	232.003	--	--	4.1	.01	--	--	--	--	--	.02	.01
Selenium	196.026	--	--	--	--	--	--	.01	--	--	.05	--
Sodium	589.592	--	--	--	--	--	--	--	--	--	--	--
Thallium	190.800	--	--	.03	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	--	--	--	--	--	--	--	--	--
Zinc	213.856	--	--	--	.26	.006	--	--	.71	--	--	--

Dashes indicate that no interference was observed at the interferent concentrations used to generate this table. The concentrations used are listed below:

Al	-	100 mg/L	Mg	-	100 mg/L
Ca	-	100 mg/L	Mn	-	100 mg/L
Cr	-	100 mg/L	Tl	-	100 mg/L
Cu	-	100 mg/L	V	-	100 mg/L
Fe	-	100 mg/L	Zn	-	100 mg/L

8.0 APPARATUS

8.1 Inductively coupled argon plasma emission spectrometer, ThermoJarrell Ash Model 61E or Perkin-Elmer Model 3000XL purged spectrometer :

8.1.1 Computer-controlled emission spectrometer with background correction.

8.1.2 Radio frequency generator compliant with FCC regulations.

8.1.3 ICP torch and load coil assembly.

8.1.4 Nebulizer and spray chamber.

8.1.5 Peristaltic pump.

8.1.6 Mass flow controller.

8.1.7 Autosampler

8.1.8 Water chiller (if necessary)

8.1.9 Drain assembly

8.1.10 Ventilation system

8.2 Argon gas supply - Welding grade or better.

8.3 Nitrogen gas supply - Welding grade or better.

8.4 Sample uptake tubing.

8.5 Variable and fixed volumetric pipetters. (100-1000µL, 1-10 mL)

8.6 Analytical balance capable of weighing 0.01 g.

8.7 Volumetric flasks (1 L).

8.8 Plastic screw top sample containers.

8.9 16mm x 125mm Plastic disposable culture tubes for Autosampler.

9.0 REAGENTS AND STANDARDS

9.1 Reagent or trace metal grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question, analyze the reagent for contamination. If the concentration of the contamination is less than the MDL then the reagent is acceptable for use.

9.1.1 Concentrated Nitric acid (HNO_3). DataChem Laboratories, Cincinnati currently uses Mallinkrodt reagent grade nitric acid.

9.1.2 Concentrated Hydrochloric acid (HCL). DataChem Laboratories, Cincinnati currently uses Mallinkrodt reagent grade hydrochloric acid.

9.2 ASTM Type II Water [ASTM D1193-77 (1983)]. All references to water in the method refer to ASTM Type II unless otherwise specified.

9.3 Standard stock solutions may be purchased. DataChem Laboratories, Cincinnati is currently purchasing High-Purity Standards certified 1000 ppm stock solutions. These standards are NIST traceable. The shelf-life of all stock solutions is one year from the day received. Alternatively, stock solutions may be prepared from ultra-high purity grade chemicals or metals (99.99 to 99.999% pure). All salts must be dried for 1 hour at 105°C, unless otherwise specified.

CAUTION: Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow. Concentrations are calculated based upon the weight of pure metal added, or upon the mole fraction and the weight of the metal salt added.

$$\text{Metal Concentration (ppm)} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

Metal salts

$$\text{Concentration (ppm)} = \frac{\text{weight (mg) x mole fraction}}{\text{volume (L)}}$$

9.3.1 Aluminum solution, stock, 1 mL = 100 ug Al: Dissolve 0.10 g of aluminum metal, weighed accurately to at least four significant figures, in an acid mixture of 4 mL of (1:1) HCl and 1 mL of concentrated HNO_3 in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 mL of (1:1) HCl and dilute to 1,000 mL with water.

9.3.2 Antimony solution, stock, 1 mL = 100 ug Sb: Dissolve 0.27 g $K(SbO)C_4H_4O_6$ (mole fraction Sb = 0.3749), weighed accurately to at least four significant figures, in water, add 10 mL (1:1) HCl, and dilute to 1,000 mL with water.

9.3.3 Arsenic solution, stock, 1 mL = 100 ug As: Dissolve 0.13 g of As_2O_3 (mole fraction As = 0.7574), weighed accurately to at least four significant figures, in 100 mL of water containing 0.4 g NaOH. Acidify the solution with 2 mL concentrated HNO_3 and dilute to 1,000 mL with water.

9.3.4 Barium solution, stock, 1 mL = 100 ug Ba: Dissolve 0.15 g $BaCl_2$ (mole fraction Ba = 0.6595), dried at 250°C for 2 hours, weighed accurately to at least four significant figures, in 10 mL water with 1 mL (1:1) HCl. Add 10.0 mL (1:1) HCl and dilute to 1,000 mL with water.

9.3.5 Beryllium solution, stock, 1 mL = 100 ug Be: Do not dry. Dissolve 1.97 g $BeSO_4 \cdot 4H_2O$ (mole fraction Be = 0.0509), weighed accurately to at least four

significant figures, in water, add 10.0 mL concentrated HNO_3, and dilute to 1,000 mL with water.

9.3.6 Cadmium solution, stock, 1 mL = 100 ug Cd: Dissolve 0.11 g CdO (mole fraction Cd = 0.8754), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with water.

9.3.7 Calcium solution, stock, 1 mL = 100 ug Ca: Suspend 0.25 g $CaCO_3$ (mole fraction Ca = 0.4005), dried at 180°C for 1 hour before weighing, weighed accurately to at least four significant figures, in water and dissolve cautiously with a minimum amount of (1:1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with water.

9.3.8 Chromium solution, stock, 1 mL = 100 ug Cr: Dissolve 0.19 g CrO_3 (mole fraction Cr = 0.5200), weighed accurately to at least four significant figures in water. When dissolution is complete, acidify with 10 mL concentrated HNO_3 and dilute to 1,000 mL with water.

9.3.9 Cobalt solution, stock 1 mL = 100 ug Co: Dissolve 0.100 g of cobalt metal, weighed accurately to at least four significant figures, in a minimum of (1:1) HNO_3. Add 10.0 mL (1:1) HCl and dilute to 1,000 mL with water.

9.3.10 Copper solution, stock, 1 mL = 100 ug Cu: Dissolve 0.13 g CuO (mole fraction Cu = 0.7989), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with water.

9.3.11 Iron solution, stock, 1 mL = 100 ug Fe: Dissolve 0.14 g Fe_2O_3 (mole fraction Fe = 0.6994), weighed accurately to at least four significant figures, in a warm mixture of 20 mL (1:1) HCl and 2 mL of concentrated HNO_3. Cool, add an additional 5.0 mL of concentrated HNO_3, and dilute to 1,000 mL with water.

9.3.12 Lead solution, stock, 1 mL = 100 ug Pb: Dissolve 0.16 g $Pb(NO_3)_2$ (mole fraction Pb = 0.6256), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10 mL (1:1) HNO_3 and dilute to 1,000 mL with water.

9.3.13 Lithium solution, stock, 1 mL = 100 ug Li: Dissolve 0.5324 g lithium carbonate (mole fraction Li = 0.1878), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HCl and dilute to 1,000 mL with water.

9.3.14 Magnesium solution, stock, 1 mL = 100 ug Mg: Dissolve 0.17 g MgO (mole fraction Mg = 0.6030), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL (1:1) concentrated HNO_3 and dilute to 1,000 mL with water.

9.3.15 Manganese solution, stock, 1 mL = 100 ug Mn: Dissolve 0.100 g of manganese metal, weighed accurately to at least four significant figures, in acid mixture (10 mL concentrated HCl and 1 mL concentrated HNO_3) and dilute to 1,000 mL with water.

9.3.16 Molybdenum solution, stock, 1 mL = 100 ug Mo: Dissolve 0.200 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (mole fraction Mo = 0.5772), weighed accurately to at least four significant figures, in water and dilute to 1,000 mL with water.

9.3.17 Nickel solution, stock, 1 mL = 100 ug Ni: Dissolve 0.100 g of nickel metal, weighed accurately to at least four significant figures, in 10.0 mL hot concentrated HNO_3, cool and dilute to 1,000 mL with water.

9.3.18 Phosphate solution, stock, 1 mL = 100 ug P: Dissolve 0.4393 g anhydrous KH_2PO_4 (mole fraction P = 0.2276), weighed accurately to at least four significant figures, in water. Dilute to 1,000 mL.

9.3.19 Potassium solution, stock, 1 mL = 100 ug K: Dissolve 0.19 g KCl (mole fraction K = 0.5244) dried at 110°C, weighed accurately to at least four significant figures, in water and dilute to 1,000 mL.

9.3.20 Selenium solution, stock, 1 mL = 100 ug Se: Do not dry. Dissolve 0.17 g H_2SeO_3 (mole fraction Se = 0.6123), weighed accurately to at least four significant figures, in water and dilute to 1,000 mL.

9.3.21 Silver solution, stock, 1 mL = 100 ug Ag: Dissolve 0.16 g $AgNO_3$ (mole fraction Ag = 0.6350), weighed accurately to at least four significant figures, in water and 10 mL concentrated HNO_3. Dilute to 1,000 mL with water.

9.3.22 Sodium solution, stock, 1 mL = 100 ug Na: Dissolve 0.25 g NaCl (mole fraction Na = 0.3934), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with water.

9.3.23 Strontium solution, stock, 1 mL = 100 ug Sr: Dissolve 0.2415 g of strontium nitrate $[Sr(NO_3)_2]$ (mole fraction 0.4140), weighed accurately to at least four significant figures, in a 1-liter flask containing 10 mL of concentrated HCl and 700 mL of water. Dilute to 1000 mL with water.

9.3.24 Thallium solution, stock, 1 mL = 100 ug Tl: Dissolve 0.13 g $TlNO_3$ (mole fraction T1 = 0.7672), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with water.

9.3.25 Vanadium solution, stock, 1 mL = 100 ug V: Dissolve 0.23 g NH_4O_3 (mole fraction V = 0.4356), weighed accurately to at least four significant figures, in a minimum amount of concentrated HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with water.

9.3.26 Zinc solution, stock, 1 mL = 100 ug Zn: Dissolve 0.12 g ZnO (mole fraction Zn = 0.8034), weighed accurately to at least four significant figures, in a minimum amount of dilute HNO_3. Add 10 mL concentrated HNO_3 and dilute to 1,000 mL with water.

9.4 Mixed calibration standard solutions - Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions with 50 mL of concentrated HNO_3 and 50 mL of concentrated HCL in 1000 mL volumetric flasks (see Table 4). Dilute to 1000 mL with water. Add the appropriate types and volumes of acids so that the standards are matrix matched with the sample digestates. Prior to preparing the mixed standards, each stock solution should be analyzed separately to check for possible spectral

interferences and/or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Record all standard preparation information in the working standard (WS) logbook.

Note: If the addition of silver results in an initial precipitation, add 15 mL of water and warm the flask until the solution clears. Cool and dilute to 1000 mL with water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap-water matrix for 30 days. Higher concentrations of silver require additional HCl.

TABLE 4
CALIBRATION AND ICV* STANDARD CONCENTRATIONS (µg/mL)

ELEMENT	Calibration Standard #1	Calibration Standard #2	Calibration Standard #3	Calibration Standard #4
Al	0.10	0.50	1.00	
Sb	0.10	0.50	1.00	
As	0.10	0.50	1.00	
Ba	0.10	0.50	1.00	
Be	0.10	0.50	1.00	
Cd	0.10	0.50	1.00	
Ca	0.10	0.50	1.00	
Cr	0.10	0.50	1.00	
Co	0.10	0.50	1.00	
Cu	0.10	0.50	1.00	
Fe	0.10	0.50	1.00	200.
Pb	0.10	0.50	1.00	
Li	0.10	0.50	1.00	
Mg	0.10	0.50	1.00	
Mn	0.10	0.50	1.00	
Mo	0.10	0.50	1.00	
Ni	0.10	0.50	1.00	
K	1.00	5.00	10.0	
Se	0.10	0.50	1.00	
Ag	0.10	0.50	1.00	
Na	0.10	0.50	1.00	
Sr	0.10	0.50	1.00	
Tl	0.10	0.50	1.00	
V	0.10	0.50	1.00	
Zn	0.10	0.50	1.00	

*ICV concentrations are spiked at levels similar to the calibration standards.

9.5 Two types of blanks are required. The calibration blank is used to establish and verify the calibrations. The reagent, or preparation, blank is analyzed to check for possible sample contamination. Potential sources of contamination include: the reagents used in the sample preparation, and/or contaminated equipment used in the sample preparation process.

9.5.1 The calibration blank is prepared by diluting 50 mL of concentrated HNO_3 and 50 mL of concentrated HCL to 1000 mL with water. This solution should also be used to flush the system between each standard and sample analysis. The calibration blank will also be used for all initial and continuing calibration blank determinations.

9.5.2 The reagent blank must contain all the reagents, and at the same volumes, as used in the processing of the samples. The reagent blank must be carried through the entire sample digestion procedure at the same time that the samples are prepared and contain the same acid concentration in the final solution as the sample solution used for analysis.

9.6 The initial calibration verification (ICV) check standard must be purchased, or prepared from stock solutions which are independent of those used for the preparation of the calibration standards. The acid content in the ICV should be the same as in the calibration standards and samples. The concentrations of analytes in the ICV must be different than those used for calibration, but within the linear working range of the instrument. The ICV check standard concentration is described in Table 4.

9.7 The interference check samples (ICSA and ICSAB) contain known concentrations of interferents that will provide an adequate test of the correction factors. They are analyzed to verify the validity of the inter-element correction (IEC) factors. These solutions may be purchased, or prepared by spiking a blank with the elements of interest, particularly those with known interferences at 0.5 to 1 mg/L. The acid content in these two solutions should be the same as in the calibration standards and samples.

9.8 The continuing calibration verification (CCV) check sample should be prepared in the same acid matrix as the calibration standards and samples with concentrations near the mid-range of calibration. The CCV may be prepared from the stock solutions used for the preparation of the calibration standards.

10.0 CALIBRATIONS

10.1 Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Groundwater sample, which have been prefiltered and acidified, will not need acid digestion. Samples, which are not digested, must either use an internal standard or be matrix-matched with the standards. Solubilization and digestion procedures are described in Section 5.0.

10.2 Operating conditions.

10.2.1 The analyst must follow the instructions in section 11.0, Procedure, or the manufacturer's recommended conditions, which ever is applicable. When analyzing samples in organic solvents, solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power is recommended to obtain stable operation and precise measurements. Sensitivity, instrumental detection limits, precision, linear dynamic ranges, and interference effects must be established for each individual analyte line on each particular instrument. All measurements must be within the instrument linear range where correction factors are valid. The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and

(2) maintain control data confirming instrument performance and analytical results.

10.2 Set up the instrument using proper operating parameters as discussed in section 11.0. The instrument must be allowed to become thermally stable before beginning (usually requires at least 30 minutes of operation prior to calibration).

10.2.1 Before using this procedure to analyze samples, there must be data available documenting initial demonstration of performance. The required data document the selection criteria of background correction points; analytical dynamic ranges, the applicable equations, and the upper limits of those ranges; the method and instrument detection limits; and the determination and verification of interelement correction equations or other routines for correcting spectral interferences. This data must be generated using the same instrument, operating conditions and calibration routine to be used for sample analysis. This documented data must be kept on file and available for review by the data user or auditor.

10.2.2 Specific wavelengths are listed in Table 2. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality to the program and data user. The analyst should follow the instruction provided by the instrument manufacturer unless other conditions provide similar or better performance for the task. Operating conditions for aqueous solutions usually vary from 1100 to 1200 watts forward power, 14 to 18 mm viewing height, 15 to 19 liters/min argon coolant flow, 0-6 to 1.5 L/min. argon nebulizer flow, 1 to 1.8 mL/min. sample pumping rate with a 1 minute preflush time and measurement time near 1 second per wavelength peak for sequential instruments and 10 seconds per sample for simultaneous instruments. For an axial plasma, the conditions will usually vary from 1100 to 1500 watts forward power, 15 to 19 liters/min. argon coolant flow, 0.6 to 1.5 L/min. argon nebulizer flow, 1 to 1.8 mL/min. sample pumping rate with a 1 minute preflush time and measurement time near 1 second per wavelength peak for sequential instruments and 10 seconds per sample for simultaneous instruments. Reproduction of the Cu/Mn intensity ratio at 324.754 nm and 257.610 nm respectively, by adjusting the argon aerosol flow has been recommended as a way to achieve repeatable interference correction factors.

10.2.3 The plasma operating conditions need to be optimized prior to use of the instrument. This routine is not required on a daily basis, but only when first setting up a new instrument or following a change in operating conditions. Follow the manufacturer's recommendations or the following procedure. The purpose of plasma optimization is to provide a maximum signal to background ratio for some of the least sensitive elements in the analytical array. The use of a mass flow controller to regulate the nebulizer gas flow or source optimization software greatly facilitates the procedure.

10.2.3.1 Ignite the radial plasma and select an appropriate incident RF power. Allow the instrument to become thermally stable before beginning, about 30 to 60 minutes of operation. While aspirating a 1000 µg/L solution of yttrium, follow the instrument manufacturer's instructions and adjust the aerosol carrier gas flow rate through the nebulizer so a

definitive blue emission region of the plasma extends approximately from 5 to 20 mm above the top of the coil. Record the nebulizer gas flow rate or pressure setting for future reference. The yttrium solution can also be used for coarse optical alignment of the torch by observing the overlay of the blue light over the entrance slit to the optical system.

10.2.3.2 After establishing the nebulizer gas flow rate, determine the solution uptake rate of the nebulizer in mL/min. by aspirating a known volume of calibration blank for a period of at least three minutes. Divide the volume aspirated by the time in minutes and record the uptake rate; set the peristaltic pump to deliver the rate in a steady even flow.

10.2.3.3 Profile the instrument to align it optically as it will be used during analysis. The following procedure can be used for both horizontal and vertical optimization in the radial mode, but is written for vertical. Aspirate a solution containing 10 µg/L of several selected elements. These elements can be As, Se, Tl, or Pb as the least sensitive of the elements and most needing to be optimized or others representing analytical judgement (V, Cr, Cu, Li and Mn are also used with success). Collect intensity data at the wavelength peak for each analyte at 1 mm intervals from 14 to 18 mm above the load coil. (This region of the plasma is referred to as the analytical zone.) Repeat the process using the calibration blank. Determine the net signal to blank intensity ratio for each analyte for each viewing height setting. Choose the height for viewing the plasma that provides the best net intensity ratios for the elements analyzed or the highest intensity ratio for the least sensitive element. For optimization in the axial mode, follow the instrument manufacturer's instructions.

10.2.3.4 The instrument operating condition finally selected as being optimum should provide the lowest reliable instrument detection limits and method detection limits.

10.2.3.5 If either the instrument operating conditions, such as incident power or nebulizer gas flow rate are changed, or a new torch injector type with a different orifice internal diameter is installed, the plasma and viewing height should be re-optimized.

10.2.3.6 After completing the initial optimization of operating conditions, but before analyzing samples, the laboratory must establish and initially verify an interelement spectral interference correction routine to be used during sample analysis. A general description concerning spectral interference and the analytical requirements for background correction in particular are discussed in Section 5.0. Criteria for determining an interelement spectral interference is an apparent positive or negative concentration for the analyte that falls within ± one reporting limit from zero. The upper control limit is the analyte instrument detection limit. Once established the entire routine must be periodically verified every six months. Only a portion of the correction routine must be verified more frequently or on a daily basis. Initial and periodic verification of the routine should be kept on file.

10.2.3.7 Before daily calibration and after the instrument warm-up period, the nebulizer gas flow rate must be reset to the determined optimized flow. If a mass flow controller is being used, it should be set to the recorded optimized flow rate, in order to maintain valid spectral interelement correction routines. The nebulizer gas flow rate should be the same (<2% change) from day to day.

10.2.4 For operation with organic solvents, use of the 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.

10.2.5 Sensitivity, instrumental detection limit, precision, linear dynamic range and interference effects must be established for each individual analyte line on each particular instrument. All measurements must be within the instrument linear range where the correction equations are valid.

10.2.5.1 Method detection limits must be established at least annually for all wavelengths utilized for each type of matrix commonly analyzed. The matrix used for the MDL calculation must contain analytes of known concentrations within 3 to 5 times the anticipated detection limit. The soil MDL concentration will be calculated from the water MDL data due to lack of a suitable matrix.

10.2.5.2 Determination of limits using reagent water represent a best case situation and do not represent possible matrix effects of real world samples.

10.2.5.3 If additional confirmation is desired, re-analyze the seven replicate aliquots on two more non-consecutive days and again calculate the method detection limit values for each day. An average of the three values for each analyte may provide for a more appropriate estimate. Successful analysis of samples with added analytes or using the method of standard additions can give confidence in the method detection limit values determined in reagent water.

10.2.5.4 The upper limit of the linear dynamic range must be established for each wavelength utilized by determining the signal responses from a minimum of three, and preferably five, different concentration standards across the range. One of these should be near the upper limit of the range. The ranges, which may be used for the analysis of samples, should be judged by the analyst from the resulting data. The data, calculations and rationale for the choice of range made should be documented and kept on file. The upper range limit should be an observed signal no more than 10 % below the level extrapolated from lower standards. Determined analyte concentrations that are above the upper range limit must be diluted and re-analyzed. The analyst should also be aware that if an interelement correction from an analyte above the linear range exists, a second analyte where the interelement correction has been applied may be inaccurately reported. New dynamic ranges should be determined whenever there is a significant change instrument response. For those analytes that periodically approach the upper limit, the range should be checked every six

months. For those analytes that are known interferences, and are present at or above the linear range, the analyst should ensure that the interelement correction has not been inaccurately applied.

Note: Many of the alkali and alkaline earth metals have non-linear response curves due to ionization and self-absorption effects. These curves may be used id the instrument allows; however the effective range must be checked and the second order curve fit should have a correlation coefficient of 0.995 or better. Third order fits are not acceptable. These non-linear response curves should be re-validated and re-calculated every six months. These curves are much more sensitive to changes in operating conditions than the linear lines and should be checked whenever there have been moderate equipment changes.

10.2.5.5 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.

10.3 Profile and calibrate the instrument daily, according to the instrument manufacturer's recommended procedures using the typical mixed calibration standard solutions described in Section 9.4. Flush the system with the calibration blank (Step 9.5.1) between each standard and sample. (Report the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.) The calibration curve must consist of a minimum of a blank and a standard.

10.4 For all analytes and determinations, the laboratory must analyze an ICV (Section 9.6), a calibration blank (Section 9.5.1), and a continuing calibration verification (CCV) (Section 9.8) immediately following daily calibration. A calibration blank and either a CCV or an ICV must be analyzed after every tenth sample and at the end of the sample run. Analysis of the check standard and calibration verification must verify that the instrument is within ±10% of the calibration with relative standard deviation <5% from replicate (minimum of two) integrations. If the calibration cannot be verified within the specified limits, the sample analysis must be discontinued, the cause determined and the instrument re-calibrated. All samples following the last acceptable ICV, CCV, or check standard must be re-analyzed. The analysis data of the calibration blank, check standard, and ICV or CCV must be kept on file with the sample analysis data.

10.5 Rinse the system with the calibration blank solution (Section 9..5.1) before the analysis of each sample. The rinse time will be one minute. Each laboratory may establish a reduction in this rinse time through a suitable demonstration.

10.6 The MSA should be used if an interference is suspected or a new matrix is encountered. When the method of standard additions is used, standards are added at one or more levels to portions of a prepared sample. This technique compensates for enhancement or depression of an analyte signal by a matrix. It will not correct for additive interferences, such as contamination, interelement interferences or baseline shifts. This technique is valid in the linear range when the interference effect is constant over the range, the added analyte responds the same as the endogenous analyte, and the signal is corrected for additive interferences. The simplest version of this technique is the single addition method. This procedure calls for two identical aliquots of the sample solution to be taken. To the first aliquot, a small volume of standard is added; while to the second

aliquot, a volume of acid blank is added equal to the standard addition. The sample concentration is calculated by: multiplying the intensity value for the unfortified aliquot by the volume (liters) and concentration (mg/L or mg/kg) of the standard addition to make the numerator; the difference in intensities for the fortified sample and unfortified sample is multiplied by the volume (liters) of the sample aliquot for the denominator. The quotient is the sample concentration. For more than one fortified portion of the prepared sample, linear regression analysis can be applied using the computer software program to obtain the concentration of the sample solution.

11.0 EXAMPLE OF THE ANALYTICAL PROCEDURE

11.1 **NOTE:** Inexperienced analysts should not attempt to operate the ICP without the supervision of a trained analyst. Many components of the instrument, especially the sample introduction system and torch assembly, are easily damaged. Improper use of the instrument may result in very costly repairs and extended down-time.

SUMMARY: The optical spectrometer measures element-emitted light. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic-line emission spectra are induced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the lines are monitored by photomultiplier tubes. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines during sample 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 correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical results. The possibility of additional interferences should also be investigated, and appropriate corrections made.

11.2 **Instrument Startup**. To turn the instrument on, locate the surge protector underneath the computer table, and turn it on. This surge protector turns on the computer, monitor and printer. The spectrometer and radio frequency (RF) generator should already be in **standby** mode. Thermospec^{tm} , which is a version of ICP operations software, should automatically load and display the main menu bar. If an error message is displayed, notify the Section Manager before proceeding. Continuing without first correcting the error could result in the loss of data.

11.3 Inspect the spray chamber and baffle for any residue left from previous analyses. If residue is observed, disassemble the spray chamber and clean the components with soap and water. Perform a final rinse with deionized water. Assemble the spray chamber and install it on the instrument.

11.4 The nebulizer should be cleaned every other day. A second nebulizer may be found in the spectroscopy prep lab. This nebulizer is sitting in a 400 mL beaker, which contains a 2 % nitric acid solution. Placing the nebulizer in a dilute nitric acid solution for a few days safely and effectively leaches any built up residue, which would otherwise degrade instrument performance. The beaker is in the fume hood. Take the nebulizer presently sitting in the beaker, rinse it with deionized water and install it on the ICP. Place the other nebulizer in the acid solution and leave it there until it is needed.

11.5 The peristaltic pump tubing should also be inspected. Any tubing that has "yellowed" or become crimped should be replaced to ensure a consistent sample uptake rate.

11.6 If the autosampler is to be used, make sure that the rinse solution bottle is full and the waste bottle is empty.

11.7 Record all instrument maintenance in the maintenance log.

11.8 After insuring that the sample introduction system is in good working order, the plasma may be ignited. A macro program has been set up on the computer to ignite the plasma, set the proper analysis parameters, and to turn on the peristaltic pump.

11.9 Place the sampling probe into the calibration blank or cadmium profile solution.

11.10 Press and hold the **Ctrl** key and then press the **F3** key. This will display the macro command line.

11.11 Type **On** and then press the **Enter** key. The plasma will ignite in approximately two minutes. If an error message is displayed, notify the Section Manager before proceeding. Do not attempt manual ignition as serious damage may result if done improperly.

11.12 Check the spray chamber for an even sample aerosol flow. If a sporadic mist or no mist is observed, check for improperly connected tubing. Also, inspect the pump tubing for excessive wear, and check the pump clamp for proper tension. If the problem is not obvious, ask the Section Manager for assistance.

11.13 It is important to maintain an aerosol flow through the torch at all times. Make sure that the rinse solution bottle does not run dry. Do not allow the sample introduction system to aspirate air, except during the time it takes to move the sampling probe from one solution to the next.

11.14 Once the plasma has ignited and the sample introduction system is performing properly, allow the instrument to warm up and stabilize for thirty minutes. If the plasma does not ignite, ask the Section Manager for assistance.

11.15 Press the **SELECT** button on the printer. Press the **TYPE STYLE** button a few times until the **Draft Gothic** LED is illuminated. Press the **SELECT** button again to bring the printer back on-line.

11.16 After the instrument has stabilized it must be profiled. Profiling aligns the spectrometer optics with respect to the detector array. Alignment ensures that the correct analyte spectral line is received by each detector and that instrument sensitivity is optimized.

11.17 Place the sampling probe into the profile solution.

11.18 Highlight the **Analysis** prompt on the main menu and press the **Enter** key. This will display the method command line.

11.19 Type **the appropriate method** and press **Enter**. The method screen will be displayed, which contains an options menu in the lower right corner.

11.20 Press **F5** which will select the profile option. Then press **F3** to perform an automatic profile and **F1** to start the scan.

11.21 Once scanning is completed, a peak profile and its **peak position** will be displayed. The peak profile should be a symmetric bell shape. If a non-symmetric peak is observed, a problem with the sample introduction system should be suspected. Repeat step 11.12, and then step 11.20.

11.22 Once a proper bell-shaped peak is observed, peak profiling may be performed. The spectrometer is considered properly profiled if the peak position is within +/- 0.05 nanometers of the **profile line** position.

11.23 If the peak position is within +/- 0.05 nanometers of the profile line, proceed to step 11.24. Otherwise, adjust the vernier position and repeat step 11.20. The vernier position should be adjusted to a higher value if the peak position is negative, and should be adjusted to a lower value if the peak position is positive. The vernier position adjustment and automatic profile may have to be done several times before achieving a peak position within +/- 0.05 nanometers of the profile line. For best results, change the vernier position a little at a time.

11.24 Once an acceptable peak position is attained, press the **F9** key.

11.25 The instrument is now ready to be calibrated. Calibration can be done manually or using the autosampler. For manual calibration press the **F3** key.

11.26 Place the sample probe into the blank solution. Using the arrow keys on the lower-right corner of the key pad, highlight **STD1-Blank** and press **F1** to begin the scan.

11.27 When the analysis is completed, the results will be displayed on the screen. Press **F9** to accept and print the results. This will automatically return you to the screen where the standards are displayed.

11.28 Using the arrow keys, select the next standard to be analyzed, if applicable. Place the sample probe in the standard solution and press **F1** again to begin the scan, and then **F9** to accept and print the results.

11.29 After analyzing all of the applicable standards, press **F9** to accept the calibration and return to the method screen. Check the relative standard deviation of the standard intensity measurements. Generally, 1% RSD is observed. If significantly larger RSD's are observed problems in the sample introduction system should be suspected. Repeat step 11.12, and then recalibrate the instrument by repeating steps 11.24 through 11.27.

11.30 Once an acceptable calibration is obtained, record the standard intensities for copper and silver in the calibration log. Place the sample probe in the blank solution. If the intensities are significantly different (> +/- 15 %) than the values obtained over the last several days, report this observation to the Section Manager before proceeding to step 11.31.

11.31 The instrument is now ready for sample analysis. Sample analysis can be done manually or using the autosampler. The autosampler is recommended for large groups of samples when the matrices are not expected to be complicated. For small groups of samples or samples with suspected difficult matrices, manual analysis is recommended. Place the sample probe in the solution to be analyzed.

11.32 If the solution to be analyzed is a sample, select **F1.** If the solution is a QC standard, press **F2**.

11.33 A sample information page will be displayed on which the sample name, analyst's initials, and correction factor, if applicable, should be entered.

11.34 For all quality control standards a check table has been created which will automatically validate the QC standard data against the established control limits. Press **F2** to recall the QC check table screen. Enter the appropriate check table name opposite the **QC CHK TABLE** prompt. If necessary, consult with the Team Leader or Section Manager to obtain a listing of the check table names. Press **F9**.

11.35 Press **F1** to begin the scan. When the analysis is complete, the results will automatically be displayed on screen and printed.

11.36 The samples and QC standards must be run in the proper sequence and at the proper frequency as defined in sections 8.0 (Calibration) and 13.0 (Quality Assurance). If any QC results fall outside of the control limits for the ICV/ICB, CCV/CCB, Prep Blank, or ICSAB analyses, the run must be terminated, the problem must be corrected, and any samples not bracketed by valid QC results must be re-analyzed.

11.37 After completing all analyses for the day the instrument must be shut down. A macro has been set up to turn off the plasma, printer and the peristaltic pump. Press and hold the **Ctrl** key and then press the **F3** key. This will display the macro command line. Type **OFF** and then press the **Enter** key. The instrument will shut down in approximately 30 seconds.

11.38 Once the plasma is off press the **ESC** key to return to the Main Menu.

11.39 Use the right arrow key until the **Exit** prompt is highlighted. Use the down arrow key to highlight the **Quit to DOS** prompt. Press the **Enter** key.

11.40 When the screen goes black turn off the surge protector under the table.

11.41 Open the torch box door and release the peristaltic pump tubing clamps. This will extend the life of the tubes.

11.42 All QC results are entered in the QC database.

12.0 CALCULATIONS

12.1 Results from the instrument are reported in µg/mL (equals mg/l) of the prepared solution. To obtain the analyte concentrations in the original sample, preparation weights and dilution volumes must be taken into consideration, where applicable. Examples of proper dilution correction and units conversion are shown below.

For solid samples:

$$\text{Sample Concentration } (\mu g/g) = \frac{[(\mu g/mL) \text{ From Instrument}] * [\text{Final Volume } (mL)]}{[\text{Sample Weight } (g)]}$$

For aqueous samples:

$$\text{Sample Concentration } (\mu g/L) = \frac{[(\mu g/mL) \text{ From Instrument}] * [\text{Final Volume } (mL)]*[1000(mL/L)]}{[\text{Sample Aliquot } (mL)]}$$

For filter and wipe samples:
Sample Concentration (ug/sample) = [(µg/mL) From Instrument] * [Final Volume (mL)]

12.2 Determination of dry weight fraction.

12.2.1 Weigh 5 to 10 grams of sample onto a preweighed watch glass. Dry in oven overnight at 105 degrees Celsius. Cool in desiccater before final weighing. To determine dry weight concentration of analyte in sample, divide sample results by the dry weight fraction.

$$\% \text{ Dry Weight} = 100 * \frac{\text{Weight dry sample}}{\text{Weight of sample}}$$

12.3 Percent recovery calculation:

$$\text{Percent Recovery} = 100 * \frac{\text{Measured Value}}{\text{Target Value}}$$

Matrix Spike Percent Recovery =

$$100 * \frac{\text{Spiked Sample Value} - \text{Unspiked Sample Value}}{\text{Spike Amount}}$$

12.4 Precision calculation:

$$\text{Relative Percent difference} = 100 * \frac{|V_1 - V_2|}{(V_1 + V_2)/2}$$

where:

V_1, V_2 = found concentrations

13.0 QUALITY ASSURANCE PROVISIONS

13.1 All quality control data must be maintained and readily available for reference and for auditing purposes.

13.2 Check the instrument standardization by analyzing appropriate check standards as follows:

13.2.1 Verify the instrument calibration by analyzing a high standard (1 ppm) as a sample. Results obtained from this analysis must agree within +/- 5% of the true value for each reported analyte. If the criteria is not satisfied, terminate the analysis, correct the problem, and re-calibrate the instrument.

13.2.2 Verify the instrument calibrations using the ICV and ICB standards described in Section 9.5 and 9.6. Results obtained from the analysis of the ICV must be within +/- 10 % of the true values for all analytes. If not, terminate the analysis, correct the problem, and re-calibrate the instrument. The results of the ICB are to agree 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, terminate the analysis, correct the problem, and recalibrate.

13.2.3 Verify stability of the calibration every 10 samples and at the end of the analytical run, using the CCB (section 9.5.1) and the CCV (section 9.6) standards. The results of the CCV analyses must agree to within ±10% of the true values. If not, terminate the analysis, correct the problem, re-calibrate the instrument and re-analyze the previous 10 samples. The results of the CCB are to agree 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, terminate the analysis, correct the problem, recalibrate, and re-analyze the previous 10 samples.

13.3 Verify the interelement and background correction factors at the beginning of the analytical run or twice during every 8-hour work shift, whichever is more frequent, using the ICSA and ICSAB standards. The results obtained for all analytes in ICSAB must agree to within +/- 20 % of the true value. If not, terminate the analysis, correct the problem, re-calibrate the instrument, and re-analyze all samples since the last valid ICSAB analysis.

13.4 Employ a minimum of one reagent blank per sample digestion batch to determine if contamination or memory effects are occurring. A reagent blank is a volume of reagent water acidified with the same amounts of acid as were added to the standards and samples (Section 9.5.2).
The reagent blank control limits and corrective actions are as follows:

Control limits: Less than the highest of either:
(1) The method detection limit,
(2) Five percent of the regulatory limit for that analyte, or
(3) Five percent of the measured concentration in the sample.

Corrective Actions:
1) Check for calculation errors, instrument performance
2) Re-analyze blank and samples
3) Re-prepare and re-analyze samples
4) Flag data

13.5 Prepare and analyze one laboratory control sample (LCS) per sample batch or per new matrix type, whichever is more frequent. A solid LCS is a reference standard of similar matrix as the samples. An aqueous LCS should contain the same reagents used to prepare aqueous samples and known amounts of certified stock standards (see Table 5). The ICV solution may be used for the aqueous LCS. The results obtained for solid and aqueous LCS's must be within the laboratory specified control limits If there is insufficient data to generate control limits (minimum 20 analyses), the results must be within +/- 20 % of the true value for aqueous LCS's, and within the vendor specified control limits for solid LCS's. If any reported analytes fall outside of the control limits for the LCS, the problem

must be corrected, and the associated samples must be re-prepped and re-analyzed for those analytes.

13.6 Analyze one pair of matrix spike samples (MS and MSD) per analytical batch or per new matrix type, whichever is more frequent. A MS/MSD pair are duplicate aliquots of one of the samples, spiked with known amounts of analytes (see Table 5), and brought through the entire sample preparation and analysis process. Recoveries should be within the established control limits, when the sample result does not exceed 4x the spike added. If there is insufficient data to generate control limits (minimum 20 analyses), advisory limits of +/- 25% will be used. If any reported analytes fall outside of the control limits, a matrix effect should be suspected and a post-digestion spike should be performed as described in section 13.8.2. At the client's request, flag all samples associated with the out of control matrix spike results. The relative percent difference (RPD) of the duplicate analyses, when both the matrix spike and duplicate results are greater than or equal to 10 times the detection limit, should be less than the laboratory established control limits. If there is insufficient data to generate control limits (minimum 20 analyses), advisory limits of <20% will be used. If the duplicate analysis exceeds the control limit for any analytes, then a heterogeneous sample should be suspected. At the client's request, flag all samples associated with the out of control duplicate results.

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$$RPD = \left| [(D1-D2)/((D1 + D2)/2)] * 100 \right|$$

where:

RPD = relative percent difference
D1 = first sample value
D2 = second sample value

13.8 Dilute and re-analyze samples that exceed the linear calibration range or use an alternate, less sensitive line for which quality control data is already established.

13.9 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in steps 13.8.1 and 13.8.2, 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 value.

13.9.1 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. At the clients request, flag all samples associated with the out of control serial dilution results.

13.9.2 A post-digestion matrix spike should be performed for any analytes (exception: Ag) for which the pre-digestion matrix spike recovery did not fall within control limits, and the sample result did not exceed 4x the spike added. An analyte spike added to a portion of a prepared sample, or its dilution, when applicable, should be recovered to within 75% to 125% of the true value. The concentration of the spike addition should be within 10 times and a 100 times the detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected and flagged as such.

CAUTION: If spectral overlap is suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

13.10 For dust wipe and filter samples only, analyze a laboratory control spike sample (LCS) and duplicate (LCSDup.). Prepare the LCS/LCSDup. by aliquoting equal amounts of standard solution onto blank sample collection media. Analyze the pair with the frequency of one pair per batch of samples using the control limits established by the laboratory.

13.12 An IDL study must be performed semi-annually, or every time the instrument is adjusted in a way which may affect the IDL's, whichever is more frequent. The IDL's are determined by first creating a standard which contains all of the analytes at concentrations between 3x and 5x the instrument manufacturer's suggested IDL's. This standard is then analyzed, under normal operating conditions, seven consecutive times per day, on three non-consecutive days. Each analysis must be performed in the same manner as typical analytical samples are measured, including rinsing between analyses with the reagent blank. The standard deviations obtained from the three sets of seven analyses, for each analyte, are averaged. The IDL's are obtained by multiplying by three the average of the three standard deviations for each analyte.

13.13 On a semi-annual basis, the linear range of each analyte must be confirmed or every time the instrument is adjusted in a way which may affect the linear range, whichever is more frequent. This is accomplished by analyzing a linear range verification check standard during a routine analytical run. The results obtained for all analytes must be within +/- 5 % of the true value. Otherwise, the problem must be corrected and the standard re-analyzed. The concentrations of each analyte in this check standard are the highest concentrations which can be reported in samples or QC standards. When results are obtained which exceed these values, the sample or QC standard must be diluted and re-analyzed.

13.14 Inter-element correction (IEC) factors, which compensate for spectral interferences on analyte wavelengths, must be determined semi-annually, or every time the instrument is adjusted in a way that would affect the correction factors, whichever is more frequent. The validity of the IEC's is verified by analyzing the ICSAB solution described in section 13.3. As described in this section, the results obtained for all analytes in this sample must be within +/- 20 % of the true value. When out-of-control results are obtained, and the bracketing ICV/ICB and/or CCV/CCB results are within control limits, erroneous IEC's are the probable cause. The analysis must be terminated, the problem corrected, and any samples not bracketed by valid ICSAB results re-analyzed.

13.15 Responsibility for inspection.

13.15.1 The Section Manager, or designee, is responsible for inspecting the work performed by the analysts to verify completeness, accuracy, and compliance to the referenced methods. The analysts are responsible for maintaining complete and detailed log books. The Section Manager is responsible for reviewing, signing, and dating all completed logbook pages.

13.15.2 The analysts performing these procedures have the responsibility of inspecting the sample containers for damage and for proper sample labeling. Any non-conformance's must be documented on an **Non-conformance/Corrective Action** form as described in the standard operating procedure for

nonconformances. The Section Manager must be notified for further instructions and for client notification.

14.0 REPORTING RESULTS

14.1 Results should be reported in the units and format specified by the client or contract.

14.2 It is the responsibility of the Section Manager, or designee, to check the final report for transcription errors, proper rounding of numbers and correct number of significant figures, compliance with the method, and compliance with the requirements listed in section 14.1.

14.3 All validated reports must be signed by the reviewer.

15.0 PREVENTIVE MAINTENANCE

15.1 Preventative maintenance should be performed in accordance with the instrument manufacturer's recommendations. All service and maintenance performed is to be recorded in the appropriate equipment maintenance logbook. Refer to preventive maintenance standard operating procedure for specifics.

16.0 DIAGRAMS OR TABLES

16.1 Table 1: Recommended Sampling Volumes for Metals Analysis

16.2 Table 2: Recommended Wavelengths and Estimated Instrument Detection Limits

16.3 Table 3: Example of Potential Interferences

16.4 Table 4: Calibration and ICV Standard Concentrations

16.5 Table 5: LCS and MS Spiking Information

16.6 Table 6: Method 6010B LCS and MS control limits

16.7 Table 7: Reporting Limits

17.0 REFERENCES

17.1 Winge, R.K.; Peterson, V.J.; Fassel, V.A. *Inductively Coupled Plasma-Atomic Emission Spectroscopy: Prominent Lines* (Final Report, March 1977-February 1978); EPA-600/4-79-017, Environmental Research Laboratory, Athens, GA, March 1979; Ames Laboratory: Ames IA.

17.2 *Test Methods: Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater*; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1982; EPA-600/4-82-057.

17.3 Patel, B.K.; Raab, G.A.; et al. *Report on a Single Laboratory Evaluation of Inductively Coupled Optical Emission Method 6010*; EPA Contract No. 68-03-3050, December 1984.

17.4 *Sampling and Analysis Methods for Hazardous Waste Combustion*; U.S. Environmental Protection Agency; Air and Energy Engineering Research Laboratory, Office of Research and Development: Research triangle Park, NC, 1986; Prepared by Arthur D. Little, Inc.

17.5 Bowmand, P.W.J.M. *Line Coincidence Tables for Inductively Coupled Plasma Atomic Emission Spectrometry*, 2nd ed.; Pergamon: 1984.

17.6 Rohrbough, W.G.; et al. *Reagent Chemicals, American Chemical Society Specifications*, 7th ed.; American Chemical Society: Washington, DC, 1986.

17.7 *1985 Annual Book of ASTM Standards*, Vol. 11.01; "Standard Specification for Reagent Water;" ASTM: Philadelphia, PA, 1985; D1193-77.

17.8 “Test Methods for Evaluating Solid Waste Physical/Chemical Methods,” Version 2, USEPA SW-846, December 1997.

TABLE 5
LCS AND MS SPIKING INFORMATION

Method	Analyte	*Concentration (mg/mL)	**Soil Amount Spiked (mL)	Water Amount Spiked (mL)
6010B	Al	200	0.5 mL	0.1 mL
	Cd	5		
	Pb	50		
	V	50		
	Sb	50		
	Cr	20		
	Mn	50		
	Zn	50		
	As	200		
	Co	50		
	Ni	50		
	Ba	200		
	Cu	25		
	Se	200		
	Be	5		
	Fe	100		
	Tl	200		
	Ag	5		

*Soil LCS is purchased pre-spiked by vendor.

Spiking solution is purchased at above listed concentration from vendor.

TABLE 6
METHOD 6010B LCS AND MS/MSD RECOVERY LIMITS

Analyte	WATER			SOIL		
	% LCS Recovery	%MS/MSD Recovery	RPD Limits	% LCS Recovery	%MS/MSD Recovery	RPD Limits
Al	82-136	80-136	63	57-124	--	63
Sb	85-115	56-148	25	17-138	32-120	25
As	76-138	89-125	65	79-115	40-147	34
Ba	71-147	69-134	68	56-135	24-166	49
Be	86-111	85-128	75	78-112	11-180	25
Cd	62-152	81-125	41	68-103	47-129	69
Ca	--	--	--	73-102	--	50
Cr	84-125	70-135	82	74-109	23-162	46
Co	86-110	83-124	40	63-88	19-169	39
Cu	84-116	83-136	52	83-113	34-166	69
Fe	51-154	74-127	38	74-150	--	66
Pb	82-136	73-136	30	68-108	10-186	52
Mg	--	--	--	83-114	--	42
Mn	75-136	57-145	14	81-107	--	55
Mo	--	--	--	76-102	--	57
Ni	79-114	81-125	65	78-119	18-180	31
K	--	--	--	58-162	--	83
Se	59-163	86-126	67	73-106	23-153	25
Ag	62-145	73-126	85	84-123	24-166	96
Na	--	--	--	71-128	--	65
Sr	--	--	--	95-197	--	30
Tl	40-140	54-138	77	37-131	23-157	25
V	65-124	78-135	55	78-114	36-193	51
Zn	73-142	55-151	65	74-103	30-194	54

-- indicates that the compound is not spiked.

Note: Control limits are subject to revision annually as per laboratory requirements.

TABLE 7
METHOD 6010B REPORTING LIMITS

Analyte	WATER	SOIL
Units	**mg/L**	**mg/Kg**
Al	200.	20.
Sb	30.	3.0
As	50.	5.0
Ba	200.	10.
Be	4.0	.40
Cd	5.0	.50
Ca	200.	20.
Cr	10.	1.0
Co	50.	5.0
Cu	25.	2.5
Fe	100.	10.
Pb	15.	1.5
Mg	200.	20.
Mn	15.	1.5
Mo	50.	5.0
Ni	40.	4.0
K	200.	20.
Se	30.	3.0
Ag	10.	1.0
Na	200.	20.
Sr	50.	5.0
Tl	30.	3.0
V	50.	5.0
Zn	50.	5.0

The reporting limits listed are routinely used by the laboratory. Other reporting limits may be used to fulfill individual project requirements but must be supported by the laboratory verified method detection limit study.

APPENDIX B

ELPAT CERTIFICATE OF ANALYSIS SHEET

Supplied by: American Industrial Hygiene Association

ELPAT ROUND 36

ENVIRONMENTAL LEAD PROFICIENCY ANALYTICAL TESTING PROGRAM

CERTIFICATE OF ANALYSIS

	Sample Number	Reference Value	STD	RSD%	Lower Limit	Upper Limit
PAINT CHIPS (%)	1	1.5576	.094	6.0	1.2763	1.8389
	2	3.2953	.219	6.6	2.6385	3.9521
	3	0.0598	.006	9.4	0.0429	0.0767
	4	0.2851	.016	5.6	0.2373	0.3329
SOIL (mg/kg)	1	113.1	12.3	10.8	76.3	150
	2	141.9	12.6	8.9	104.1	179.8
	3	791.7	47.9	6.1	647.9	935.5
	4	289.5	24.6	8.5	215.7	363.3
DUST WIPES (*u*g)	1	162.3	14.3	8.8	119.2	205.3
	2	17.6	3.39	19.3	7.4	27.9
	3	418.1	30.7	7.3	326	510.3
	4	49	5.88	12.0	31.3	66.7