Municipal Water Service Extension
Sampling and Analysis Plan
Pines Area of Investigation
AOC II
Docket No. V-W-'04-C-784

ENSR International
October 19, 2004
Document Number 01776-020-124

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ACRONYMS

AOC I	Administrative Order on Consent, 2003 and as amended; Docket No. V-W-03-730
AOC II	Administrative Order on Consent, 2004; Docket No. V-W-'04-C-784
bgs	Below Ground Surface
CAS	Columbia Analytical Services
CCB	Coal Combustion By-Product
CCBk	Continuing Calibration Blank
CLP	Contract Laboratory Program
COC	Chain-of-Custody
CVAA	Cold Vapor Atomic Absorption
DQO	Data Quality Objectives
EDD	Electronic Data Deliverable
FS	Feasibility Study
GPS	Global Positioning System
HASP	Health and Safety Plan
IC	Ion Chromatography
ICBk	Initial Calibration Blank
ICP	Inductively Coupled Plasma
ICV	Initial Calibration Verification
ID	Identification
IDW	Investigation-Derived Waste
IDEM	Indiana Department of Environmental Management
LCS	Laboratory Control Sample
LIMS	Laboratory Information Management System
MDL	Method Detection Limit
MPC	Measurement Performance Criteria
MS/MSD	Matrix Spike/Matrix Spike Duplicate
NIPSCO	Northern Indiana Public Service Company
PE	Performance Evaluation
PPE	Personal Protective Equipment
PQL	Practical Quantitation Limit
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RAL	Removal Action Level
RI	Remedial Investigation
RI/FS	Remedial Investigation/Feasibility Study
RPD	Relative Percent Difference
SAP	Sampling and Analysis Plan
SOP	Standard Operating Procedure

SOW	Statement of Work
TAL	Target Analyte List
TBD	To Be Determined
USEPA	United States Environmental Protection Agency

DISCLAIMER

This document is a document prepared under a federal administrative order on consent and revised based on comments received from the U.S. Environmental Protection Agency (USEPA). This revised document has not undergone formal review by USEPA. The opinions, findings, and conclusions expressed are those of the author and not necessarily those of USEPA.

1.0 INTRODUCTION

In April 2004, the United States Environmental Protection Agency (USEPA) and the Respondents (Brown, Inc., Ddalt Corp., Bulk Transport Corp., and Northern Indiana Public Service Company (NIPSCO)), signed an Administrative Order on Consent (AOC II) (Docket No. V-W-'04-C-784) to conduct a Remedial Investigation and Feasibility Study (RI/FS) at the Pines Area of Investigation, as set forth in Exhibit I to AOC II, located in the environs of the Town of Pines, Indiana, as shown on Figure 1.

In June 2004, the Respondents submitted the first major document for the RI/FS, a Site Management Strategy document (ENSR, 2004), which outlined a preliminary conceptual model, data gaps, and the strategy for certain elements of the RI/FS. Upon approval from the USEPA, the Site Management Strategy will serve as the basis for development of the RI/FS work plans, including the Field Sampling Plan, Quality Assurance Project Plan (QAPP), and other supporting documents. The Site Management Strategy notes that excavations for the installation of municipal water service lines will start in the summer of 2004. These excavations provide an opportunity to observe the nature of the sub-surface within the excavations, to assist in identifying the locations of suspected coal combustion by-products (CCBs), where they occur within the excavations, and to collect samples to assist in the RI/FS. This work is scheduled in advance of the RI/FS work plans. This Municipal Water Service Extension Sampling and Analysis Plan (SAP) is a plan under which such sampling can be accomplished at the time the excavations are made.

1.1 Historical Background

Between 2000 and 2003, the Indiana Department of Environmental Management (IDEM) and USEPA conducted sampling of private water supply wells in a portion of the Town of Pines. In some of these samples, boron and molybdenum were detected at concentrations above Removal Action Levels (RALs) (USEPA, 1998). These elevated concentrations in groundwater are suspected by the USEPA to be derived from CCBs particularly fly ash, one type of CCB. Fly ash has been disposed at a permitted Restricted Waste Facility known as Yard 520 located within the Area of Investigation, and CCBs appear to have been used as fill in areas within the Area of Investigation outside of Yard 520. Yard 520 is operated by Brown, Inc., and most of the fly ash placed at Yard 520 was generated by combustion of coal at NIPSCO's Michigan City Generating Station.

To address the boron and molybdenum detections above the RALs, the Respondents agreed to extend the municipal water service from Michigan City to selected portions of the Town of Pines. This agreement was documented in an Administrative Order on Consent, referred to as AOC I (Docket No. V-W-03-730). Additional sampling by USEPA of other private wells indicated some concentrations near or exceeding current RALs. To address this, the Respondents voluntarily approached the USEPA to discuss extending the municipal water service to a larger area, which incorporates the

primary areas of interest, under an amendment to AOC I (April 5, 2004). The Respondents also signed AOC II to conduct an RI/FS for the Area of Investigation, as identified in the order.

Figure 1 shows the Pines Area of Investigation, including areas previously connected to municipal water (North Area and South Area) and areas to be connected to municipal water under AOC I (amended).

1.2 Objectives for the RI/FS

The objectives of the RI/FS, as outlined in the Statement of Work (SOW) attached to AOC II, are:

(a) To determine the nature and extent of constituents in the Area of Investigation and any threat to the public health, welfare, or the environment caused by releases or threatened releases of constituents related to CCBs at or from the Area of Investigation, by conducting a Remedial Investigation.

(b) To collect data necessary to adequately characterize, for the purpose of developing and evaluating effective remedial alternatives:
   i) Whether the water service extension installed pursuant to AOC I and AOC I as amended is sufficiently protective of current and reasonable future drinking water use of groundwater in accordance with Federal, State, and local requirements;
   ii) Whether there are any human health risks at the Area of Investigation associated with exposure to CCBs; and,
   iii) Whether CCB-derived constituents may be causing unacceptable risks to ecological receptors.

(c) To determine and evaluate alternatives for remedial action to prevent, mitigate, control or eliminate risks posed by any release or threatened release of constituents related to CCBs at or from the Area of Investigation, by conducting an FS.

The purpose of the RI is to obtain the data necessary to appropriately evaluate current and potential future risks to human health and ecological receptors. The risk assessments will evaluate these risks. If risks are found to be unacceptable, the FS will evaluate the merits of alternative remedial technologies to address these risks.

1.3 Proposed Sampling

As documented in the Site Management Strategy, there are reports of CCBs used as road base and/or fill in certain areas of the Area of Investigation. As part of the extension of the municipal water service, utility trenches will be excavated along many streets, including areas where CCBs are reported to have been placed. These excavations provide an opportunity to observe the nature of the subsurface in those areas and collect samples of suspected CCBs early in the RI so that information obtained can be

used throughout the RI. At the same time, the trenches allow for sampling of native soils to evaluate background conditions. Therefore, during implementation of this sampling plan, samples of native soils will also be collected from the trenches. In addition, the utility trenches will expose a large amount of the subsurface (relative to traditional investigation methods). Using these trenches to support sampling activities takes advantage of these benefits and may also reduce the need for third-party access in later phases of the RI.

This document outlines a sampling and analysis plan for the suspected CCBs and native soils. This sampling plan includes the objectives of the sampling (Section 2), project organization (Section 3), sampling design and field and analytical protocols (Section 4), documents and records (Section 5), data management activities (Section 6), and assessments and corrective action (Section 7). Supporting attachments to this SAP include ENSR Standard Operating Procedures (SOPs) (Appendix B) and example chain-of-custody documents (Appendix B).

Although this plan pre-dates the RI/FS work plans, including the Field Sampling Plan and QAPP, the sampling performed under it is designed to be consistent with procedures and protocols that will be used for the remainder of the RI/FS.

2.0 PROJECT OBJECTIVES

The sampling proposed in this sampling plan is intended to take advantage of the open trenches that will be excavated during the extension of the municipal water service. The benefits of collecting samples at this time include use of existing trenches, obtaining preliminary data that can be used to guide additional RI activities, and potentially decreasing the need for third-party access in future sampling events. The geologic information and chemical analytical data obtained during the sampling will be used in the RI and FS. Potential uses may include characterization of the physical description and chemistry of CCBs and native soils, the estimation of potential location and extent of CCBs within the municipal water service area, and use of collected data in future risk assessments.

It is not an objective of this sampling effort to develop a complete delineation of the extent of CCBs in the Area of Investigation. The locations of suspected CCBs will only be noted when they are encountered during excavations. Additional delineation of CCB extent may be performed during the RI.

As described in the preliminary conceptual model (presented in the Site Management Strategy), the native soils in the Area of Investigation are typically white to tan sands in uplands and fine-grained organic soils in the lowlands. It is expected that fill materials, including potential CCBs, will have a distinctly different appearance in the field. Although encountered materials may appear different from native soils, the identification of whether they are CCBs or other types of fill material, and what type of CCB (e.g., fly ash, bottom ash, etc.) will not be conclusively made in the field. For example, bottom slag from coal combustion (a CCB) may have an appearance in the field similar to steel-making slag (not a CCB). Therefore, the non-native materials that are encountered during implementation of this sampling plan with the visual appearance consistent with CCBs will be referred to as suspected CCBs. It is understood that the use of the term CCB with respect to sampling medium is based on visual appearance in the field and is not a conclusive determination. The sampling conducted under this plan may provide information to aid in characterizing CCBs and types of CCBs in the RI/FS.

2.1 Data Quality Objectives

Data Quality Objectives (DQOs) are qualitative and quantitative statements that specify the quality of results required to support decisions made during project activities and are based on the end uses of the data to be collected. As such, different data uses may require different levels of data quality. The design of this sampling program is based on the DQO process (USEPA, 2000), a multi-step, iterative process that ensures that the type, quantity, and quality of environmental data used in decision-making is appropriate for its intended application. This DQO process is summarized below.

DQO Step	Description
State the Problem	As documented in the Site Management Strategy, there are reports of CCBs used as road base and/or fill in certain areas of the Area of Investigation. As part of the extension of the municipal water service, utility trenches will be excavated along many streets, including areas where CCBs are reported to have been placed.
Identify the Decision	The purpose of collecting samples during the municipal water service extension work is to provide preliminary information on description, location, extent, and chemistry of CCBs in the Area of Investigation and to provide information on the chemistry of native soils in the Area of Investigation. This information will be used in the RI and FS for purposes such as characterization and risk assessment. Specific decisions to be made will be identified in the RI/FS work plans.
Identify Inputs to the Decision	Samples of suspected CCBs and native soils will be collected and analyzed for inorganics. Other information will include logging of the utility trenches with regard to the presence of native and non-native soils encountered in the field, and determination of sampling locations.
Define Study Boundaries	During extension of the municipal water service, sampling will occur from the utility trenches excavated along many streets in certain areas of the Area of Investigation.
Develop a Decision Rule	No specific decision will be made at this time. The data will be used for a variety of purposes during the RI/FS.
Specify Decision Error Limits	A formal statistical design will not be developed for this sampling. However, the data will be considered acceptable if they are collected according to this Sampling and Analysis Plan and they meet the appropriate quality objectives for field and laboratory activities.
Optimize the Study Design	Since a formal statistical design is not being utilized, the iterative process for optimizing the sample design will not be used.

2.2 Specific Objectives and Associated Tasks

The objective for this SAP is to collect samples of suspected CCBs as well as native soils present within the Pines Area of Investigation that may be encountered during municipal water service line installation activities, for characterization purposes. To accomplish this objective, the following tasks will be implemented:

- Visual logging of utility trenches with regard to the presence of suspected CCBs and native soils; and
- Collection of samples (both suspected CCBs and native soils) for laboratory analysis for Target Analyte List (TAL) metals, plus boron, molybdenum, sulfur, and silicon.

Table 1 provides the laboratory reporting levels, including practical quantitation limit (PQL) and method detection limit (MDL), for each analyte. These levels were established to be sufficiently conservative to generate data of a quality that would be usable in a human health risk assessment.

The native soil samples will be collected to provide a baseline for comparison with the suspected CCB samples, especially for parameters such as silica that do not have risk-based levels associated with them.

2.3 Project Schedule

The proposed schedule for the Municipal Water Service Extension Sampling and Analysis Program is outlined below.

Activity	Dates
Sample Collection Activities	September 2004 through July 2005
Laboratory Analysis	September 2004 through August 2005[1]
Data Validation	October 2004 through September 2005
Database Activities	October 2004 through September 2005
Data Submittal	November 2004 through October 2005
[1] Analytical turnaround time is 3 weeks	

3.0 PROJECT ORGANIZATION AND RESPONSIBILITY

The lines of authority and communication for this project are presented in the project organization chart (Figure 2). The responsibilities of key personnel are outlined below.

Respondents' Project Manager

The Project Managers for the individual Respondents will be responsible for project direction and decisions concerning technical issues and strategies, budget, and schedule.

ENSR Project Manager

The ENSR Project Manager, Lisa Bradley, will be responsible for technical, financial, and scheduling matters. The ENSR Project Manager also will be responsible for project coordination between the Respondents and USEPA as required.

ENSR Task Manager

The ENSR Task Manager, Gordon Ferguson, will have the overall responsibility for implementing the sampling activities. Specific responsibilities of the ENSR Task Manager will include, but not be limited to, the following:

- Providing personnel and equipment for site activities;
- Ensuring that ENSR's associates perform their designated duties in accordance with this SAP and Health and Safety Plan (HASP);
- Ensuring required quality assurance/quality control (QA/QC) procedures are properly implemented and documented;
- Ensuring the sampling activities are completed within the approved schedule;
- Preparing documents and reports as required under this SAP;
- Communicate any request for modifications to the approved SAP to the ENSR Project Manager; and
- Promptly notifying the ENSR Project Manager if unforeseen field conditions and/or analytical issues are encountered that affect achievement of the project DQOs.

ENSR Corporate Health and Safety Officer

The ENSR Corporate Health and Safety Officer, Joe Sanders, will coordinate and provide oversight for the health and safety issues at the site. He will develop the HASP prior to any field work within the Area of Investigation.

ENSR Project Quality Assurance Officer

The ENSR Project QA Officer, Debra McGrath, will have overall QA oversight for the project and will report to the ENSR Project Manager. Specific responsibilities include:

- Reviewing and approving QA procedures;
- Ensuring the QA audits of the various phases of the project are conducted as required by this SAP;
- Providing QA technical assistance to the field staff;
- Ensuring that data validation is conducted as required by this SAP; and,
- Reporting on the adequacy and efficiency of the QA Program to the ENSR Project Manager.

ENSR Field Technical Staff

The Field Technical Staff will be responsible for implementing sampling activities according to this SAP. Other responsibilities may include gathering and analyzing data, and preparing various task reports. The field technical staff will report directly to the ENSR Task Manager.

Laboratory Project Manager

The Laboratory Project Manager for Columbia Analytical Services (CAS) is Janice Jaeger. Ms. Jaeger will be the point of contact at the laboratory. Specific responsibilities include:

- Acting as a liaison between the laboratory and ENSR;
- Reviewing project data packages for completeness and conformance to project-specific requirements; and,
- Monitoring, reviewing, and evaluating the progress of the performance of the project in the laboratory.

4.0 FIELD SAMPLING PROCEDURES

4.1 Health and Safety

A site-specific HASP will be developed and utilized by the field sampling team to ensure sampling activities are conducted in a safe manner. The plan will address potential physical and chemical hazards associated with sampling and discuss the use of appropriate personal protective equipment (PPE).

4.2 Visual Inspection of Utility Trenches

Sampling will be conducted within municipal water service line excavations to collect analytical data on native soils as well as suspected CCBs that have been reported as being used as road base material or placed as fill in the Pines Area of Investigation. Information about potential locations of CCBs in the Area of Investigation was compiled in the Site Management Strategy (ENSR, 2004). The map in Figure 3 shows the reported distribution of these materials. The information on which the map was based is presented in Appendix A (from Appendix F of the Site Management Strategy).

As described in the preliminary conceptual model (presented in the Site Management Strategy), the native soils in the Area of Investigation are typically white to tan sands in uplands and fine-grained organic soils in the lowlands. It is expected that fill materials, including suspected CCBs, will have a distinctly different appearance in the field. Although encountered materials may appear different from native soils, the identification of whether they are CCBs or other types of fill material, and what type of CCB (e.g., fly ash, bottom ash, etc.) will not be conclusively made in the field. For example, bottom slag from coal combustion (a CCB) may have an appearance in the field similar to steel-making slag (not a CCB). Therefore, the non-native materials that are encountered during implementation of this sampling plan with a visual appearance consistent with CCBs will be referred to as suspected CCBs. It is understood that the use of the term CCB with respect to sampling medium is based on visual appearance in the field and is not a conclusive determination. The sampling conducted under this plan may provide information to aid in characterizing CCBs and types of CCBs in the RI/FS.

When suspected CCBs are encountered by the excavation contractor, ENSR field sampling personnel will be called into the field. While field personnel are en route to the site, trenching and installation of the water line will continue. The excavation contractor will leave the trench open at expected sample locations (described below). Between sample locations, the contractor will complete their work, which may include backfilling of the trenches. At the sample locations, the contractor will construct slopes that may be used to provide access into the trench. Alternatively, the excavation contractor may chose to dig test pits at sampling locations in advance of the utility trench if that is more convenient for them. Upon arrival at the site, the field samplers will inspect any visible suspected CCBs. The horizontal and vertical extent and physical appearance of the suspected CCBs exposed in the trench will be noted. At each sample location, the material encountered (both native soils and suspected CCBs) will be logged

in accordance with Indiana guidance (IDEM, 1988). In particular, it will be noted whether the suspected CCBs appear homogeneous, or whether there are visual differences, suggesting different types of CCBs. Specific aspects of the suspected CCBs and native soils to be noted include: color, grain size, sorting (consistency of grain sizes), glassy appearance (if any), and whether the material seems to be a mixture (of CCBs and/or with native soils).

4.3 Selection of Suspected CCB Sample Locations and Frequency

Suspected CCBs may be encountered at the ground surface and in the subsurface during extension of the municipal water service. However, it is unclear exactly where these may be encountered or how extensive the individual deposits might be. In addition, there are several different types of CCBs (fly ash, bottom ash, bottom slag) that will be sampled if encountered. Therefore, specific numbers and locations of samples cannot be established at this time. Instead, this plan outlines a rationale for selecting locations and frequencies of samples based on conditions encountered in the field. A summary of the estimated number of samples, including field quality control (QC) samples, is presented as Table 2.

The sample locations and depths for materials that are suspected of being CCBs will be selected as follows:

- As noted above, each utility trench excavated through suspected CCBs will be inspected, and the material encountered will be logged. In particular, it will be noted whether the materials appear homogeneous, or whether there are visual differences, suggesting different types of suspected CCBs.

- Where suspected CCBs are used as road-bed (i.e., surface filling only, less than 2 feet deep), one sample will be collected for every 500 feet of trenching or at a visible change in appearance. Each sample will be collected from the side-wall of the utility trench, from the mid-depth point of the suspected CCB horizon. Where the physical appearance of the suspected CCBs change along the length of the trench, one sample will be collected on each side of this change. If the materials are highly heterogeneous with frequent changes in appearance, only the 500-foot samples will be collected.

- Where suspected CCBs are used as fill (i.e., deeper filling, greater than 2 feet), sampling locations will be established every 100 feet of trenching. At each of these locations, one sample will be collected from each different layer or visual horizon of suspected CCBs, based on physical appearance. This may result in more than one sample at each location. If the materials are highly heterogeneous with frequent changes in appearance at any location, only two samples will be collected, one near the surface and one near the base of the trench. If there are additional horizons visible in the trench between the 100-foot sampling locations, additional samples may be collected.

- Samples will be collected from the trench side-walls from the middle of each visually distinct layer of suspected CCBs at a minimum depth of one foot below ground surface (bgs) and a maximum depth of one foot above the bottom of the trench floor. Collection of samples at least one foot below ground surface will minimize the influence of surface deposition or other fill materials on analytical results. Using a maximum sample depth of one foot above the bottom of the excavation trench will minimize potential for inclusion of extraneous material that may have eroded off of sidewalls onto the excavation floor during trenching. Samples will not be collected below the water table, if encountered.

4.4 Selection of Native Soil Sampling Locations

Samples of native soils will be collected from utility trenches at 10 locations outside the areas where suspected CCBs are encountered. These 10 locations will be selected to generally cover the extent of the area (north to south and east to west) and the expected range of variability, for example, including both uplands and lowlands, both residential and commercial areas. Two native soil samples will be collected at each location: one at a depth of approximately 1 foot bgs and one approximately one foot above the base of the trench to correspond with the depths at which suspected CCBs samples are to be collected (see Section 4.3). If the appearance of the soil at the selected sampling location is variable, additional samples may be collected. Samples will not be collected below the water table, if encountered. Table 2 presents a summary of the number of native soil samples.

4.5 Sampling Methods for Suspected CCBs and Native Soils

4.5.1 Field Measurements

Field measurements for this program will be limited to horizontal and vertical determination of sampling locations. At each sample location, the location will be surveyed using a global positioning system (GPS) hand held unit (Garmin eTrex Legend® or equivalent) with an accuracy of 3 to 5 meters (10 to 16 feet). The GPS will be calibrated according to the manufacturer's instructions prior to use and checked periodically. The coordinate system being used will be recorded. The depth interval of each sample will be measured from the ground surface.

4.5.2 Photographs

At each selected sampling location, one or more photographs will be taken with a digital camera to document the sampling location and appearance of the material in the field. Photographs will be taken of the sidewall(s) of the open trench showing the visual appearance of the material in relation to its surrounding within the trench, including the ground surface for shallow sample locations. Each photograph will include an indication of scale (e.g., sampling equipment, backhoe, or actual scale). Where appropriate, additional photographs may be taken of the area surrounding the trench if this would be helpful, for example, in documenting the sample location based on proximity to landmarks.

It is often difficult to obtain useful photographs of the insides of trenches due to the contrast in lighting between the shaded interior of the trench and the bright surroundings. Every attempt will be made to obtain useful photographs on sunny days by adjusting the location/angle of the photograph and/or adjusting the camera settings if applicable. The resulting digital photo will be reviewed in the field and re-taken, if necessary.

4.5.3 Sampling Methods

Samples will be collected in a manner such that field personnel do not descend into unsafe trench conditions. For sample depths less than approximately 4 feet, samples may be collected directly from the sidewalls either from the ground surface by leaning over the sides of the trench (for samples less than 2 ft deep), or by descending along the re-graded slopes constructed by the excavation contractor to depths no greater than 4 feet. Where samples must be collected at greater depths, the contractor's excavation equipment (e.g., backhoe, rubber-tire excavator, or track-mounted excavator) will be used to obtain a bucket of material. Because the backhoe is not able to sample with precision, the sample depth interval may be two to three feet wide. The sample interval will be measured and documented. The excavator will place the bucket of material on plastic sheeting on the ground surface a minimum distance of two to three feet from the trench wall to minimize hazards of a side wall collapse.

Sampling will be conducted in accordance with ENSR SOP No. 7110 (Surface Soil Sampling), included in Appendix B. A disposable plastic implement (e.g., spoon, spatula) will be used to scrape off any miscellaneous material on the surface of the sidewall or the pile of excavated material to limit carryover of non-target material. This plastic implement will be discarded and a new plastic spoon (or equivalent) used to transfer sample material to a disposable plastic bowl. No material directly in contact with the excavator bucket, shovel, or other tools will be included in the sample. Once sufficient volume has been placed in the bowl, the material will be homogenized with the plastic spoon (or equivalent) and transferred into the certified clean sample containers provided by the laboratory. The label of the sample container will be completed, and the sample placed in a cooler and chilled with ice pending packaging and shipment to the analytical laboratory as described in Section 4.7.2 below. Samples will be shipped under chain of custody to CAS in Rochester, NY for analysis (Section 4.8).

Sample container, preservation, and holding time requirements are shown in the following table. For this sampling event, glass containers cannot be used due to interferences with the analysis for silicon.

Parameter	Matrix	Container[1]	Preservative	Maximum Holding Time[2]
Inorganics[3]	Suspected CCBs or Native Soils	One wide-mouth 500-mL plastic	Cool 4°C	Six months to analysis; 28 days for mercury and sulfur

[1] Alternative sample containers may be provided by the laboratory under the condition that sufficient sample volume is provided and the project data quality objectives are met. If glass containers are used, they must be certified clean for boron and silicon.
[2] Sample holding time begins at time of collection.
[3] Refer to Table 1 for the list of analytes.

At each sample location, additional volume of suspected CCBs will be collected. This material will be taken directly from the plastic sheeting and placed, unhomogenized, in a clean, wide-mouth glass jar (approximately 1 to 2 liters). This sample will be retained and may be used for later visual inspection and chemical/physical analysis if needed for further characterization of suspected CCBs.

4.5.4 Equipment Decontamination

Disposable plastic implements and bowls will be used to collect the samples. No equipment decontamination is necessary.

4.6 Quality Control

Quality control will be exercised in the field as well as at the laboratory, as discussed below.

4.6.1 Field

Field duplicate and matrix spike/matrix spike duplicate (MS/MSD) samples will be analyzed to assess the quality of data resulting from this sampling and analysis program. Field duplicates will be collected by placing the sample material in a plastic bowl, homogenizing it, and dividing it between two identical containers. The samples will be labeled as two separate samples (see Section 4.7) and carried through analysis and reporting. The field duplicate will be analyzed for the same parameters as its associated field sample. Field duplicate samples will be collected at a frequency of one per 10 (or less) field samples of suspected CCBs. One field duplicate of the native soil will be collected (that is, one in 10).

MS/MSDs will be designated in the field and will be collected at a frequency of one per 20 (or less) field samples of suspected CCBs. One MS/MSD of the native soil will be collected (i.e., one in 20). Double

sample volume (or the amount requested by the laboratory) will be collected to provide sufficient material for the analysis. MS/MSDs will be identified as described in Section 4.7.

The number of field QC samples for each matrix is summarized in Table 2.

4.6.2 Laboratory

The laboratory's QC program is documented in their QA Manual. Analytical procedures are documented in writing as SOPs and each SOP includes the minimum requirements for the procedure. Internal QC checks associated with the analyses for this sampling program include, as applicable to the method:

- Blanks (preparation, calibration);
- MS/MSDs;
- Laboratory control samples (LCSs);
- Inductively coupled plasma (ICP) interference checks; and
- Serial dilutions.

A summary of the QC applicable to this program is presented in Table 3. The measurement performance criteria (MPC) utilized for this project are shown in Table 4.

4.7 Sample Custody

Sample custody will be tracked both in the field and in the laboratory, as discussed below.

4.7.1 Sample Labeling

Immediately upon collection, the adhesive sample label on each container will be completed with the unique sample identification (ID) (as described below), the time and date of sample collection, the sampler's initials, parameters to be analyzed, and preservation, if applicable. The unique sample identification will be an alphanumeric code consisting of the following elements:

- Name of location in five digits (e.g., TP002, etc.). These location names will correspond to logs of the geologic materials, as well as sample locations posted on maps.

- Single letter signifying depth of sample (A, B, C, etc. for suspected CCB/soil samples taken at increasing depth, X if this field is not being used). The actual depth measured in the field in feet will be recorded in the field records.

- Two letters signifying the sample matrix (CB for suspected CCBs, SS for surface soil, SB for subsurface soil).

- Sampling date consisting of the number corresponding to the month (2 digits), day (2 digits) and year (2 digits), for example, 061404 for samples collected on June 14, 2004.

- Letter denoting the type of sample. Codes for this field include: S – sample; D – field duplicate.

No dashes will be used to separate fields. An example sample ID for this sampling would be: TP011BCB071404D indicating a suspected CCB sample collected at location TP011 on July 14, 2004. This sample is a duplicate, and collected at depth greater than another sample at the same location.

Samples designated as MS/MSDs will be noted as such in the comments field of the COC form.

4.7.2 Field Custody

The field sampler(s) are responsible for the care and custody of the samples until they are shipped to the laboratory. As few people as possible will handle the samples.

Samples will be packaged for shipment to the laboratory under the COC procedures described in ENSR SOP No. 1007 and ENSR SOP No. 7510 (See Appendix B).

After sample containers are labeled and filled, samples will be placed in plastic ziplock bags to contain material in the event of container spillage during shipment. Containers will then be packaged in a cooler for shipment, using inert packing material (e.g., bubble wrap, rubber foam, or equivalent) to prevent breakage during shipment. A multi-form COC form will be completed (an example COC form is presented in Appendix B). The original COC will be placed in a ziplock bag that is taped to the lid inside each cooler of samples being submitted to the laboratory for analyses. The back copy of the COC will be maintained with the field records. The cooler will be locked or sealed, and custody seals placed on the outside of the cooler in such a way that the cooler cannot be opened without breaking the seals. Samples will be shipped to the laboratory via commercial overnight courier (e.g., Federal Express).

4.7.3 Laboratory Custody

Samples will be received and logged in by a designated sample custodian. Any issues concerning sample breakage, temperature exceedances, or anomalies between the COC forms and the samples will be communicated to the Laboratory Project Manager, who will be responsible for contacting the ENSR Project QA Officer within 24 hours of sample receipt. Following sample receipt, the samples will be logged in to the Laboratory Information Management System (LIMS) and stored under the appropriate conditions until taken for analysis.

Specific details of laboratory custody procedures for sample receiving, identification, sample control, and record retention are described in the laboratory SOPs.

4.8 Laboratory Analyses

Samples will be submitted to CAS for analysis of all parameters:

Columbia Analytical Services
1 Mustard Street, Suite 250
Rochester, NY 14609
(585) 288-5380

Contact: Janice Jaeger

The specific parameters to be analyzed are listed in Table 1. Analytical methodologies are presented below. Laboratory SOPs are included as Appendix C.

Analyte Group[1]	Laboratory SOP Number[2]	Equivalent USEPA Method
Mercury	MET-7471APines	SW-846 Method 7471A
Sulfur	MET-ICSPines GEN-300Pines	EPA Method 300.0
Metals	MET-3050BPines MET-6010BPines	SW-846 Method 3050B SW-846 Method 6010B

[1] See Table 1 for the specific analytes

[2] The version of the SOP that is current at the time of sample analysis will be utilized. Any modification to the approved SOPs will require USEPA notification and concurrence.

Analytical instrument calibration and preventative maintenance are summarized in Tables 5 and 6, respectively.

4.9 Investigation Derived Waste (IDW)

Excess suspected CCB material and native soils provided by the contractor on plastic sheeting will be handled by the contractor. Native soils and CCBs are non-hazardous. Therefore, disposable sampling equipment and PPE that have come into contact with sample media will be placed in plastic garbage bags and handled as trash.

5.0 DOCUMENTS AND RECORDS

5.1 Field Records

Field logbooks will provide the primary means of recording the data collecting activities performed during the sampling activities. As such, entries will be described in as much detail as possible so that persons going to the field could reconstruct a particular situation without reliance on memory.

Field logbooks will be bound field survey books or notebooks. Logbooks will be assigned to field personnel, but will be stored in the project files when not in use. Each logbook will be identified by a project-specific document number.

Entries into the logbook will contain a variety of information. At the beginning of each entry, the date, start time, weather, names of all sampling team members present, and the signature of the person making the entry will be entered. The names of visitors to the site, and the purpose of their visit, will also be recorded in the field logbook.

Measurements made and samples collected will be recorded. All entries will be made in permanent ink, signed, and dated and no erasures or obliterations will be made. If an incorrect entry is made, the information will be crossed out with a single strike mark and the correct entry will be made, signed and dated by the person making the correction. Whenever a sample is collected, or a measurement is made, a detailed description of the sampling location, which includes compass and distance measurements, or, latitude and longitude information (e.g., obtained by using GPS) will be recorded. All equipment used to make measurements will be identified, along with the date of calibration. The coordinate system that the GPS unit displays will be recorded.

Information specific to sample collection will include:

- Sample identification number;
- Time and date of sample collection;
- Sample description (color, texture, etc.);
- Depth of sample interval bgs, as measured with a steel measuring tape; and
- Location (GPS coordinates and street address).

To streamline data recording, information will be recorded on standardized forms when this approach is logical.

Descriptions of geologic materials and suspected CCBs will be logged in accordance with Indiana guidance (IDEM, 1988).

Representative photographs of sample locations will be taken with a digital camera and the camera picture frame number, date, direction facing, and subject will also be recorded in the logbook.

COC forms will be maintained as part of the field records as described in Section 4.7.2.

5.2 Laboratory Deliverables

Data deliverables will be provided within standard turnaround time (21 calendar days). The laboratory will provide at least one copy each of the hard copy report and an electronic data deliverable (EDD). The EDD will be provided in four-file EQuIS® format. The hard copy data package will be "CLP-like", i.e., consisting of all the information presented in a Contract Laboratory Program (CLP) package, including CLP-like summary forms. This information is summarized below:

- Case narrative (see description below);
- Cross reference of field sample IDs and laboratory IDs;
- Method summary;
- COC documentation;
- Sample receipt checklist;
- Dates of sample preparation and analysis;
- Description of any data qualifiers used;
- Sample results, including units;
- Sample preparation information;
- Raw data for initial and continuing calibrations;
- Run logs;
- QC summaries (equivalent to CLP forms) for MS/MSDs, method or preparation/calibration blanks, LCSs, laboratory duplicates, ICP serial dilutions, and ICP interference check samples; and
- Raw data for samples and laboratory QC samples.

The case narrative will include the client name, project name and number, date of issuance, and a discussion of any deviations from analytical strategy, technical problems, and QC failures or nonconformances. The cover page of the report will be signed by the Laboratory Project Manager.

5.3 Project Files

The project file will be the central repository for all documents which constitute evidence relevant to sampling and analysis activities as described in this SAP. The project files will include at a minimum:

- Plans;
- Field logbooks;
- Photographs;
- Drawings;
- Laboratory data deliverables;
- Progress reports, QA reports, interim project reports, etc.; and
- All custody documentation (tags, forms, airbills, etc.).

Records associated with this sampling will be retained with all the project records for the duration of AOC II and for a minimum of 10 years after its termination. USEPA, NIPSCO and Brown will be notified in writing 90 days prior to destruction of the records (per AOC II Section XIII. 44.).

6.0 DATA MANAGEMENT

6.1 Database Entry

Sampling analytical data will be transmitted from the laboratory contractor in electronic format (the EDD) and uploaded into ENSR's relational database. ENSR will upload the data into an EQuIS® database which will include GPS coordinates to allow for posting of sample locations and/or results on Pines Area of Investigation base maps. At the completion of data validation, validation qualifiers will be added to the database.

6.2 Data Validation

Validation procedures will be derived from the USEPA's *Contract Laboratory Program, National Functional Guidelines for Inorganic Data Review* (USEPA, 2002), but will be modified to reflect SW-846 procedures and the project-specific criteria defined in Section 4.6.2 of this SAP. Essentially, all technical holding times will be reviewed, instrument performance check samples will be evaluated, results of initial and continuing calibrations will be reviewed and evaluated by trained reviewers independent of the laboratory. Also, the results of all blanks, surrogate spikes, MS/MSDs, LCSs, and target compound identification and quantitation will be reviewed/evaluated by the data validator.

Ten percent of the analytical data collected for this sampling program will be validated as described above. The remaining data will be reviewed using the same USEPA guidelines and data validation protocols, but the review will be limited to holding times, the results of site-specific QC samples (field duplicates), and the following parameters as presented on the CLP-like summary forms:

- Preparation and calibration blanks;
- Initial and continuing calibration;
- MS/MSD recoveries and relative percent differences (RPDs); and
- LCS recoveries.

The overall completeness of each data package will also be evaluated by the data validator. Completeness checks will be administered on all data to determine whether the required deliverables are present.

Upon completion of the validation, a report will be prepared. This report will summarize the samples reviewed, elements reviewed, any nonconformances with the established criteria, and validation actions (including application of data qualifiers). Data qualifiers will be consistent with USEPA guidelines (2002b).

6.3 Transmittal of Data

Validated sampling analytical results will be submitted to the USEPA in accordance with the requirements of AOC II.

7.0 ASSESSMENTS AND CORRECTIVE ACTION

7.1 Performance and Systems Audits

Performance and systems audits of field and laboratory activities will be conducted. For field activities, performance audits are not applicable. A systems audit will be conducted by the Project QA Officer or designee and will consist of a review of field documentation to ensure that the records are complete and accurate, instruments were calibrated properly, sampling was conducted according to the procedures stated in this SAP, and that chain-of-custody was maintained. Audit findings will be communicated to the ENSR Project Manager, who will be responsible for taking corrective action as described below.

The performance audit for the laboratory will consist of the analysis of a single blind performance evaluation (PE) sample. The Project QA Officer will evaluate the results of the PE sample analysis and submit an evaluation of the laboratory's performance to the ENSR Project Manager.

The systems audit of the laboratory will include a review of the following areas:

- QA organization and procedures;
- Personnel training and qualifications;
- Sample log-in procedures;
- Sample storage facilities;
- Analyst technique;
- Adherence to laboratory SOPs and project QAPP;
- Compliance with QA/QC objectives;
- Instrument calibration and maintenance;
- Data recording, reduction, review, and reporting; and
- Cleanliness and housekeeping.

Preliminary results of the systems audit will be discussed with the Laboratory Manager, Laboratory Project Manager, and Laboratory QA Manager. A written report that summarizes audit findings and recommended corrective actions will be prepared by the Project QA Officer and submitted to the Laboratory Manager for response, and to the ENSR Project Manager.

7.2 Corrective Action

Corrective action is the process of identifying, recommending, approving, and implementing measures to counter unacceptable procedures or out-of-limit QC performance that can affect data quality. Corrective action can occur during field activities or laboratory analyses. Where nonconformance is identified and if the nonconformance causes project objectives not to be achieved, it may be necessary to inform all levels of project management, including USEPA.

7.2.1 Field Corrective Action

Corrective action in the field can be needed when the sample network is changed or when sampling procedures and/or field analytical procedures require modification due to unexpected conditions. The ENSR field staff in consultation with the ENSR Task Manager and ENSR Project QA Officer will recommend the corrective action. The ENSR Task Manager will approve the corrective measure, which will be implemented by the ENSR field staff. It will be the responsibility of the ENSR Task Manager and the ENSR Project Manager to ensure that corrective action has been implemented.

If the corrective action will supplement the existing sampling plan using existing and approved procedures in this SAP, corrective action approved by the ENSR Task Manager will be documented. If corrective actions result in fewer samples, alternate locations, etc., which may cause project DQOs not to be achieved, it may be necessary that all levels of project management be notified, including USEPA.

Corrective actions will be implemented and documented in the field record book. No staff member will initiate corrective action without prior communication of findings through the proper channels.

7.2.2 Laboratory Corrective Action

The need for corrective action within the laboratory may be identified by the analyst, supervisor, QA staff, or Laboratory Project Manager. The corrective action will be performed prior to the release of data from the laboratory. If the corrective action does not rectify the situation, the laboratory will contact the ENSR Project QA Officer. If the nonconformance causes project objectives not to be achieved, it may be necessary to inform all levels of project management, including USEPA.

8.0 REFERENCES

ENSR. 2004. Site Management Strategy, Pines Area of Investigation. Submitted to USEPA June 4, 2004.

IDEM. 1988. Technical Guidance Document, Volume 1 – Requirements for Describing Unconsolidated Deposits. Indiana Department of Environmental Management. Draft, Revised November 18, 1988.

USEPA. 1998. Retransmittal of the Latest Superfund Removal Action Levels. From Stephen Luftig, Office of Emergency and Remedial Response, to Regional Emergency Response Managers. U.S. Environmental Protection Agency. November 10, 1998.

USEPA. 2000. Guidance for the Data Quality Objectives Process, EPA QA/G-4. EPA/600/R-96/055. U.S. Environmental Protection Agency. August, 2000.

USEPA. 2002. USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review. U.S. Environmental Protection Agency. Final, July 2002.

9.0 TABLES

Table 1. Laboratory Reporting Levels

Constituent	CAS Number	Laboratory Detection Limits (mg/kg)	
		PQL	MDL
Aluminum	7429-90-5	10	4.98
Antimony	7440-36-0	6	1.99
Arsenic	7440-38-2	1	0.297
Barium	7440-39-3	2	0.46
Beryllium	7440-41-7	0.5	0.0217
Boron	7440-42-8	20	1.06
Cadmium	7440-43-9	1	0.291
Calcium	7440-70-2	50	5.79
Chromium (total)	7440-47-3	1	0.173
Cobalt	7440-48-4	5	0.302
Copper	7440-50-8	2	0.292
Iron	7439-89-6	10	1.19
Lead	7439-92-1	5	2.17
Magnesium	7439-95-4	50	2.04
Manganese	7439-96-5	1	0.0247
Mercury	7439-97-6	0.05	0.00321
Molybdenum	7439-97-7	2.5	0.885
Nickel	7440-02-0	4	0.292
Potassium	7440-09-7	200	2.24
Selenium	7782-49-2	20	4.84
Silicon	7631-86-9	100	2.33
Silver	7440-22-4	1	0.0809
Sodium	7440-23-5	50	31.2
Sulfur	7704-34-9	200	110
Thallium	7440-28-0	1	0.18
Vanadium	7440-62-2	5	1.29
Zinc	7440-66-6	2	0.516

Notes:
PQL - Practical Quantitation Limit. Actual PQLs may differ based on sample-specific factors.
MDL - Method Detection Limit. MDLs are determined periodically; actual MDLs may vary.
CAS - Chemical Abstracts Service.

Table 2. Summary of Sampling and Analytical Program

Matrix	Field Parameters	Analytical Parameters	Sample Nos.	Field Duplicates	Equip Blanks	MS/MSD	Total by Matrix
Suspected CCB	None	TAL metals, boron, molybdenum,silicon, and sulfur	25[1]	3[2]	0	2 pairs[2]	31
Native Soil	None	TAL metals, boron, molybdenum,silicon, and sulfur	10	1	0	1 pair	13

[1] May change based on field conditions (Section 4.3).

[2] Based on number of estimated field samples. Actual field duplicate and MS/MSD frequency will be one per 10 field samples for field duplicates and one per 20 field samples for MS/MSDs.

TAL – Target Analyte List

Table 3. Summary of Analytical Quality Control Checks

Parameter/ Method	QC Check	Frequencies	Control Limits[1]	Laboratory Corrective Actions
Metals 6010B SOP: MET 6010B -Pines	Reagent/prep blanks	One per analytical batch of 20 samples or less	No analytes above MRL	Redigest/reanalysis of entire prep batch
	MS samples	One per analytical batch of 20 samples or less.	75-125%R	Analyzed post digestion spike (PDS)
	Duplicate samples	One per analytical batch of 20 samples or less	RPD <20	Check analytical system, flag results
	LCS	One per analytical batch of 20 samples or less	80-120%R	Reanalyze the LCS for confirmation; if still out and <80% redigest and reanalyze the entire batch; if >120% redigest positive samples only
	Dilution test	One per analytical batch	Within 10% of original sample results	Flag results
	Interference check	Beginning and end of each analytical run	80-120%R	Stop run; recalibrate and rerun any samples with interfering elements present.
Mercury 7471A SOP: MET 7471A- Pines	Reagent/prep blanks	One per analytical batch of 20 samples or less	Not detected above MRL	Repreparation/reanalysis of entire batch
	MS samples	One per analytical batch of 20 samples or less	75-125%R (lab limits)	Repreparation/reanalysis of entire batch
	Duplicate samples	One per analytical batch of 20 samples or less	RPD <20	Check analytical system, flag results
	LCS	One per analytical batch of 20 samples or less	ERA Vendor listed limits.	Repreparation/reanalysis of entire batch
Sulfur EPA 300.0 SOP: GEN 300-Pines	ICBlk/CCBlk	One after the ICV and one per ten samples	Not detected above MRL	Reanalyze samples bracketed by noncompliant CCBlks Sample results less than the MRL do not require reanalysis
	MS samples	One per analytical batch of 20 samples or less	70-130%R	Check LCS, flag results
	Duplicate samples	One per analytical batch of 20 samples or less	RPD <20	Reanalyze, flag results
	LCS	One per analytical batch of 20 samples or less	90-110%R	Stop run Reanalyze LCS and any associated samples above the MRL

Parameter/ Method	QC Check	Frequencies	Control Limits[1]	Laboratory Corrective Actions

QC = Quality Control
MS/MSD = Matrix Spike/Matrix Spike Duplicate
MRL = Method Reporting Limit
%R = Percent Recovery
LCS = Laboratory Control Standard
RPD = Relative Percent Difference
IDL = Instrument Detection Limit
SOP = Standard Operating Procedure
ICP = Inductively Coupled Plasma
ICBk = Initial calibration blank
CCBk = Continuing calibration blank

Analytical batch defined as maximum of 20 field samples of a similar matrix

Table 4. Measurement Performance Criteria

Constituent	Blank	Field Duplicate %RPD	LCS % Recovery		Matrix Spike % Recovery		Duplicate % RPD[1]
			Water	Solid	Water	Solid	
Method 6010B							
Aluminum	<RL	50%	NA	C of A[2]	NA	75-125	20
Antimony	<RL	50%	NA	C of A[2]	NA	75-125	20
Arsenic	<RL	50%	NA	C of A[2]	NA	75-125	20
Barium	<RL	50%	NA	C of A[2]	NA	75-125	20
Beryllium	<RL	50%	NA	C of A[2]	NA	75-125	20
Boron	<RL	50%	NA	C of A[2]	NA	75-125	20
Cadmium	<RL	50%	NA	C of A[2]	NA	75-125	20
Calcium	<RL	50%	NA	C of A[2]	NA	75-125	20
Chromium (total)	<RL	50%	NA	C of A[2]	NA	75-125	20
Cobalt	<RL	50%	NA	C of A[2]	NA	75-125	20
Copper	<RL	50%	NA	C of A[2]	NA	75-125	20
Iron	<RL	50%	NA	C of A[2]	NA	75-125	20
Lead	<RL	50%	NA	C of A[2]	NA	75-125	20
Magnesium	<RL	50%	NA	C of A[2]	NA	75-125	20
Manganese	<RL	50%	NA	C of A[2]	NA	75-125	20
Molybdenum	<RL	50%	NA	C of A[2]	NA	75-125	20
Nickel	<RL	50%	NA	C of A[2]	NA	75-125	20
Potassium	<RL	50%	NA	C of A[2]	NA	75-125	20
Selenium	<RL	50%	NA	C of A[2]	NA	75-125	20
Silver	<RL	50%	NA	C of A[2]	NA	75-125	20
Sodium	<RL	50%	NA	C of A[2]	NA	75-125	20
Thallium	<RL	50%	NA	C of A[2]	NA	75-125	20
Vanadium	<RL	50%	NA	C of A[2]	NA	75-125	20
Zinc	<RL	50%	NA	C of A[2]	NA	75-125	20

Constituent	Blank	Field Duplicate %RPD	LCS % Recovery		Matrix Spike % Recovery		Duplicate % RPD[1]
			Water	Solid	Water	Solid	
Method 7471A							
Mercury	<RL	50%	NA	C of A[2]	NA	75-125	35
Method 300.0							
Sulfur	<RL	50%	NA	90-110%	NA	70-130	20

[1]RPD criteria applies to both aqueous and solid samples.

[2]C of A – Certicate of Analysis QC limits provided by manufacturer.

LCS – Laboratory Control Sample

NA - Not applicable

RL - Reporting Limit

PPD – Relative Percent Difference

Table 5. Summary of Calibration Frequency and Criterion Laboratory Analytical Instruments

Instrument and Method	Calibration Frequency	Calibration Standards	Acceptance Criteria
ICP Metals SW-846 Method 6010B	Initial: Daily	Initial: Per manufacturer's instructions. Minimum of one standard and calibration blank.	ICV 10% of true value
	Continuing: Every 10 samples	Mid-level of each metal	±10% true value
	Ending	Mid-level of each metal	±10% true value
CVAA Mercury SW-846 Method 7471A	Initial: Daily and/or after recalibration	Calibration 6 standards plus blank Initial Mid-Level standard	$r \geq 0.995$ ICV ±10% of true value
	Continuing: Every 10 samples	Mid-level standard	±10% of true value of original prepared standard
	Ending	Mid-level standard	±10% of original prepared standard
Sulfur by IC EPA Method 300.0	Initial: Prior to analysis	Initial Mid-Level standard Minimum 3 standards plus blank	ICV ±10% of true value $r \geq 0.995$
	Continuing: Every 10 samples	Mid-level standard	±10% of true value
	Ending	Mid-level standard	±10% of true value

CVAA – Cold Vapor Atomic Absorption

ICP – Inductively Coupled Plasma

ICV – Initial Calibration Verification

Table 6. Preventive Maintenance for Laboratory Instruments

Instrument	Parts	Activity	Frequency
ICP (SW-846 Method 6010B)	Gases O-rings Tubing	Maintenance includes but not limited to: Check cooling water system Check nebulizer Clean nebulizer and drain chamber Clean plasma torch assembly Clean filters Replace tubing	 As needed As needed As needed As needed As needed As needed
CVAA (SW-846 Method 7471A)	Tubing Lamps	Maintenance includes but not limited to: Check tubing/change tubing Check gas pressure Clean optical tubes Check filter membrane for moisture	 As needed As needed As needed As needed
IC (EPA Method 300.0)	Filters Lamps Tubing	Check eluant and regenerant levels Check waste lines Check Helium pressure Check Conductivity Release gas pressure in eluant/suppressor bottles Rinse IC pump and valves	Prior to analysis Prior to analysis Prior to analysis Prior to analysis After analysis Weekly

ICP – Inductively Coupled Plasma
CVAA – Cold Vapor Atomic Absorption
IC – Ion Chromatography

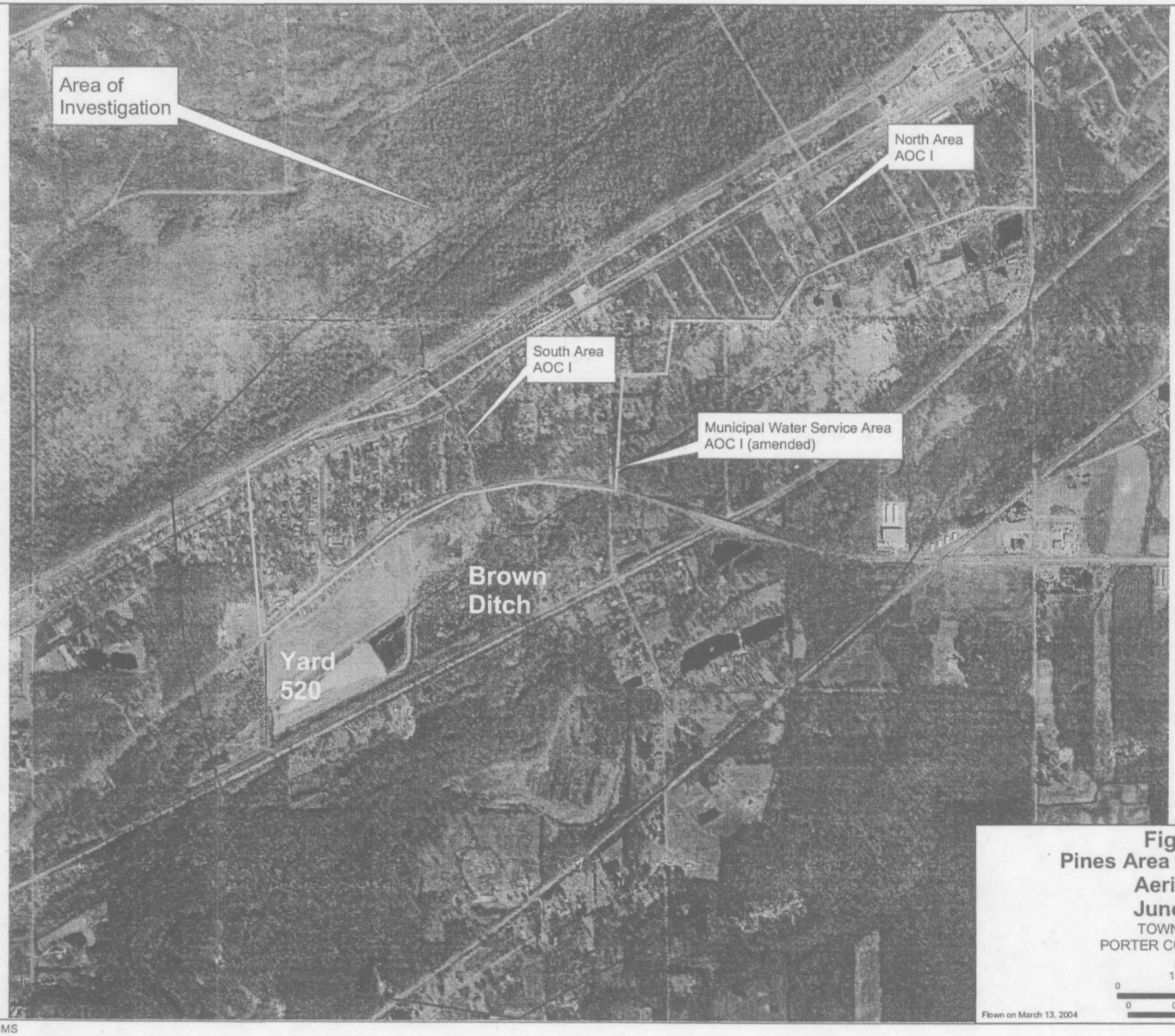


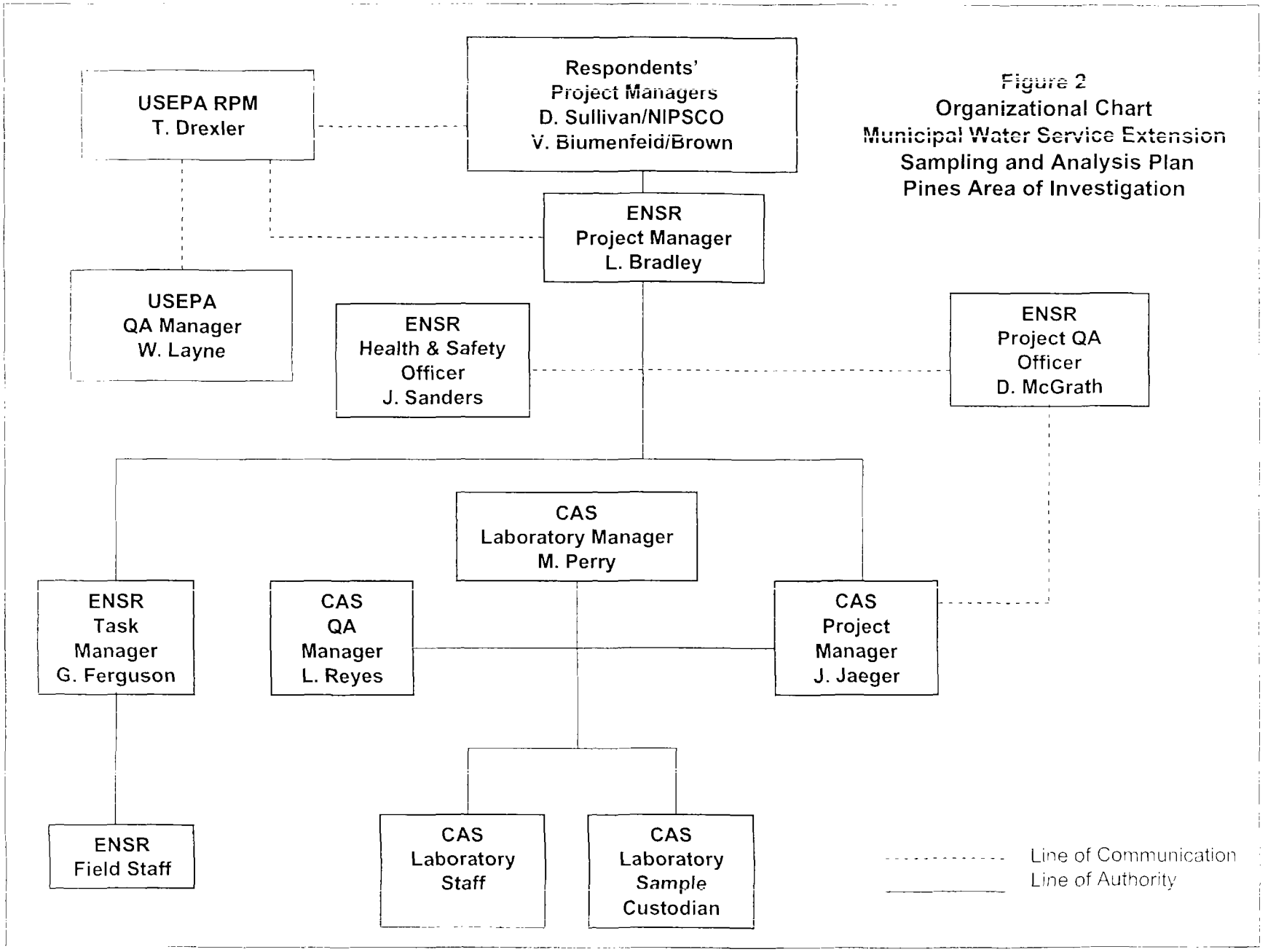
Figure 1
Pines Area of Investigation
Aerial Photo
June 4, 2004
TOWN OF PINES
PORTER COUNTY, INDIANA

Scale
1:13,000
0 750 1,500 Feet
0 0.1 0.2 Miles

N

Flown on March 13, 2004

ENSR INTERNATIONAL


USEPA RPM
T. Drexler
Respondents'
Project Managers
D. Sullivan/NIPSCO
V. Blumenfeld/Brown
Figure 2
Organizational Chart
Municipal Water Service Extension
Sampling and Analysis Plan
Pines Area of Investigation
ENSR
Project Manager
L. Bradley
USEPA
QA Manager
W. Layne
ENSR
Health & Safety
Officer
J. Sanders
ENSR
Project QA
Officer
D. McGrath
CAS
Laboratory Manager
M. Perry
ENSR
Task
Manager
G. Ferguson
CAS
QA
Manager
L. Reyes
CAS
Project
Manager
J. Jaeger
ENSR
Field Staff
CAS
Laboratory
Staff
CAS
Laboratory
Sample
Custodian
Line of Communication
Line of Authority

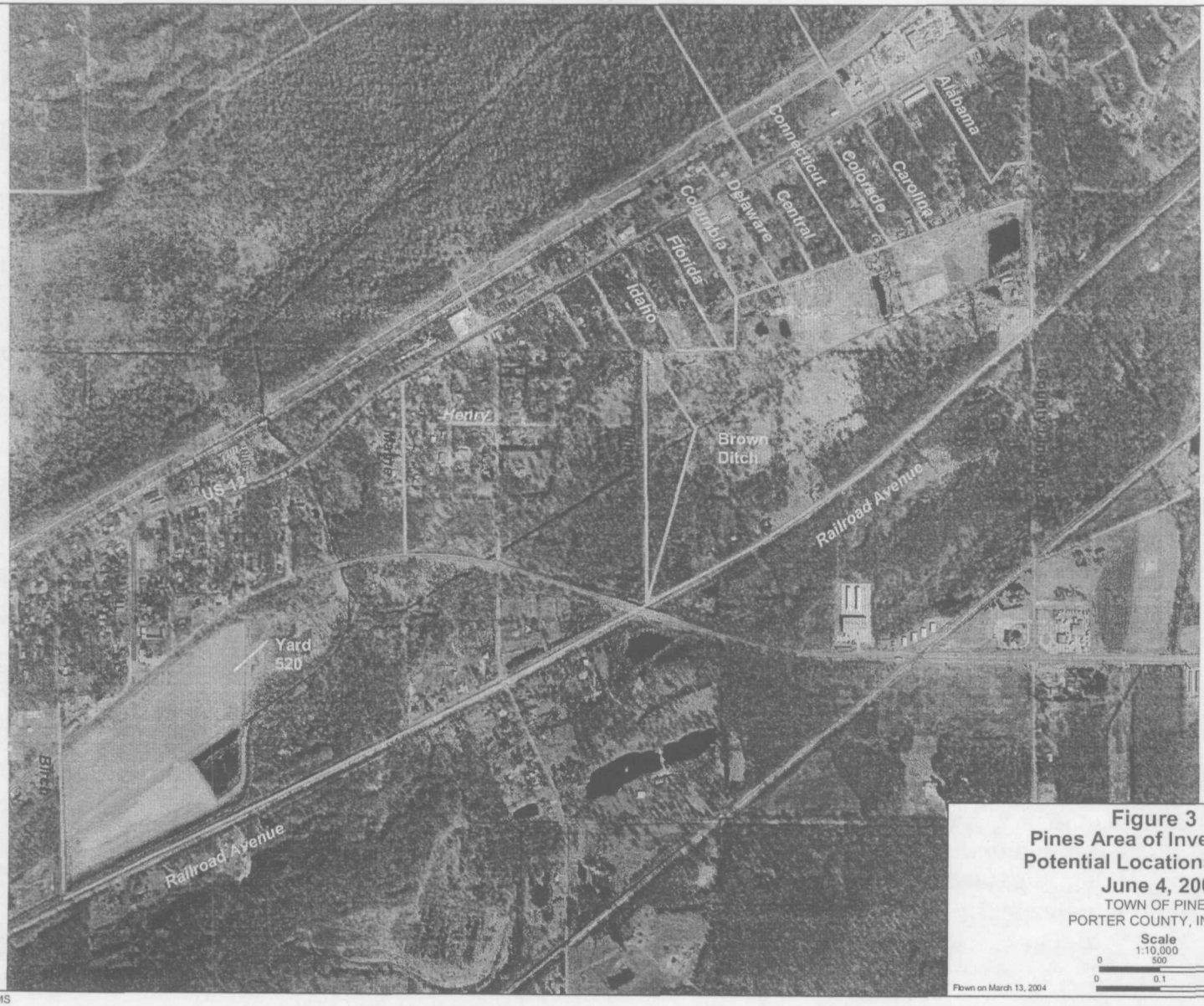


Figure 3
Pines Area of Investigation
Potential Locations of CCBs
June 4, 2004
TOWN OF PINES
PORTER COUNTY, INDIANA

Scale
1:10,000
0 500 1,000 Feet
0 0.1 0.2 Miles

N

Flown on March 13, 2004

ENSR INTERNATIONAL

APPENDIX A

Summary of Information about CCBs in Pines Area of Investigation

APPENDIX A
SUMMARY OF INFORMATION ABOUT CCBs IN PINES AREA OF INVESTIGATION

Information in this appendix has been compiled from various sources relating to possible locations of coal combustion by-products placed in the Town of Pines. All of this information is anecdotal and has not been field verified.

Reference: Combined PA/SI Report for the Town of Pines Fly Ash Dump (IDEM, July 2002)

"It appears that the coal combustion waste had been possibly used as a road base"

"...a synopsis of where the alleged fly ash was dumped throughout the town.

FERN STREET: From Alabama, east to County Line Road. This has been paved with asphalt in the last few years...

ALABAMA STREET: From Fern north to the ditch. This portion of Alabama has not been paved. The county put down some sort of stone to minimize dust. Additional information: in the 1980's, a ditch was dug on the east side of this road to allow for runoff to the ditch. This ditch runs from the east side of County Line Road west and then north.

RAILROAD AVENUE: From County Line Road west to Ardendale. This road has been paved over from County Line Road to Illinois. It remains to be mostly fly ash the rest of the way. This road also had various stone applications over the years and may have had oil sprayed on it at one time. There is still considerable fly ash remaining along the southern edge of this road.

SECOND PLACE: From Carolina Avenue west to Columbia then south on Columbia to East Johns Avenue. This has been completely paved over. Ash was put down on the south side of this road from County Line Road west to Carolina.

CONNECTICUT STREET: This is the one remaining road in town that has only ash on it. There is swamp land on both sides of this road.

ILLINOIS STREET: From East Johns Avenue south to Railroad Avenue. Some railroad ballast was put down a couple of years ago.

VARIOUS: Starting with Carolina Avenue, going west to Delaware Street all these roads were not connected through to Second Place until the fly ash was put down on Second Place. At that time

approximately the last most southerly portions of these roads have fly ash as their base prior to paving."

Reference: Unknown, but includes the information presented above, so assumed to be from IDEM. Obtained from USEPA files.

"...the south side of RR avenue was 'shored' up with fly ash after paving was done to prevent the road from caving in....the same thing was done on the south side of E. Johns Ave. between Columbia & at least Idaho St."

"Someone has said that the Town Hall and the park next to it are built completely on fly ash."

"Someone has also said that many people in town (especially on Main) had their driveways replenished with fly ash..."

"1534 Idaho – his whole back yard was filled in with the fly ash."

"Corner of Idaho & E. Johns Ave. – also supposedly had a lot of the fly ash dumped on his property."

From Additional Comments 9-10-01

"When the fly ash was first brought into the town, it was offered to the residents for their driveways, etc. The fly ash was later put on shoulders of roads in the town including the east side of the 520 cutoff."

According to sources within the Indiana State Prison where they had a coal fired heating facility, "at least during the years of 1987/1988 the waste product from this facility was, in addition to being put on the roads in the Town of Pines, was put into large trucks and hauled over to the 'Summit Farm' located on Johnson Road in LaPorte County. It was dumped in a pile and then when necessary, used as fill on the farm road."

"Just recently, the Town hall had a new septic system installed. Supposedly, the well company told a resident they had to dig down at least six feet before they cleared the flyash that had been dumped on the property when the hall was built to fill it in."

"Just learned on 6-11-02, that while this was going on, flyash was also dumped on the east side of Kintzle Ditch at Lake Park Ave. The flyash supposedly extended from Lake Park to the east but not as far as the area where Rt. 12 curves to the north at this point."

Reference: Expanded Site Inspection for Town of Pines Groundwater Plume (IDEM, July 2002)

IDEM reports taking soil samples labeled Ash 1 to Ash 3 (2001IN02S65 to 2001IN02S67). Ash 1 is described as "grey, gravely" material collected from "ash pile along Birch at US 20." Ash 2 is described as "black soil with gravel" taken at the "Fire Department parking lot" and Ash 3 is described at "light grey gravel" from 1580 Highway 520."

During an investigation of the Town of Pines, IDEM noted "piles of what appears to be ash are present along two streets." The location of these piles or the names of the streets were not identified in the report.

Reference: Construction/Operation Application for Solid Waste Management Permits for Yard 520 (Brown, Inc., November 1981)

"As of November 1, 1981 approximately 15 of the 45 acres have been covered with up to 20 feet of flyash. This has been placed in the original depression that fell off sharply at the highway's edge. Frontage here had been subdivided into lots prior to 1920, though no homes are there today."

"The Vernier China Co., 3986 W. U.S. Highway 20, carves a nine lot notch out of highway frontage on the almost 20-acre site. Vernier, whose residence is directly north across U.S. 20, has requested that their property to the south of the retail store be filled along with Brown Inc.'s operation."

"There will be no further flyash disposal within the 600' radii of the other structures across U.S. Highway 20. These areas are already finished to street level with the slopes and top surface sporting a think stand of grass."

"Any accumulation of flyash here [areas paved with asphalt] resulting from driving between the working face and exit is washed off with one of two 4,800 gallon and 3,600 gallon water trucks equipped with pressure spray bars."

Reference: EPA Water main installation photo observations (Kevin Herron, Spring 2003)

"They were taken at the south end of Florida Street. Columbia also had about 11-12 feet of fly ash, but I did not get any pictures of this area during excavation activities. I did take pictures of the fly ash that was left exposed on the surface in this area, including on the streets, which was part of the complaints at the time."

Reference: Shallow Ground-water Flow and Drainage Characteristics of the Brown Ditch Basin near the East Unit, Indiana Dunes National Lakeshore, Indiana, 1982 (U.S. Geological Survey, Report 83-4271)

"The stratigraphy shown for Section A-A' is not necessarily representative of the Calumet-Glenwood wetland because the test holes were drilled along a road constructed of coal ash."

Borings B-6, B-5, and B-4 show approximately 5 feet of fill containing fly ash. The location of Section A-A' is outlined on Figure 6 of the USGS Report. Figure 7 of the Report depicts the geohydrologic cross-section of A-A' and includes the boring locations along A-A'.

Reference: ATEC/Weaver Boos Boring Logs for Yard 520

Boring PL-1 (not converted to MW, was located in the northeast corner of the site): Fill and fly ash material to 29.5 ft bgs. Note – This was not in the former fill area. PL-1 was in the parking lot area.

Boring PL-2 (Currently MW-2 and located near clay barrier): Fly ash to 5.5 ft bgs

Boring PL-3 (Currently MW-3A and located near Railroad Avenue west of the southeastern corner of the southern area – approx. 600 ft east of PL-4): Fill material to 3.0 ft bgs

Boring PL-4 (Currently MW-4A and located near Railroad Avenue east of the southwestern corner of the southern area): Fill material to 3.0 ft bgs.

Boring PL-5 (abandoned, was located near MW-1 in northwestern corner of Yard 520): Fly ash to 5.5 ft bgs.

Reference: Map provided by USEPA to Respondents in January 2004 meetings.
USEPA provided a draft map with boron concentrations in groundwater posted as color-coded dots and "fly ash areas" shaded as green. These areas include:

Yard 520
Railroad and/or Railroad Ave from Ardendale eastward to County Line Road
Extension of Illinois from East Johns southward, crossing Brown Ditch, to the Railroad
Most (but not all) of Second Pl from Illinois eastward to County Line Road
Connecticut from US Rte 12 to Second Pl
Extension of Carolina north of US Rte 12 from railroad tracks northward to Beverly Drive

Reference: *Town of Pines Town Board Meeting Notes* (May 6, 1975), received from USEPA May 11, 2004

"The town board is using the ash on Birch Street south of 20 and along Railroad Ave. to the County Line; to fill Henry between Louisiana Ave. and Ardendale Ave.; to extend E. Johns Ave. to Columbia; and to join E. John Ave. with Idaho Ave. and Florida Ave."

Reference: Letter from Calumet Trucking Company to the State of Indiana Solid Waste Management Office (February 23, 1976), received from USEPA, May 11, 2004

"There is approximately 40,000 cubic yards of a mixture of fly ash and boiler bottom ash from the Michigan City Generating Station Lagoons. This material will be deposited as a land fill in the location as shown on the enclosed map."

The map shows four disposal areas. Area #1 is along the south side of 2nd Place near California. Area #2 is along the south side of 2nd Place and west of Area #1. Area #2 is described as the "back of 101 Junk Shop". Area #3 is located along the northwest corner of County Line Road and the railroad tracks. Area #4 is located in the northeast corner of Idaho Street and E. John Street.

APPENDIX B

ENSR Standard Operating Procedures

Chain-of-Custody Procedures

SOP Number 1007Pines

Revision Number: 1.0

October 2004

ENSR Project Manager
October 15, 2004

ENSR Project QA Officer
October 15, 2004

ENSR Corporation
October 2004
Document Number 01776-020-124

SOP NUMBER: 1007Pines

Chain-of-Custody Procedures

CONTENTS

LIST OF ACRONYMS

COC	Chain-of-Custody
EPA	Environmental Protection Agency
NEIC	National Enforcement Investigations Center
SOP	Standard Operating Procedure

1.0 SCOPE AND APPLICABILITY

This standard operating procedure (SOP) describes chain-of-custody procedures applicable to ENSR sampling and analysis programs.

2.0 SUMMARY OF METHOD

The National Enforcement Investigations Center (NEIC) of EPA defines custody of evidence in the following manner:

- it is in your actual possession;
- it is in your view, after being in your physical possession;
- it was in your possession and then you locked or sealed it up to prevent tampering; or
- it is in a secure area.

Samples are physical evidence and should be handled according to certain procedural safeguards described in of this SOP.

3.0 HEALTH AND SAFETY WARNINGS

Not applicable.

4.0 INTERFERENCES

Not applicable.

5.0 PERSONNEL QUALIFICATIONS

Individuals responsible for completing chain-of-custody (COC) documentation must have read this SOP and have worked under the oversight of experienced personnel.

6.0 EQUIPMENT SUPPLIES

- Chain-of-Custody Form (Figure 1)
- Sample Labels
- Chain-of-Custody Tape (Figure 2)

7.0 METHODS

7.1 Field Custody

7.1.1 The field sample custodian or sampler is required to complete the following information on the COC form (Figure 1):

- Project Number
- Client or Project Name
- Project Location
- Field Sample Identification Number
- Date and Time of Sample Collection
- Sample Matrix
- Preservative
- Analysis Requested
- Sampler's Signature
- Signature of Person Relinquishing Sample Custody (Field Sample Custodian)
- Date and Time Relinquished
- Sampler Remarks
- Chain-of-Custody Tape Number

7.1.2 The COC must be filled out completely and legibly. Corrections will be made, if necessary, by drawing a single line through and initialing and dating the error. The correct information is then recorded with indelible ink. All transfers from field personnel to laboratory personnel are recorded on the chain-of-custody form in the "relinquished by" and "received by" sections.

7.1.3 If samples are to be shipped, the field sample custodian must complete a chain-of-custody form for each package of samples and place a copy of each completed form inside the associated package before the package is sealed. Each completed chain-of-custody form must accurately list the sample identification numbers of the samples with which it is packaged, and must contain the identification number of the chain-of-custody seal on the package.

7.1.4 If samples are hand carried to a laboratory, the person hand carrying the samples is the sample custodian. If the carrier is a different person than the one who filled out the chain-of-custody form and packaged the samples, then that person must transfer custody to the carrier by signing and dating each form in the

"Relinquished By" section. The carrier must then sign and date each form in the adjacent "Received By" section. When the carrier transfers the samples to the laboratory, he or she must sign and date each form in the next "Relinquished By" section, and the laboratory sample custodian must sign and date each form in the adjacent "Received By" section.

7.2 Laboratory Sample Receipt and Inspection

7.2.1 Upon sample receipt, the coolers or packages are inspected for general condition and the condition of the COC tape. The coolers or boxes are then opened and each sample is inspected for damage.

7.2.2 Sample containers are removed from packing material and sample label field identification numbers are verified against the COC form.

7.2.3 The following information is recorded in the laboratory's records:

- Airbill Number
- Presence/absence of COC forms and custody tape
- Condition of samples
- Discrepancies noted
- Holding time and preservatives
- Sample storage location

7.2.4 The COC form is completed by signing and recording the date and time of receipt.

7.2.5 The ENSR Project Manager or designate must be notified of any breakage, temperature exceedances, or discrepencies between the COC paperwork and the samples.

8.0 DATA AND RECORDS MANAGEMENT

The records generated in this procedure will become part of the permanent record supporting the associated measurements. Copies of these records will be retained in the applicable project files, and in the files of the laboratories who have performed the sample analyses.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

- The records generated in this procedure are subject to senior review in accordance with ENSR's senior review procedures.

10.0 REFERENCES

SOP 7510Pines - Packaging and Shipment of Environmental Samples. Revision 1.

FIGURE 1 Example Chain of Custody Form

M901376

ENSR **CHAIN OF CUSTODY RECORD** Page ____ of ____

Client/Project Name.	Project Location:	Analysis Requested
Project Number:	Field Logbook No	
Sampler: (Print Name) /Affiliation	Chain of Custody Tape No..	
Signature:	Send Results/Report to	

Field Sample No./ Identification	Date	Time	Grab	Comp	Sample Container (Size/Mat'l)	Sample Type (Liquid, Sludge, Etc.)	Preservative	Field Filtered								Lab I D	Remarks

Relinquished by: (Print Name)	*Date*	*Received by:* (Print Name)	*Date:*	Analytical Laboratory (Destination)
Signature.	Time:	Signature:	Time.	ENSR 4303 W. LaPorte Ave. Fort Collins, CO 80521 (970) 416-0916
Relinquished by: (Print Name)	Date.	Received by: (Print Name)	Date:	
Signature.	Time:	Signature:	Time:	
Relinquished by: (Print Name)	Date:	Received by (Print Name)	Date:	
Signature:	Time:	Signature	Time:	Serial No.

FIGURE 2 Example Chain of Custody Tape

Surface Soil Sampling

SOP Number 7110Pines

Revision Number: 1.0

October 2004

ENSR Project Manager
October 15, 2004

ENSR Project QA Officer
October 15, 2004

ENSR Corporation
October 2004
Document Number 01776-020-124

SOP NUMBER: 7110Pines

Surface Soil Sampling

CONTENTS

LIST OF ACRONYMS

HASP	Health and Safety Plan
IDW	Investigation-derived Waste
MS/MSDs	Matrix spike/matrix spike duplicates
OSHA	Occupational Safety and Health Adminstration
QAPP	Quality Assurance Project Plan
SAP	Sampling and Analysis Plan
SOP	Standard Operating Procedure

1.0 SCOPE AND APPLICABILITY

This standard operating procedure (SOP) describes the method used for obtaining surface soil samples at the Pines Site for analysis of inorganic parameters. The purpose of this SOP is to provide a specific method and/or procedure to be used in the collection of surface soil samples which, if followed properly, will promote consistency in sampling and provide a basis for sample representativeness.

This SOP is generally applicable to surface and shallow depth soils which are unconsolidated and are of low to moderate density. Higher density or compacted soils may require use of drill rigs or other powered equipment to effectively obtain representative samples.

2.0 SUMMARY OF METHOD

Surface soil sampling generally involves use of hand-operated equipment to obtain representative soil samples from the ground surface and or from shallow depths below the ground surface exposed by excavating equipment. If soil conditions are appropriate, surface soil sampling, following the procedures described in this SOP, can provide representative soil samples in an efficient manner.

3.0 HEALTH AND SAFETY WARNINGS

Surface soil sampling may involve chemical exposure hazards associated with the type of contaminants present in surface soil. When surface soil sampling is performed, adequate Health and Safety measures must be taken to protect sampling personnel. These measures must be addressed in the project Health and Safety Plan (HASP). This plan must be approved by the project Health and Safety Officer before work commences, must be distributed to all personnel performing sampling, and must be adhered to as field activities are performed.

4.0 INTERFERENCES

Potential interferences could result from cross contamination. Minimization of the cross contamination will occur through the following:

- The use of clean, disposable plastic sampling tools at each location.
- Avoidance of material that is not representative of the media to be sampled. Material that has been in contact with the excavator bucket will not be sampled.

5.0 PERSONNEL QUALIFICATIONS

Surface soil sampling is a relatively simple procedure requiring minimal training and a relatively small amount of equipment. It is, however, recommended that initial attempts be supervised by more experienced personnel. Sampling personnel should be health and safety certified as specified by OSHA (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous materials may be present.

6.0 EQUIPMENT AND SUPPLIES

6.1 Spoons or Scoops

Commercially purchased plastic spoons or scoops will be utilized to collect the samples to be analyzed for inorganic parameters. These tools will be dedicated to each sampling location and will be discarded after use.

6.2 Collection Bowl

A plastic bowl will be used as the intermediate sample container between removal of the sample from the ground and containerization of the sample. Plastic bowls will be purchased new and dedicated to each sample location.

6.3 Supporting Materials

- Sample kit (i.e., bottles, labels, custody records, cooler, etc.)
- Sample logs/boring logs
- Six-foot folding rule or tape measure for depth measurement
- Personal protective equipment (as required by the HASP)
- Field project notebook/pen

7.0 METHODS

7.1 Equipment Decontamination

Not applicable. Clean, plastic equipment (trowels or spatulas and bowls) will be dedicated to each sample location and will be disposed of after each use.

7.2 Sample Collection Preparation

7.2.1 Surface preparation will include removal of the surface layer which was in contact with the excavator bucket.

7.2.2 Select the sampling location and "dress" the surface of the excavation wall or pile of excavated material by scraping to remove any loose surface soil or smearing residues.

7.2.3 Replace the dressing tool with a clean sampling tool.

7.3 Sampling Procedure

7.3.1 Insert the sampling tool into the soil and rotate the tool so that a representative "column" of soil is removed from the ground. One or more scoops of material may be needed until the desired sample volume is achieved.

7.3.2 Place each scoop into an intermediate sample container (plastic bowl) until sufficient sample volume is collected.

7.3.3 Once sufficient material has been collected, thoroughly homogenize the sample within the collection pan prior to bottling. Sample homogenizing is accomplished by manually mixing the entire sample in the collection pan with the sampling tool until a uniform mixture is achieved.

7.3.4 Fill the sample containers with material from the plastic bowl. The sampling tool may be used to fill the sample bottles. Use of fingers/hands to fill or pack sample containers is not allowed.

7.4 Sample Handling and Preservation

7.4.1 Once each sample container is filled, clean the rim and threads of the sample container by wiping with a paper towel.

7.4.2 Cap and label the container with the sample identifier, sampling date and time, preservation information, and analytical tests.

7.4.3 Place the sample containers into a cooler and maintain on ice.

7.4.4 Complete sample chain-of-custody and other documentation per SOP 1007Pines.

7.4.5 Package the samples for shipment to the laboratory per SOP 7510Pines.

7.4.6 Handle any investigation-derived waste (IDW) per the SAP.

8.0 DATA AND RECORDS MANAGEMENT

Various forms are required to ensure that adequate documentation is made of the sample collection activities. These forms include:

- Field log books
- Sample collection records
- Chain-of-custody forms
- Shipping labels

The field book will be maintained as an overall log of all samples collected throughout the study. Sample collection records are generated for each sample collected and include specific information about the sample (Figure 1). Chain-of-custody forms are transmitted with the samples to the laboratory for sample tracking purposes. Shipping labels are required if sample coolers are to be transported to the laboratory by a third party (courier service). Original and/or copies of these documents will be retained in the appropriate project files.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

- Collection of representative samples will be ensure through adherence to the procedures in this SOP and the sampling strategy outlined in the Sampling and Analysis Plan (SAP).
- The field quality control samples identified in the SAP must be collected. These samples include field duplicates and matrix spike/matrix spike duplicates (MS/MSDs)

10.0 REFERENCES

SOP 1007Pines. Chain-of-Custody Procedures. Revision 1.0.

SOP 7510Pines. Packaging and Shipment of Environmental Samples. Revision 1.0.

ENSR Health and Safety Policy and Procedures Manual.

FIGURE 1 Surface Soil Sample Log

SURFACE SOIL SAMPLE LOG

Project Number: _____ Project Location: _____

Sample Point No.: _____

Date: _____ Time:

Sample Point Description/Designation: _____

_____

_____

_____

SAMPLE COLLECTION

Equipment Used: _____

No. of Samples Collected: Container Size: _____

Sample Number	Depth	Type of Material	Analyses Requested

Comments:

Lab Designation _____

Shipping ID Number: _____

Collector's Name _____

Package and Shipment of Environmental Samples

SOP Number 7510Pines

Revision Number: 1.0

October 2004

Lesa J. Bradley
ENSR Project Manager
October 15, 2004

Debra L. McGrath
ENSR Project QA Officer
October 15, 2004

ENSR Corporation
October 2004
Document Number 01776-020-124

CONTENTS

LIST OF ACRONYMS

COC	Chain-of-Custody
DOT	Department of Transportation
HASP	Health and Safety Plan
OSHA	Occupational Safety and Health Adminstration
RCRA	Resource Conversation and Recovery Act
SOP	Standard Operating Procedure

1.0 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the procedures associated with the packaging and shipment of environmental samples consisting of water and soil submitted for routine environmental testing. Environmental samples are not considered a hazardous waste by definition; therefore, more stringent Department of Transportation (DOT) regulations regarding sample transportation do not apply. Environmental samples do, however, require fairly stringent packaging and shipping measures to ensure sample integrity as well as safety for those individuals handling and transporting the samples.

This SOP is designed to provide a high degree of certainty that environmental samples will arrive at their destination intact. This SOP assumes that samples will often require shipping overnight by a commercial carrier service, therefore, the procedures are more stringent than may be necessary if a laboratory courier is used or if samples are transported directly to their destination by a sampling team member. Should the latter occur, the procedures may be modified to reflect a lesser degree of packaging requirements.

2.0 SUMMARY OF METHOD

Sample packaging and shipment involves the placement of individual sample containers into a cooler or other similar shipping container and placement of packing materials and coolant in such a manner as to isolate the samples, maintain the required temperature, and to limit the potential for damage to sample containers when the cooler is transported.

3.0 HEALTH AND SAFETY WARNINGS

Sampling personnel should be aware that packaging and shipment of samples involves potential physical hazards primarily associated with handling of occasional broken sample containers and lifting of heavy objects. Adequate health and safety measures must be taken to protect sampling personnel from these potential hazards. The project Health and Safety Plan (HASP) generally addresses physical and other potential hazards. This plan must be approved by the project Health and Safety Officer before work commences, must be distributed to all personnel performing sampling, and must be adhered to as field activities are performed. In the absence of a HASP, work will be conducted according to the ENSR Health and Safety Policy and Procedures Manual and/or direction from the Regional Health and Safety Manager.

4.0 INTERFERENCES

Sample containers with presumed high contaminant concentrations should be isolated within their own cooler with each sample container placed into a Zipper-lock bag.

5.0 PERSONNEL/QUALIFICATIONS

Sample packaging and shipment is a relatively simple procedure requiring minimal training and a minimal amount of equipment. It is, however, recommended that initial attempts be supervised by more experienced personnel. Sampling technicians should be health and safety certified as specified by OSHA (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous waste materials are considered to be present.

6.0 EQUIPMENT AND SUPPLIES

- Sample coolers
- Sample containers
- Shipping labels
- Chain-of-custody (COC) form (Figure 1)
- Custody tape (Figure 2)
- Bubble wrap
- Vermiculite (granular), or styrofoam pellets
- Ice
- Transparent tape, or rubber bands
- Fiber tape
- Duct tape
- Zipper-lock plastic bags

- Trash bags
- Health and safety supplies
- Temperature blank
- Field project notebook/pen

7.0 METHODS

7.1 Preparation

The extent and nature of sample containerization will be governed by the type of sample, and the most reasonable projection of the sample's hazardous nature and constituents. The EPA regulations (40 CFR Section 261.4(d)) specify that samples of solid waste, water, soil or air, collected for the sole purpose of testing, are exempt from regulation under the Resource Conservation and Recovery Act (RCRA) when any of the following conditions are applicable:

- Samples are being transported to a laboratory for analysis;
- Samples are being transported to the collector from the laboratory after analysis;
- Samples are being stored (1) by the collector prior to shipment for analyses, (2) by the analytical laboratory prior to analyses, (3) by the analytical laboratory after testing but prior to return of sample to the collector or pending the conclusion of a court case.

7.1.1 Laboratory Notifications

Prior to sample collection, the Project Manager, or designated alternative must notify the laboratory project manager of the number, type and approximate collection and shipment dates for the samples. If the number, type or date of sample shipment changes due to program changes which may occur in the field, the Project Manager or alternate must notify the laboratory of the changes. Additional notification from the field is often necessary when shipments are scheduled for weekend delivery.

7.1.2 Cooler Inspection and Decontamination

Laboratories will often re-use coolers. Every cooler received at a project location should be inspected for condition and cleanliness. Any coolers that have cracked interior or exterior linings/panels or hinges should be discarded as their insulating properties are now compromised. Any coolers missing one or both handles should also be discarded if replacement handles (i.e., knotted rope handles) can not be fashioned in the field. Replacement coolers may be purchased in the field if necessary.

The interior and exterior of each cooler should be inspected for cleanliness before using it. Excess strapping tape and old shipping labels should be removed. If the cooler interior exhibits visible contamination or odors it should not be used. Drain plugs should be sealed on the inside with duct tape.

7.2 Sample Packaging

7.2.1 Place plastic bubble wrap matting over the base of each cooler or shipping container as needed. A 2- to 3-inch thickness layer of vermiculite may be used as a substitute base material.

7.2.2 Insert a clean trash bag into the cooler to serve as a liner.

7.2.3 Check that each sample container is sealed, labelled legibly, and is externally clean. Re-label and/or wipe bottles clean if necessary. Clear tape should be placed over the labels to protect them. Wrap each sample bottle individually with bubble wrap secured with tape or rubber bands. Place bottles into the cooler in an upright single layer with approximately one inch of space between each bottle. Do not stack bottles or place them in the cooler lying on their side. If plastic and glass sample containers are used, alternate the placement of each type of container within the cooler so that glass bottles are not placed side by side.

7.2.4 Insert the cooler temperature blanks supplied by the laboratory.

7.2.5 Place additional vermiculite, bubble wrap, and/or styrofoam pellet packing material throughout the voids between sample containers within each cooler to a

level which meets the approximate top of the sample containers. Packing material may require tamping by hand to reduce the potential for settling.

7.2.6 Double bag cubed ice in heavy duty Zipper-lock type plastic bags, close the bags, and distribute the packages in a layer over the top of the samples. Loose ice should never be used. Cold packs should be used only if the samples are chilled before being placed in the cooler.

7.2.7 Add additional bubble wrap/styrofoam pellets or other packing materials to fill the balance of the cooler or container.

7.2.8 Obtain two pieces of custody tape as shown in Figure 2 and enter the custody tape numbers in the appropriate place on the COC form. Sign and date the custody tape.

7.2.9 Complete the COC form per SOP 1007Pines. If shipping the samples involves use of a third party commercial carrier service, sign the COC record thereby relinquishing custody of the samples. Shippers should not be asked to sign COC records. If a laboratory courier is used, or if samples are transported to the laboratory by field personnel, the receiving party should accept custody and sign the COC records. Remove the last copy from the multi-form COC and retain it with other field notes. Place the original (with remaining copies) in a Zipper-lock type plastic bag and tape the bag to the inside lid of the cooler or shipping container.

7.2.10 Close the top or lid of the cooler or shipping container.

7.2.11 Place the custody tape at two different locations (i.e., one tape on each side) on the cooler or container lid and overlap with transparent packaging tape.

7.2.12 Packaging tape should be placed entirely around the sample shipment containers. A minimum of two full wraps of packaging tape will be placed at least two places on the cooler.

7.2.13 Repeat the above steps for each cooler or shipping container.

7.3 Sample Shipping

Transport the cooler to the package delivery service office or arrange for package pick-up at the site. Fill out the appropriate shipping form or airbill and affix it to the cooler. Some courier services may use multi-package shipping forms where only one form needs to be filled out for all packages going to the same destination. If not, a separate shipping form should be used for each cooler. Keep the receipt for package tracking purposes should a package become lost. Please note that each cooler also requires a shipping label which indicates point of origin and destination. This will aid in recovery of a lost cooler if a shipping form gets misplaced. Never leave coolers unattended while waiting for package pick-up. Airbills or waybills will be maintained as part of the custody documentation.

7.4 Sample Receipt

Upon receipt of the samples, the analytical laboratory will open the cooler or shipping container and will sign "received by laboratory" on each COC form. The laboratory will verify that the custody tape has not been broken previously and that the tape number corresponds with the number on the COC record. The laboratory will note the condition of the samples upon receipt and will identify any discrepancies between the contents of the cooler and COC. The analytical laboratory will then forward the back copy of the COC record to the Project Manager to indicate that sample transmittal is complete.

8.0 DATA AND RECORDS MANAGEMENT

Documentation supporting sample packaging and shipment consists of COC records and shipping records. All documentation will be retained in the project files following project completion.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

- The potential for samples to break during transport increases greatly if individual containers are not snugly packed into the cooler. Completed coolers may be lightly shake-tested to check for any loose bottles. The cooler should be repacked if loose bottles are detected.

- Environmental samples are generally shipped so that the samples are maintained at a temperature of approximately 4°C. Temperature blanks may be required for some projects as a quality assurance check on shipping temperature conditions. These blanks usually are supplied by the laboratory and consist of a 40-ml vial or plastic bottle filled with tap water. Temperature blanks should be placed near the center of the cooler.

10.0 REFERENCES

SOP 1007Pines. Chain-of-Custody Procedures. Revision 1.0.

ENSR Health and Safety Policy and Procedures Manual.

FIGURE 1 Example Chain of Custody Form

M901376

ENSR **CHAIN OF CUSTODY RECORD** Page ____ of ____

Client/Project Name:	Project Location.	Analysis Requested
Project Number.	Field Logbook No :	
Sampler (Print Name) /Affiliation	Chain of Custody Tape No.	
Signature	Send Results/Report to:	

Field Sample No / Identification	Date	Time	Grab	Comp	Sample Container (Size/Matl)	Sample Type (Liquid Sludge, Etc)	Preservative	Field Filtered							Lab I D	Remarks

Relinquished by (Print Name)	Date:	Received by. (Print Name)	Date	Analytical Laboratory (Destination):
Signature	Time:	Signature:	Time:	ENSR 4303 W. LaPorte Ave. Fort Collins, CO 80521 (970) 416-0916
Relinquished by (Print Name)	Date:	Received by (Print Name)	Date	
Signature:	Time.	Signature	Time	
Relinquished by: (Print Name)	Date.	Received by: (Print Name)	Date:	
Signature:	Time:	Signature.	Time:	Serial No

FIGURE 2 Example Chain of Custody Tape

APPENDIX C

Laboratory Standard Operating Procedures

STANDARD OPERATING PROCEDURE

DETERMINATION OF SULFUR IN SOILS USING ION CHROMATOGRAGPHY AFTER ALKALINE DIGESTION FOR INDIANA PINES SITE

GEN-300Pines

Revision 0

September 24, 2004

Approved By:	_____ Supervisor	9/24/04 Date
	_____ QA Coordinator	9/24/04 Date
	_____ Laboratory Manager	9/24/04 Date

One Mustard St., Suite 250
Rochester, NY 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: _____ **Date:** _____
Initials: _____ **Date:** _____
Initials: _____ **Date:** _____

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Table of Contents **Page**

1 SCOPE AND APPLICABILITY

1.1 This SOP uses Method 300.0 for the analysis of sulfate by Ion Chromatography in soil samples prepared by alkaline digestion according to MET-ICS.

1.2 Range

Using the settings and calibration techniques outlined in this SOP, the upper range for sulfate is 10 ppm (solution concentration). Higher concentrations of sulfate may be determined using appropriate dilutions. Review current calibration for specific ranges.

1.3 The PQL for the current system is 0.20 mg/L

2 SUMMARY OF METHOD

Sample digested by alkaline digestion. The extract is filtered and injected into an ion chromatograph (Dionex Series 4000i). Sulfate is chromatographically separated and measured with a conductivity detector. Suppression is accomplished using an ion exchange membrane. It is assumed that all of the sulfur is converted to sulfate during the digestion. The sulfate results are converted by calculation to concentration of sulfur in the original soil sample.

3 DEFINITIONS

3.1 **Initial Calibration** - analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the system.

3.2 **Independent Calibration Verification (ICV)** - ICV solutions are made from a stock solution which is different from the stock used to prepare calibration standards and is used to verify the validity of the standardization. The ICV is analyzed immediately following the calibration standards.

3.3 **Relative Percent Difference (RPD)** – The absolute value of the difference of two values *divided by the average of the same two values. Used to compare the precision of the* analysis. The result is always a positive number.

3.4 **Batch** - Samples processed together as a unit, not to exceed 20 investigative samples.

3.5 **Method Detection Limit (MDL):** a statistically derived value representing the lowest level of target analyte that may be measured by the instrument with 99% confidence that the value is greater than zero

3.6 **Method Reporting Limit (MRL):** The minimum amount of a target analyte that can be measured and reported quantitatively. The MRL is equivalent to Practical Quantitation Level (PQL) and Estimated Quantitation Level (EQL). Typically, the MRL is calculated as five times the MDL (although this is a rule of thumb and not intended to be a strict policy of establishing the MRL for a compound).

3.7 **QA/QC Samples**: Samples added to a sample preparation batch, or an analytical batch to provide quality assurance checks on the analysis.

3.7.1 **Matrix Spike (MS)** - In the matrix spike analysis, predetermined quantities of standard solutions of certain analytes are added to a sample matrix prior to analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the methods used for the analyses. Percent recoveries are calculated for the analyte detected. In this method, spikes are very useful in determining proper retention times when a low concentration of an analyte is detected or expected to be adjacent to a large concentration of analyte. When a spike is used to verify retention time, calculation of recovery is not necessary.

3.7.2 **Duplicate Sample (DUP)** - A laboratory duplicate. The duplicate sample is a separate field sample aliquot that is processed in an identical manner as the sample proper. The relative percent difference between the samples is calculated and used to assess analytical precision.

3.7.3 **Continuing Calibration Verification Standard (CCV)** - A standard analyzed at specified intervals and used to verify the ongoing validity of the instrument calibration.

3.7.4 **Instrument Blank (ICB/CCB)** - The instrument blank (also called initial or continuing calibration blank) is a volume of blank reagent of composition identical to the samples (ie. not chemically preserved). The purpose of the ICB/CCB is to determine the levels of contamination associated with the instrumental analysis. The ICB is performed once, immediately after the ICV.

3.7.5 **Laboratory Control Standard (LCS)** - In the LCS or blank spike analysis, predetermined quantities of standard solutions of certain analytes are added to a blank prior to sample analysis. Percent recoveries are calculated for the analyte detected.

4 HEALTH AND SAFETY WARNINGS

- Take all appropriate safety precautions for handling reagents and samples when performing this procedure. This includes the use of personnel protective equipment, such as safety glasses, lab coat and the correct gloves.

- Handle chemicals, reagents and standards as described in the CAS safety policies, approved methods and in MSDSs where available.

- The use of pressurized gases is required for this procedure. Exercise care when moving cylinders. All gas cylinders must be secured to a wall or an immovable counter with a chain or a cylinder clamp at all times. Sources of flammable gases (e.g., pressurized hydrogen) should be clearly labeled.

- When releasing the cap on the suppressor reagent, wear a face shield and exercise caution. The container is pressurized and the reagent will emit a fine mist. Turn the cap slowly.

5 INTERFERENCES

5.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or spiking can be used to solve most interference problems. The most common examples of this are:

5.1.1 Sulfite will interfere with the sulfate peak.

5.1.2 Thiosulfate can interfere if the run time of the entire chromatogram is too short.

6 PERSONNEL QUALIFICATIONS

At a minimum, personnel must have attained at least a 4-year degree (or 2-yr degree plus one year experience) in a science-related field and have successfully completed an Initial Demonstration of Capability and the Training Plan Form (attached). Training and Demonstration of Capability are in accordance with NELAC 2002 standard.

7 EQUIPMENT AND SUPPLIES

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

7.2 Anion guard column: A protector of the separator column. If omitted from the system the retention times will be shorter. Dionex Ionpac AG4A-SC 4×50 mm (P/N 43175)

7.3 Anion separator column: Dionex AS14 4x250 (P/N 046124). Expires when separation between the anions of interest is no longer acceptable or upon manufacturer's indications, whichever occurs first.

7.4 Anion suppressor device: Dionex anion micro membrane suppressor (P/N 53946).

7.5 Detector-Conductivity Cell: approximately 1.25 µL internal volume.

7.6 Dionex PeakNet 5.1 Chromatography Workstation software or equivalent. Personal computer connected to network, capable of running the PeakNet software.

7.7 Calibrated MicroPipettor and tips.

7.8 Calibrated repipettor.

7.9 System configuration

An automated sampler	(Dionex P/N 39534)
An analytical gradient pump	(Dionex System 4000i)
A separator column	(Dionex AS14 4x250mm P/N 046124)
A conductivity detector	(Dionex P/N 40157)
A 50µL sample loop	
Pump rate of 2.0 mL/min	

7.10 **Standards Preparation General Information**

- Bring any cooled parent stocks to room temperature before use.
- All standards and reagents are to be tightly capped when not in immediate use. Protect standards and reagents from light whenever possible.

7.11 Reagent water: Distilled or deionized water, free of the anions of interest.

7.12 Stock Eluent solutions for AS14 column

7.12.1 0.5 M Sodium Carbonate Concentrate– Dissolve 26.49g Na2CO3 in 400 mLs DI. Bring to volume in a 500 mL volumetric flask. Expires one year. Store at room temperature.

7.12.2 0.5M Sodium Bicarbonate Concentrate – Dissolve 21.00 g of $NaHCO_3$ in 400 mL DI. Dilute to a final volume of 500 mLs with DI. Store at room temperature. Expires in one year.

7.13 Working Eluent Solution for AS 14 Column – 3.5 mM Sodium Carbonate / 1.0 mM Sodium Bicarbonate – Filter a sufficient volume of each of the 2 eluent reagents through 0.2 µm syringe filters into separate dispo cups. Pipette 7.0 mL of 0.5 M Na_2CO_3 and 2.0 mL of 0.5 M $NaHCO_3$ into a 2 Liter volumetric flask. Dilute to volume with DI. Degas for 5 minutes with ultra high purity Helium at a rate of 1-5 bubbles per second. Store at room temperature. Expires in 1 week.

7.14 Regeneration solution (micro membrane suppressor): Sulfuric acid 0.1N. Dilute 5.6 mL of conc. sulfuric acid (H_2SO_4) to 2L with reagent grade water. Degas for 5 minutes with ultra high purity Helium at a rate of 1-5 bubbles per second. This solution is stable for one week from date of preparation. Store at room temperature in plastic.

7.15 Stock standard solutions

7.15.1 Sodium Sulfate – ACS reagent grade dried at 103-105°C for 30 mins. Store dried material in a small glass beaker. Enclose the beaker in aluminum foil to protect from light. Store the covered beaker in a desiccator. Expires in one year.

7.15.2 Sulfate (SO_4^-) 1000 mg/L: Dissolve 1.479 g prepared (as above) sodium sulfate (Na_2SO_4) in reagent water and dilute to 1 L. Store at 0-6°C in amber glass for up to 1 year.

7.16 Intermediate Calibration Standards –

7.16.1 Routine Intermediate Stock – Store at 0-6°C in plastic. Expires in 6 months. Also used as LCS and MS Intermediate stock.

Analyte:	SO_4
Stock Conc (mg/L):	1000
mLs Stock:	20.0
Final Vol (mLs):	200.0
Int. Stock Conc (mg/L):	100.0

7.17 Calibration Standards - prepared in 100 mL volumetric flask as follows: record the pipette ID used in the reagent prep logbook. Make fresh weekly. Store at 0-6°C in glass or plastic.

Standard ID		mLs of Intermediate Stock	Final Volume, mLs	Working conc. SO_4 mg/L
Std #	9	10.0	100.0	10.0
Std #	8	8.0	100.0	8.0
Std #	7	5.0	100.0	5.0
Std #	6	2.0	100.0	2.0
Std #	5	1.0	100.0	1.0
Std #	4	0.5	100.0	0.50
Std #	3	0.2	100.0	0.20
Std #	2	0.1	100.0	0.10
Std #	1	0.0	100.0	0.00

7.18 Reference Standard Stocks:

7.18.1 Potassium Sulfate – ACS reagent grade dried at 103-105°C for 30 mins. Store dried material in a small glass beaker. Enclose the beaker in aluminum foil to protect from light. Store the covered beaker in a desiccator. Expires in one year.

7.18.2 Sulfate (SO_4.) 3200 mg/L: Dissolve 5.80g dried (as above) K_2SO_4 in reagent water and dilute to 1 L. Store at 0-6 °C in amber glass for up to 1 year.

7.19 ICV/CCV Intermediate stock (12.8 mg/L) - Dilute 4.0 mL of 3200 mg/L reference stock to 1 Liter in a volumetric flask. Store at 0-6°C in plastic for up to 6 months.

7.20 ICV/CCV (6.4 mg/L) - prepare by diluting the CCV intermediate stock solution with equal parts water in small quantity (about 30 mLs DI and 30 mLs intermediate stock solution). The resulting concentrations are half of those of the intermediate solution. Prepare fresh when needed or at least once a week. Store at room temperature in plastic.

7.21 LCS (2.0 mg/L): Store at room temperature in glass or plastic for up to one week. Add 2.0 mLs of the intermediate stock solution (prepared same as the intermediate solution used for calibration standards) to DI in a 100 mL volumetric flask and bring to volume.

7.22 Matrix Spike Solution - Add 2.0 mL of the intermediate stock solution to 100 mL sample (or dilution of sample). Prepare fresh before use.

7.23 Consumable materials.

- 5 mL vials with filter caps. (Dionex P/N 038141)
- 0.2 µm syringe filters.

8 PROCEDURE

8.1 Calibration and Standardization-

8.1.1 Prepare calibration standards according to Section 7. Document preparation in standards log book. Load standards according to Autosampler Vial Loading Section. Start instrument and analyze according to sections below.

8.1.2 The initial calibration is made by linear regression. This method of quantitation uses the equation of a line ($y=mx+b$). The curve must not be forced through zero. System calibration must have correlation coefficient of 0.995 or better. Delete outlier standards. Standards must be within 10% of their true value. Method 300.0 requires a minimum of 3 standards and a blank. If the removal of outlier standards does not bring the curve into compliance, recalibrate.

8.1.3 Immediately after an acceptable calibration has been achieved, run the ICV, ICB, and an LCS. If these are compliant, continue with samples as described in the daily analytical sequence.

8.2 **Sample Collection** – Samples should be collected in purchased, certified clean glass or polyethylene bottles or jars.

8.3 **Sample Handling and Preservation** – Sulfate holding time is 28 days from collection. Samples stored at 0-6°C from receipt until analysis. Sample handling, storage, and custody procedures are in accordance with NELAC 2002 Standard.

8.4 **Sample Preparation** – Soil samples for Total Sulfur are digested according to MET-ICS. Further preparation of the extract is given below.

8.5 **Sample Analysis** –

8.5.1 **Prepare the Instrument** –

8.5.1.1 Be sure there is a current MDL and IDC for the system.

8.5.1.2 Check eluent and regenerant levels in containers. Fill to appropriate levels as necessary. Hand tighten caps of both jugs.

8.5.1.3 Remove plugs from the waste lines on the back of the instrument. Screw flow restrictor onto end of suppressor drain line (both lines are labeled).

8.5.1.4 Turn on Helium carrier gas (should be at approximately 17psi.) and compressed air (100 psi.) by turning the yellow handles to the up-down position and the small valves to IC#1. These are located along the column to the left of the computer.

8.5.1.5 Start the Dionex Gradient pump – on the bottom right half of the instrument there is a button with stop / start indicator. Press the button to light the start indicator.

8.5.1.6 Turn on the Conductivity Cell. In the middle of the instrument there is a CELL off/on indicator. Press the button to light the "on" indicator. Allow the system to warm up for about an hour.

8.5.2 **Create a schedule in the PeakNet software** -

8.5.2.1 While the system is warming up, determine whether an ICAL is to be run. The instruments must be calibrated if any of the following apply:

- when a new column is put in
- when system configuration changes warrant calibration
- every 6 months
- when QC samples indicate the old calibration is no longer acceptable.

8.5.2.2 Determine which samples are to be analyzed.

8.5.2.3 Remove any standards or reagents needed from the cooler and allow to warm to room temperature before use.

8.5.2.4 Create the schedule of the day's run in the software. This may be modified later as needed, but will help with initial organization.

8.5.2.5 If a calibration is not to be run – set up the schedule to analyze samples in the following analytical sequence: CCV, CCB, LCS, 10 samples, CCV, CCB, 10 samples, CCV, CCB, LCS, etc. with a CCV/CCB set after every 10 samples and an LCS after every 20 samples and DUP/MS where appropriate (at no particular position but one set for every 10 samples). Skip the initial calibration section. Prepare the samples and load the autosampler as described below.

8.5.2.6 If a calibration is to be run – set up the schedule to analyze the calibration standards, ICV, ICB, LCS, 10 samples, CCV, CCB, 10 samples, CCV, CCB, LCS, etc. with a CCV/CCB set after every 10 samples and an LCS after every 20 samples and DUP/MS where appropriate (at no particular position but one set for every 10 samples). Continue with initial calibration section.

8.5.3 **Prepare the extract for analysis–**

8.5.3.1 Draw the extract up into a 10 mL pipette. Place a 0.2 µm syringe filter on the end of the pipette and push some of the sample (only enough to make a dilution – 2 mLs is plenty) through the filter into a dispo cup.

8.5.3.2 Use the filtered extract to make an appropriate dilution.

8.5.4 Autosampler Vial Loading

8.5.4.1 Rinse all sample vials and caps to remove any debris present from the manufacture.

8.5.4.2 Once the sample or standard has been placed in the sample vial, place a vial cap in the vial and use the tool to press the cap down flush with the top of the vial.

8.5.4.3 Place the loaded vials into cassettes according to the schedule created and in compliance with the analytical sequence described below. Place the holder in the autosampler.

8.5.5 Start Instrumental Analysis

8.5.5.1 Open the run screen in the PeakNet software. Load the schedule. Select Start.

8.5.5.2 Push the "auto off-set" button on the IC unit to reset the conductivity baseline.

8.5.5.3 Press "Run" on the autosampler.

8.5.6 Evaluate sample analysis

8.5.6.1 Examine solution concentrations of target analytes in the samples. If the concentration is greater than the high calibration standard, reanalyze the sample at a dilution.

8.5.6.2 Check peak integrations.

8.5.6.2.1 Where possible, all integrations should be performed consistent with integration of the corresponding calibration standards.

8.5.6.2.2 Be sure the peaks on the chromatogram and the instrument calculated concentration make sense. Sometimes the software will attempt to integrate overrange peaks and will incorrectly assign them a concentration which would be acceptable for the dilution if it was a reasonable integration.

8.5.6.2.3 On occasion, the software integrates peaks incorrectly. The sample may be reanalyzed or the analyst may use the software to correct the integration. Any manual integration or manipulation of peaks must be consistent with the calibration standards and the QC samples.

8.5.6.3 Evaluate QC samples. All samples must be bracketed by acceptable CCVs and CCBs. See Section 10 for further discussion of QC and sample acceptance and corrective action.

8.5.7 Instrument Shut Down –

8.5.7.1 Take the daily readings. Then turn the auto offset & cell to off and the pump to stop.

8.5.7.2 Turn the gas and air off to each IC individually by turning the small valve handles perpendicular to the gas flow direction.

8.5.7.3 Vent the eluent first, leave the cap very loose, and then ASAP vent the suppressor. (Vent the suppressor by slowly opening both jugs. The

suppressor is acidic, so use care. Wear face shield and cover the jugs with a plastic bag for added protection).

8.5.7.4 Take the flow restrictor off of the suppressor drain line and plug both the eluent and suppressor drain lines.

8.5.7.5 After the last IC is shut off, turn both the gas and air yellow handles to the right.

8.6 Troubleshooting –

8.6.1 Rinsing the IC pump and valves. This should be done weekly, preferably Friday night or Saturday.

8.6.1.1 Disconnect the column from the valve. Plug the column with one of the solid plugs so that it doesn't dry out.

8.6.1.2 Attach the old column to the valve (the old column is in the IC "tool drawer" in the box on the left, behind the filters, B-cups, etc. Get the syringe then, too. It has to have the orange union fitting attached to its tip) Place the tube at the end of the column in the graduated cylinder.

8.6.1.3 Disconnect the eluent line, and plug it up, because it will continue to siphon all over you if you don't. Keep the brown-colored union fitting attached to the blue-colored tubing that leads to the pump heads.

8.6.1.4 Fill the carboy labeled "DI" about halfway with DI (rinse it once or twice first). Put the carboy back in the rack and feed the long tubing to the side of the IC. Attach the syringe to the fitting at the end of the tubing and pull the DI into the syringe to get the siphon going. When it is going, detach it from the syringe and attach it to the brown-colored union fitting attached to the blue-colored tubing that leads to the pump heads. Be sure to allow some of the water dribbling out of the DI carboy tubing to fill up any lost liquid in the brown-colored union fitting, so that you won't (hopefully) have to prime the pump.

8.6.1.5 Now you can turn on the pump. The DI should start flowing out the old column. Let it go for at least 15 minutes, after which time it can be turned off and you can go home.

8.6.1.6 As per Dionex Tech Support, this is to be done only every 6 months: While the DI is pumping through the pump & valves, lubricate the pump by opening up the pump drawer about 2 inches, exposing the pump motor housing. There is a little port in the front of the motor, with yellow grease in it. Attach the grease syringe (located in the cupboard below the IC) and squirt in 0.1 mL of grease (Dionex P/N 39440).

8.6.2 To re-configure back to operation mode:

8.6.2.1 Take off the DI carboy.

8.6.2.2 Attach the filled eluent carboy to the brown-colored union fitting after having starting the siphon, etc.

8.6.2.3 Allow the eluent to pump through the old column until you are sure that all DI has been displaced. Check with pH paper, or allow to pump >8-10 minutes.

8.6.2.4 Re-attach the valve to the guard column/analytical column.

8.6.3 Nightly: Release gas pressure in eluant/suppressor bottles and cap both waste ports. Fill in the daily log, recording Date, Column ID, Helium inlet pressure, System backpressure, Eluant pressure, Detector Background, and Reagent flow.

8.6.3.1 The incoming pressure of the Helium carrier is checked (should be approx. 17 psi.)

8.6.3.2 The system pressure is checked (usually around 1500 psi.).

8.6.3.3 The background of the detector should be around 22-24 µs.

8.6.3.4 The flow rate of the suppressor coming from the waste line should be 3-4 mL per minute.

8.6.4 Maintenance log – Document all preventive maintenance, as well as instrument repair, in the appropriate instrument maintenance log. Most routine maintenance and troubleshooting are performed by CAS staff. Other maintenance or repairs may, or may not require factory service, depending upon the nature of the task. Any maintenance performed by outside services must also be documented – either through notes in the log or through documents provided by the service. The log entries will include the date maintenance was performed, symptoms of the problem, serial numbers of major equipment upgrades or replacements. The datafile name of the first acceptable run after maintenance is to be documented in the maintenance log.

8.7 Data Acquisition, Calculations, and Data Reduction Requirements

8.7.1 The results which are printed on the instrument report will be adjusted for any dilution made at the instrument. Further adjustment for initial weight and final volume will be made separately. The final multiplication by 0.3338 (sulfur is 33.38% of sulfate by molecular weight) will be done by StarLIMS.

8.7.2 Data will be reviewed by the analyst and a qualified peer using the Data Quality Checklist (attached) and validated by supervisor.

8.7.3 All sample data and QC data, including calibration verification must reference the name (date or filename) of the ICAL on the raw data report

8.8 Computer Hardware and Software

8.8.1 StarLIMS v.6.11.a
8.8.2 Personal Computer running Dionex PeakNet v5.1

9 DATA AND RECORDS MANAGEMENT

9.1 **Responsibilities** - It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

9.2 **Data Flow** – Samples are entered by the Project Manager into StarLIMS on a Personal Computer running on a Novell Network. On the day that the samples are received the samples appear on a daily log printed from this computer system. The Metals Prep analyst prepares a benchsheet, digests the samples and turns the samples and digest sheet over to the IC analyst. The samples are analyzed for sulfate using PeakNet software. The results are printed and hand entered into StarLIMS. StarLIMS makes the final calculations and the results are printed for data review. When the results are approved, the StarLIMS is used for reporting, and invoicing.

9.3 Data Review - Data will be reviewed by the IC analyst and a qualified peer using a Data Review Checklist (attached) and validated by a supervisor.

10 QA/QC REQUIREMENTS

10.1 Laboratory Control Standards (LCS)

10.1.1 An LCS must be run daily and once every 20 samples.

10.1.2 The LCS must be within 10% of the true value.

10.1.3 If the LCS is outside the acceptance criteria stop the run, correct the problem and reanalyze the LCS. Exception: if the LCS recovery is high and sample results less than the reporting limit, analysis may continue and data may be reported.

10.2 Method Detection Limits (MDL)

MDLs should be performed every 6 months, when a new operator begins work or whenever there is a significant change in the background or instrument response. The result of the MDL must be less than the PQL. If it is not, correct the problem and do another MDL study or raise the PQL. See 40 CFR Part 136 Appendix B.

10.3 Initial and Continuing Calibration Verification (ICV/CCV)

10.3.1 An ICV is analyzed immediately after the standards. The ICV must be 90-110% of the true value or the curve may not be used.

10.3.2 A CCV is analyzed every 10 samples.

10.3.3 All CCVs must be within 10% of the true value. If the CCV is not in control, correct the problem, obtain a compliant CCV and reanalyze all samples bound by the non-compliant CCV. Recalibrate if necessary. Exception: if the CCV recovery is high and sample results are less than the reporting limit, analysis may continue and data may be reported.

10.4 Continuing Calibration Blanks (CCB)

10.4.1 A CCB must be analyzed every 10 samples immediately following the CCV.

10.4.2 All CCB's must be less than the PQL. If the CCB is above the PQL, correct the problem and obtain a compliant CCB following a compliant CCV. Reanalyze samples bound by non-compliant CCB. Recalibrate if necessary. Exception: If there is blank contamination and the sample results are less than the reporting limit, analysis may continue and data may be reported.

10.5 Matrix Spikes (MS)

10.5.1 A matrix spike must be analyzed once every 10 samples. Do not choose field blanks for the analysis of MS.

10.5.2 The matrix spike should be within the lab-generated limits of 69-120% for waters and 70-130 % for soils. If it is not, note the outlying recovery in the case narrative. If the MS is out and the LCS is in, matrix interference is assumed and the batch is acceptable. It is recommended that the MS be reanalyzed to confirm the outliers, however it is not required.

10.6 Duplicates (DUP)

10.6.1 A DUP must be analyzed every 20 samples. The DUP is regularly analyzed every 10 samples since the MS must be analyzed every 10 samples. Do not choose field blanks for analysis of DUP.

10.6.2 The acceptance criteria for a DUP is less than 20% RPD or ± the reporting limit if the sample is less than 5 times the reporting limit.

10.6.3 If a DUP is outside of the acceptance criteria, reanalyze to confirm and flag with an asterisk (estimated).

11 REFERENCES

- Method 300.0, *Methods for the Determination of Inorganic Substances in Environmental Samples*, EPA/600/R-93/100 Revised August 1993.
- Method 4110 B in *Standard Methods for the Examination of Water and Wastewater*, 18th Ed., 1992.
- NELAC 2002 Standard
- 40CFR Part 136 Appendix B

Ion Chromatography Analysis Training Plan

Procedure:_____

SOP:_____ Revision:_____ Date:_____

Trainee:_____

1. Read SOP Trainer:____ Trainee:____ Date:____

2. Demonstrated understanding of the scientific basis of the analysis including:
   -column separation, retention time
   -supressor and eluent functions
   -method of detection
   -Correlation co-efficients and results based on calculated curves
   Trainer:____ Trainee:____ Date:____

3. Demonstrated familiarity with related SOPs
   -ADM-BATCHSEQ -ADM-PCAL -ADM-SIGFIG
   -ADM-DATAENTRY -ADM-DIL -ADM-SPSR
   -ADM-MDL -ADM-DREV -ADM-TRANDOC
   Trainer:____ Trainee:____ Date:____

4. Observe performance of SOP
   -sample preparation (soil, water, other matrices)
   -standard and reagent prep and documentation – including pipet(s) used
   -IC start-up and warm-up procedures
   -software use, entering sample IDs in analytical sequence
   -sample dilution guidelines (1/10 or more unless F, OPO4; 1/50 or more for leachates; other nasties; use of historical data)
   -holding times
   -use and loading of vials (filter if necessary, no air in tubes)
   -use and loading of autosampler
   -sample analysis including:
      -calibration
      -software command of instrument
      -recognition of normal vs. abnormal peaks
         -linear range
         -manual integration
      -use of QC samples and QC criteria
   -IC instrument logbook use
   -data reduction, reporting, and review
   Trainer:____ Trainee:____ Date:____

5. I have read, understood and agree to perform the most recent version of the SOP:

   Signature:_____ Date:_____

6. Perform SOP with supervision
   - *including all items in 4.*
   Trainer:____ Trainee:____ Date:____

7. Independent performance of the SOP
   -*all of the item listed in 4*
   -IDC (4 mid-range standards performed before client samples are analyzed)
   -attach IDC certificate, raw data, and summary spreadsheet.
   Trainer:____ Trainee:____ Date:____

Columbia Analytical Services, Inc.
An Employee-Owned Company

WET CHEMISTRY
DATA QUALITY CHECKLIST

Analysis:_____

Date: _____

Yes	No	NA			Yes	No	NA
☐	☐	☐	1.	**Holding Times met method requirements?**	1. ☐	☐	☐
☐	☐	☐	2.	**ICAL met method requirements?**	2. ☐	☐	☐
☐	☐	☐	3.	**ICV acceptable?**	3. ☐	☐	☐
☐	☐	☐	4.	**CCVs acceptable? Analyzed per 10 samples?**	4. ☐	☐	☐
☐	☐	☐	5.	**CCBs acceptable? Analyzed per 10 samples?**	5. ☐	☐	☐
☐	☐	☐	6.	**Method Blank results <RL?**	6. ☐	☐	☐
☐	☐	☐	7.	**LCS recoveries within QC limits?**	7. ☐	☐	☐
☐	☐	☐	8.	**All reported sample concentrations within LR?**	8. ☐	☐	☐
☐	☐	☐	9.	**MS recoveries within QC limits?**	9. ☐	☐	☐
☐	☐	☐	10.	**Duplicate RPD within QC limits?**	10. ☐	☐	☐
☐	☐	☐	11.	**Dilution factors verified and calculated correctly?**	11. ☐	☐	☐
☐	☐	☐	12.	**Bench Sheet complete, initials, date, and time:**	12. ☐	☐	☐
☐	☐	☐		•Are standards and reagents traceable?	☐	☐	☐
☐	☐	☐		•Is unused space on the sheet crossed out?	☐	☐	☐
☐	☐	☐		•Pipette ID referenced?	☐	☐	☐
☐	☐	☐	13.	**All applicable Log Books filled in?**			
			14.	**Manual data entry to LIMS correct? Date? Time?**	14. ☐	☐	☐

Analyst:_____ Peer Review:_____

Date:_____ Date:_____

COMMENTS:
****Comments must be provided for any items noted above as "No"**

STANDARD OPERATING PROCEDURE

for

**METALS DIGESTION,
SOILS, SEDIMENTS, AND SLUDGE FOR ICP ANALYSIS
FOR INDIANA PINES SITE**

SOP No.: MET-3050pines

Revision: 0

September 28, 2004

Approved by: _____ Supervisor — 9/28/04 Date

_____ QA Coordinator — 9/28/04 Date

_____ Laboratory Manager — 9/28/04 Date

1 Mustard Street, Suite 250
Rochester, New York 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: _____ Date: _____
Initials: _____ Date: _____
Initials: _____ Date: _____

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1 SCOPE AND APPLICABILITY

This SOP uses EPA SW-846 Method 3050B for the digestion of soils, sludges, or sediments for analysis by ICP. As stated in the EPA method, "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." This SOP was written specifically for the Indiana Pines Site.

2 SUMMARY OF METHOD

A representative aliquot of sample is digested in nitric acid and hydrogen peroxide. Hydrochloric acid is used as a final reflux acid.

3 DEFINITIONS

3.1 **Laboratory Duplicates** - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of duplicates indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.2 **Laboratory Control Sample Soil (LCSS)** - An aliquot of a soil to which known quantities of the method analytes are added. The LCSS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

3.3 **Matrix Spike** - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The matrix spike is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.

3.4 **Preparation Blank (PB)** - An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The PB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus.

3.5 **Digestion Batch** - A digestion batch is no more than 20 samples of the same matrix digested as a unit per day.

4 HEALTH AND SAFETY WARNINGS

Nitric and Hydrochloric acids are extremely corrosive. Care should be taken while working with these chemicals. Personal protective equipment including safety glasses (with side shields), gloves, and lab coat shall be worn when handling samples or reagents.

5 CAUTIONS

Antimony is easily lost by volatilization. Do not boil the digestate.

6 INTERFERENCES

Use more sample for those samples with high moisture content to meet detection limits.

7 PERSONNEL QUALIFICATIONS

At a minimum, personnel must have attained at least a 2-year degree in a science-related field and have successfully completed an Initial Demonstration of Capability and the Training Plan Form (attached). Training and Demonstration of Capability are in accordance with NELAC 2002 standard.

8 EQUIPMENT AND SUPPLIES

8.1 Eppendorf Pipettors
8.2 Funnels
8.3 Mortar and pestle
8.4 Tongue depressors
8.5 Filter paper
8.6 Hot Block Digestor with ETR-3200 Controller by Environmental Express, LTD.
8.7 Graduated block digestor cups
8.8 Block Digestor Filters.
8.9 CPI MOD Block Digestor

8.10 Reagent water - ASTM Type II deionized water.

8.11 Concentrated nitric acid (Baker Instra-Analyzed 69-70%): Store at room temperature in the dark in the original container or in glass. Expires per manufacturer's indications or one year from receipt if no indication is given.

8.12 Concentrated hydrochloric acid (Baker Instra-Analyzed 36.5-38%): Store at room temperature in the original container or in glass. Expires per manufacturer's indications or one year from receipt if no indication is given.

8.13 Hydrogen peroxide (30%) - H_2O_2. Purchased commercially. Should be demonstrated to be free of impurities at levels which would interfere with sample determinations. Store at room temperature in the original container. Expires upon manufacturer's indications or 1 year from receipt if no indication is given.

8.14 ERA Soil Laboratory Control Sample (LCSS) - Concentrations and Performance Acceptance Limits distributed through vendor. Store at room temperature. Expires upon manufacturer's indications or 1 year from receipt if no indication is given.

8.15 Metals spiking solutions – Purchased commercially. See Table 1. Store at room temperature. Stocks expire upon manufacturer's indications or 1 year from receipt, whichever is sooner. Solutions prepared from stocks expire 6 months from preparation.

9 PROCEDURES

9.1 Sample Collection – Collect samples in purchased, certified clean glass or plastic.

9.2 Sample Handling and Preservation – Analyze samples within 6 months of sample collection. Store samples in a refrigerator or at room temperature. Sample receiving, handling, storage, and custody procedures are in accordance with NELAC 2002 Standard.

9.3 Sample Preparation

9.3.1 Set the temperature on the Block Digestor to a temperature that brings the sample temperature to 90-95°C without boiling.

9.3.2 The Hot Block is on a timer which can be set to turn on and off whenever necessary. To set timer press the timer button and choose the days M-F (Monday through Friday). Then choose the hour and minutes to start and stop the Block Digestor.

9.3.3 Label graduated hot block digestor sample cups with appropriate sample IDs for digestion.

9.3.4 Mix the sample thoroughly to achieve homogeneity using a tongue depressor or the mortar and pestle.

9.3.5 Weigh (to the nearest 0.01g) 1.00g to 1.50g of sample into labeled digestor sample cup. For sludges and sediments that have a high moisture content, use more sample. The goal is to use about 1g of dry weight sample. At this point add the appropriate spiking solutions (see Table 1) directly onto the designated spike sample prior to addition of reagents.

9.3.6 Unless otherwise specified by project requirements, the addition of acid should be as follows: Add 10ml of 1:1 HNO_3 and 1.5 mL of 1:1 HCl, cover with reflux cap and reflux for 15 minutes. The sample temperature should be 90-95°C. Allow the sample to cool, then add 5ml of concentrated HNO_3, cover and reflux for 30 minutes. Repeat the addition of 5ml of HNO_3 and reflux to 5 mLs. Do not allow the sample to go to dryness. CAUTION: Do not boil. Antimony is easily lost by volatilization.

9.3.7 Cool the sample and add 2ml of DI and 3ml of 30% H_2O_2. Cover and heat to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessive effervescence. Heat until effervescence subsides and cool the sample cup.

9.3.8 If the effervescence does not subside, add 3 mLs of hydrogen peroxide with warming to each of the samples (including blanks and LCSs) in the batch. If necessary, continue to add 30% H_2O_2 in 1ml aliquots with warming until the effervescence is minimal, or until the general sample appearance is unchanged. Do not add more than 10ml of 30% H_2O_2.

9.3.9 Add 10 mL 1:1 HCL.

9.3.10 Cover and reflux the samples for 15 minutes without boiling. Allow to cool.

9.3.11 Rinse filters with 1:1 nitric acid and DI.

9.3.12 All samples are diluted to 100 mLs with DI. Quantitatively transfer the digestate to a graduated cylinder by pouring the sample through a prepared filter into the cylinder and rinsing the beaker and reflux cap with DI into the filter. Rinse the filter with DI. Bring to volume with DI. Pour into a labeled B-cup.

9.4 **Sample Analysis** – Give digested samples and a copy of the prep sheet to the ICP analyst. Analyze according to MET-6010Bpines.

9.5 **Troubleshooting** - All hoods in the Metals Prep Lab are wiped down once a week with DI water. The tops of all digestion hot plates are wiped down daily.

9.6 **Data Acquisition, Calculations and Data Reduction Requirements**

Digestion logs are used to record all sample volumes, spike volumes, etc. The Manufacturer's lot number for the reagents used are added to the digestion log (see attached digestion log benchsheet).

10 DATA AND RECORDS MANAGEMENT

10.1 Responsibilities - It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

10.2 Data will be reviewed after ICP analysis according to MET-6010Bpines.

11 QA/QC REQUIREMENTS

11.1 Each day, digest one laboratory control sample (LCS) per digestion batch, or per 20 samples, or per EPA SDG group, whichever is more frequent. Use the appropriate solid laboratory control sample (LCSS) for soils analysis.

11.2 Each day, digest one blank per digestion batch, or per 20 samples, or per EPA SDG group, whichever is more frequent. Use D.I. water and follow the digestion procedures.

11.3 Each day, prepare one duplicate and one spiked sample with each digestion batch, or per twenty samples, or per EPA SDG group, whichever is more frequent. At times, specific samples will be assigned as duplicates of spikes depending on client requirements.

11.4 Matrix spikes are prepared by adding the appropriate volume of spiking solution (See Table 1).

11.5 See MET-6010Bpines for applicable QC limits and corrective action.

12 REFERENCES

"Test Methods For Evaluating Solid Waste, Physical/Chemical Methods". EPA SW846, Third Edition, December 1996.

NELAC, 2002 Standard.

Table 1 Spiking Concentrations for LCS and MS Samples

SPIKE SOLUTION A			1.00ml Spk A	to Final Vol of 100ml
Metal	*Conc. (ug/mL)*		*Metal*	*Conc. (ug/mL)*
AL	200		NI	50
AS	4		SE	1
BA	200		AG	5
BE	5		TL	200
CD	5		V	50
CR	20		ZN	50
CO	50		B	100
CU	25		CA	200
FE	100		MG	200
PB	50		NA	2000
MN	50		K	2000

SPIKE SOLUTION B			1.00ml Spk B	to Final Vol of 100ml
Metal	*Conc. (ug/mL)*		*Metal*	*Conc. (ug/mL)*
SB	50		TI	50
MO	50		-	-

INDIVIDUAL METALS	0.10ml Spk. to Final Volume of 100ml		INDIVIDUAL METALS	0.5ml Spk. to Final Volume of 100ml
Metal	*Conc. (ug/mL)*		*Metal*	*Conc. (ug/mL)*
SE	1000		SN	1000

CAS-Rochester ICP Soil Digestion Log 6010B/846 // 200.7/136 // ASP/CLP4.1

Batch ID:

Analyst: _____ **Date:** _____

Spike Witness / Lot Approval: _____

Batch Temp:

Prep Method: SW846 3050 // CLP

Digest: Initial // Redigest of: _____ **Report Type:** Routine // ASP // Pkg5

	Submission / Order #	Initial Wgt. (g)	Final Vol (ml)	Initial Color / Texture	Final Color / Clarity	Metals	Spike Vol (ml)
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							
21							
22							
23							
24							

Spiking Standards / Reagent Lot #:

Spike A,B: _____ Spike #4: _____

TCLP Spk: _____ TCLP Bs: _____

Se Std: _____ Sn Std: _____

HNO3: _____ HCL: _____

H2O2: _____ LCSS: _____

Color / Clarity Key:

Color: C = Colorless ; Y = Yellow ; B = Brown
BL = Black ; G = Grey ; W = White

Clarity: CDY = Cloudy ; CLR = Clear ; OP = Opaque

Texture: F = Fine ; M = Medium ; CS = Coarse ; NAQ = Non Aqueous

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Comments: _____

STANDARD OPERATING PROCEDURE

for

DETERMINATION OF METALS AND TRACE ELEMENTS BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP) FOR INDIANA PINES SITE

SOP No.: MET-6010BPINES

Revision: 1

September 29, 2004

Approved by: _____ Department Supervisor — 9/29/04 Date

_____ Laboratory Manager — 9/29/04 Date

_____ QA Coordinator — 9/29/04 Date

1 Mustard Street, Suite 250
Rochester, New York 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: _____ Date: _____
Initials: _____ Date: _____
Initials: _____ Date: _____

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1. SCOPE AND APPLICABILITY

1.1. This SOP uses EPA SW-846 Method 6010B for the determination of trace elements, including metals, in solution using Inductively coupled plasma-atomic emission spectrometry (ICP-AES). The method is applicable to all of the elements listed in Table 1. All matrices, including ground water, aqueous samples, TCLP and EP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis.

1.2. Detection limits, sensitivity, and the optimum and linear concentration ranges of the elements can vary with the wavelength, spectrometer, matrix and operating conditions. The Method Reporting Limits (MRL) are listed in Table 1. The reported MRL may be adjusted if required for specific project requirements, however, the capability of achieving other reported MRLs must be demonstrated. Results may be reported to the Instrument Detection Limits (IDLs) upon request.

1.3. This SOP was modified specifically for the Indiana Pines site project.

2. SUMMARY OF METHOD

2.1. Samples are digested according to one of the proper metals digestion methods listed in SW-846.

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. Background 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 (discussed later) should also be recognized and appropriate corrections made.

3. DEFINITIONS

3.1. Calibration Blank - A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to calibrate the ICP instrument.

3.2. Calibration Standard (CAL) - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration

3.3. Dissolved Analyte - The concentration of analyte in an aqueous sample that will pass through a 0.45 µm membrane filter assembly prior to sample acidification.

3.4. Instrument Detection Limit (IDL) - The concentration equivalent to the analyte signal which is equal to three times the standard deviation of a series of 10 replicate measurements of the calibration blank signal at the same wavelength.

3.5. Initial/Continuing Calibration Verification Solution (ICV/CCV) - A solution of method analytes, used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.6. Internal Standard - Pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component

3.7. Laboratory Duplicates - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of duplicates and indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.8. Laboratory Control Sample (LCS) - An aliquot of to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

3.9. Matrix Spike - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The matrix spike is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.

3.10. Preparation Blank (PB) - An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The PB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus.

3.11. Linear Range - The concentration range over which the instrument response to an analyte is linear.

3.12. Method Detection Limit (MDL) - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

3.13. Plasma Solution - A solution that is used to determine the optimum height above the work coil for viewing the plasma.

3.14. Interference Check Solution (ICS) - A solution of selected method analytes of higher concentrations which is used to evaluate the procedural routine for correcting known interelement spectral interferences with respect to a defined set of method criteria.

3.15. Method Reporting Limit Standard (MRL) – Standard prepared with a known concentration of elements to check accuracy at the low end of the curve.

3.16. HLCCV1 – A standard prepared at the bench at a high concentration to encompass the range of the samples being analyzed. This standard is used to assess accuracy at the high end of the linear range.

3.17. HLCCV2 – A standard prepared slightly higher than the calibration range for metals.

3.18. Batch – a group of no more than 20 field samples digested or analyzed together on the same day with the same reagents.

4. HEALTH AND SAFETY WARNINGS

4.1. Corrosives - Because all samples and standards are diluted in 2% HNO_3 and 5% HCl, there is a danger of exposure to corrosives, sufficient care must be taken in handling these solutions. Safety glasses must be worn while preparing and handling the solutions.

4.2. High Voltage - The power unit supplies high voltage to the RF generator which is used to form the plasma. The unit should never be opened. Exposure to high voltage can cause injury or death.

4.3. UV Light - The plasma when lit is a very intense light, and must not be viewed with the naked eye. Protective lenses are in place on the instrument. Glasses with special protective lenses are available.

4.4. When the nature of the sample is either unknown or is known to be hazardous, acidification should be done in a well ventilated area or fume hood

5. INTERFERENCES

There are several types of interferences by the ICP's: Spectral interferences can be from an overlap of spectral lines, background points or background from line emissions of high concentration elements. Physical interferences are effects associated with the sample introduction process, example high dissolved solids buildup on the nebulizer tip. Chemical interferences caused by the sample matrix itself. IEC's aid in eliminating some of these interferences. IECs are interelement correction factors that the instrument uses to compensate for spectral overlap when analyzing samples with complex spectra. Refer to Method 6010B Section 3.0 or Method 200.7 Section 4.0 for more detail and suggested procedures to correct and adjust the instrument due to interferences.

6. PERSONNEL QUALIFICATIONS

At a minimum, personnel must have attained at least a 4-year degree (or 2-yr degree plus one year experience) in a science-related field and have successfully completed an Initial Demonstration of Capability and the Training Plan Form (attached). Training and Demonstration of Capability are in accordance with NELAC 2002 standard.

7. EQUIPMENT AND SUPPLIES

7.1. ICP- Perkin Elmer Optima 3000XL - Inductively coupled argon plasma emission spectrometer (ICP) equipped with the following:

7.1.1. Computer-controlled emission spectrometer with background correction.

7.1.2. Mass flow controller for argon nebulizer gas supply.

7.1.3. Peristaltic pump.

7.1.4. Autosampler.

7.1.5. Argon gas supply - high purity.

7.2. Volumetric flasks, class A .

7.3. Trace metals grade chemicals shall be used in all tests.

7.3.1. Hydrochloric acid (conc), HCl. Purchased commercially. Store at room temperature. Expires three years from receipt or upon manufacturer's indications, whichever is sooner.

7.3.2. Hydrochloric acid (1:1), HCl. Add 500 mL concentrated HCl to 400 mL water and dilute to 1 liter in an appropriately sized beaker. Store at room temperature. Expires one year from preparation.

7.3.3. Nitric acid (conc), HNO_3. Purchased commercially. Store at room temperature. Expires three years from receipt or upon manufacturer's indications, whichever is sooner.

7.3.4. Nitric acid (1:1), HNO_3. Add 500 mL concentrated HNO_3 to 400 mL water and dilute to 1 liter in an appropriately sized beaker. Store at room temperature. Expires one year from preparation.

7.4. Reagent Water. All references to water in the method refer to DI Type II water unless otherwise specified. Reagent water will be interference free.

7.5. All standards are prepared from NIST traceable stock standard solutions. Manufacturers expiration dates are used to determine viability of standards. Preparatory procedures for standards and QC solutions vary between instruments due to the working ranges. All preparatory information for the QA/QC samples are provided in Appendix I.

7.5.1. Mixed Calibration Standards are prepared by combining appropriate volumes of the stock solutions in volumetric flasks. Matrix match with the appropriate acid and dilute to 100ml with water. Calibration standards should be verified using a second source quality control sample (LCS, ICV, or CCV). Calibration standards should be stored at room temperature in glass volumetric flasks with a shelf-life of 7 days.

7.5.2. Initial and Continuing Calibration Verification (ICV and CCV) Standards are prepared by combining compatible analytes at concentrations equivalent to the midpoint of their respective calibration curves. The ICV and CCV standards should be prepared from a separate source independent from that used in the calibration standards. ICV / CCV standards should be stored at room temperature in glass volumetric flasks with a shelf-life of 48 hours.

7.5.3. MRL Standards are prepared to contain known concentrations of elements at or near the Method Reporting Limit. MRL standards should be stored in plastic containers with a shelf-life of 6 months.

7.5.4. Interference Check Solutions A and AB are prepared to contain known concentrations of interfering analytes that will provide an adequate test of the correction factors. ICSA / ICSAB standards should be stored in plastic containers with a shelf-life of 6 months.

7.5.5. Laboratory Control Sample and Matrix Spike are purchased as custom mixes stored in plastic containers with a shelf-life of 6 months at the concentrations recommended in the method. Certificates of analysis are attached in Appendix I. Each sample, up to 100 mL, is spiked with 1.0 ml of spike solution.

7.6. Blanks

7.6.1. Method Blanks must contain all the reagents and in the same volumes as used in the preparation of samples. The method blanks must be carried through the complete procedure and contain the same acid concentration in the final solution as the samples.

7.6.2. The Calibration Blank is prepared by acidifying reagent water to the same concentrations of acid found in the standards and samples.

7.7. Reagent Receiving Log

The manufacturer, lot number, standard /reagent name, concentration, date received and expiration date are recorded in a reagent log.

8. PROCEDURE

8.1. Calibration and Standardization

Calibration is accomplished daily using 3 calibration standards and a blank for each element using the internal standard technique. See Sample Analysis section for more information.

8.2. Sample Collection

Containers may be glass or plastic. Samples are cooled with ice to be shipped to the laboratory.

8.3. Sample Handling and Preservation

8.3.1. Solid samples require no preservation prior to analysis other than storage at 0-6°C. Samples are analyzed within 6 months of collection.

8.3.2. Aqueous samples are acid preserved with (1+1) nitric acid to pH <2. Samples are analyzed within 6 months of sample collection.

8.3.3. Samples are checked upon receipt for all the elements listed in the Sample Acceptance Policy found in NELAC 2002 Standard.

8.3.4. For the determination of the dissolved elements, filter the sample through a 0.45 µm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. (Glass or plastic filtering apparatus are recommended to avoid possible contamination. Only plastic apparatus should be used when the determinations of boron and silica are critical.) Use a portion of the filtered sample to rinse the filter flask, discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) nitric acid immediately following filtration to pH <2.

Note: When the nature of the sample is either unknown or is known to be hazardous, acidification should be done in a well ventilated area or fume hood.

8.3.5. Samples received by the ICP lab as digestates contain nitric and hydrochloric acid. Digestates are stored at room temperature in plastic B-cups.

8.3.6. Following analysis, digestates are stored until all results have been reviewed. Digestates are diluted and disposed of through the sewer system in approximately 90 days after receipt of sample.

8.4. Sample Preparation

8.4.1. Digest samples prior to analysis. Refer to the following Metals Methods found in SW-846:

- 3005A Metals Digestion, Waters, Total Recoverable and Dissolved for ICP
- 3010A Metals Digestion, Waters for ICP
- 3020A Metals Digestion, Waters for GFAA
- 3050B Metals Digestion, Soils, Sediments and Sludges for ICP and GFAA

8.5. Sample Analysis

8.5.1. Set up the instrument with proper operating parameters established as detailed below. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 45 minutes of operation prior to calibration). Operating conditions - The analyst should follow the instructions provided in Table 3.

8.5.2. Before using this procedure to analyze samples, there must be data available documenting initial demonstration of performance. The required data documents the selection criteria of background correction points; linear ranges, 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. These documented data must be kept on file and be available for review by the data user or auditor.

8.5.3. Turn on power supply for the instrument, computer, printer and light the plasma. Allow instrument to warm-up for 45-60 minutes before operation. The cooling water and the argon are on when the instrument are on.

8.5.4. Profile the instrument on a daily basis, and when maintenance is done to align it optically for both horizontal and vertical optimization in either mode. Aspirate a 10 ppm source of manganese (as recommended by the manufacturer). Choose the Tools menu/Spectrometer Control/Optimize X&Y. The instrument automatically adjusts the torch viewing position for maximum intensity.

8.5.5. Pour the 3 calibration standards, ICV/CCV standards, MRL, ICSA, and ICSAB up to 40 mL in 50 mL centrifuge tubes and add 0.80 mL of the internal standard solution. Pour all other samples, preparation blanks and laboratory control samples up to 10 mL in 15 mL centrifuge tubes and add 0.20 mL of internal standard solution. This gives an apparent concentration of 1.00 mg/L Yttrium. The Yttrium intensity is used by the instrument to ratio the analyte intensity signals for both calibration and quantitation. Cesium is used only as a stabilizer.

8.5.6. Internal standards can be added via pump and mixing block. This technique uses a solution of 10 mg/L Y and 10 mg/L Cs.

8.5.7. Following the calibration, analyze in the following sequence:

- ICV; ICB; MRL; ICSA; ICSAB; CCV; CCB;
- 10 environmental samples (including PBs and LCSs); CCV; CCB; repeat to the end of the run.....
- Last 10 samples; CCV; CCB, MRL, ICSA, ICSAB; HLCCV1; HLCCV2; CCV; CCB.

8.5.8. Rinse the system with the calibration blank solution before the analysis of each sample for one minute.

8.5.9. Samples which exceed the linear range of the instrument must be diluted and reanalyzed.

8.5.10. Method detection limits must be established 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 3-5 times the anticipated detection limit. See Table 2 for approximate wavelengths. See 40 CFR Part136 Appendix B for more information.

8.6. Troubleshooting

8.6.1. All maintenance activities are recorded in a maintenance logbook kept for each instrument. Most routine maintenance and troubleshooting is performed by CAS staff. Other maintenance or repairs may, or may not require factory service, depending upon the nature of the task. Record the analytical run filename of the first acceptable run after major maintenance in the maintenance log book. Typical preventive maintenance measures include, but are not limited to, the following items:

- Cleaning the pump tubing as needed
- Empty waste container, as needed
- Cleaning the nebulizer, spray chamber, and torch, as needed
- Replace water and vacuum filters, as needed

8.7. Data Acquisition, Calculations, and Data Reduction Requirements

8.7.1. Calculations: If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported with up to three significant figures.

8.7.2. Sample Calculation (water)

$$\text{Conc. (mg/L)} = \frac{\text{Instrument Reading (mg/L) x Final digestion volume (L)}}{\text{Initial volume (L)}}$$

8.7.3. Sample Calculation (soils)

$$\text{Conc. (mg/g)} = \frac{\text{Instrument Reading (mg/L) x Final digestion volume (L)}}{\text{Initial mass (g) x Percent Solids expressed as a decimal}}$$

8.7.4. **Matrix Spike Recovery** is calculated to determine accuracy for matrix and blank spikes using the following equation:

$$\text{Accuracy (\%REC)} = \frac{A - B}{C} \times 100$$

Where
A = Analyte total concentration from spiked sample
B = Analyte concentration from unspiked sample
C = Concentration of spike added

8.7.5. **Precision** is measured through the use of replicate sample analyses within the same batch and is expressed as the relative percent difference (RPD) between the replicate measurements.

$$\text{RPD} = \frac{|D1 - D2|}{(D1+D2)/2} \times 100$$

Where
D1 = Original Result
D2 = Duplicate Result

Report each analyte concentration to the proper significant figures in mg/L or µg/L as required.

8.8. Computer Hardware and Software

Each ICP uses a Gateway GP5-233 running the ICP WinLab v.1.42.
Metals Analytical Review and Reporting System (MARRS) v.3.2.44
StarLIMS v.6.11.a

9. DATA AND RECORDS MANAGEMENT

9.1. **Responsibilities** - It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

9.2. **Data Flow** – Samples are entered by the Project Manager into StarLIMS on a Personal Computer running on a Novell Network. On the day that the samples are received the samples appear on a daily log printed from this computer system. The Metals Prep analyst prepares a benchsheet, digests the samples and turns the samples and digest sheet over to the ICP analyst. The samples are analyzed for metals of interest using ICP software. The results are transferred to MARRS (for reporting package work) and StarLIMS for validation, reporting, and invoicing.

9.3. Data Review - Data will be reviewed by the ICP analyst and a qualified peer using a Data Review Checklist (attached) and validated by a supervisor.

10. QUALITY CONTROL AND QUALITY ASSURANCE

10.1. Instrument values are based on duplicate readings. Precision between the emission readings shall not exceed 20 %RSD. If RSD values exceed 20%, the sample reanalyzed and reported.

10.2. Preparation Blanks must be analyzed at least one PB with each batch of 20 or fewer samples of the same matrix. PB values must not exceed the MRL. Fresh aliquots of the samples must be prepared and analyzed again for affected analytes after the source of the contamination has been corrected and acceptable PB values have been obtained. If detections are greater than the MRL, the batch needs to be redigested if sample concentration is less than 5 times the concentration found in the prep blank. If the sample concentration is less than the MRL the sample does not require redigestion.

10.3. HLCCV1 – High standard used in curve and analyzed once during daily analysis. Should agree within 10% of the true value. If HLCCV1 is > 10% different the analysis is judged to be out of control and the source of the problem should be identified and resolved before continuing analysis.

10.4. HLCCV2 – standard slightly higher than calibration for some metals. Analyzed once during daily analysis. Should agree within 10% of the true value. If out of control, client data above the HLCCV1 should be re-analyzed.

10.5. ICV/CCV - Calibration Verification Standards must immediately follow each calibration, after every tenth sample, and at the end of the sample run. Initial Calibration Verification must verify that the instrument is within 10%. Continuing Calibration Verification standards must confirm the calibration within ±10% throughout the analyses. If the recovery of an analyte falls outside the required control limits, the analysis is judged to be out of control, and the source of the problem should be identified and resolved before continuing analysis. Recalibrate the instrument.

10.6. The results of the calibration blank (CCB) must be less than the MRL. If not, terminate the analysis, correct the problem, recalibrate, and reanalyze the samples effected.

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

10.8. Analyze matrix spiked and duplicate samples at a frequency of one per matrix batch (max. 20 samples). Matrix spiked and duplicate samples are brought through the entire sample preparation and analytical process.

10.8.1. The spiked sample or spiked duplicate sample recovery is to be within ± 25% of the actual value or within the documented historical acceptance limits for each matrix. Sample concentrations greater than four times the spike concentration are not valid and shall not be evaluated. If the matrix spike does not meet these criteria, analyze a Post Digestion Spike.

10.8.2. A control limit of ± 20% RPD shall be used for original and duplicate samples greater than or equal to 5X the CRDL. A control limit of ± the CRDL shall be used if either the sample or duplicate value is less than 5 times the CRDL. CRDL values are given in Table 1.

10.9. Laboratory Control Sample – verify sample preparation and analysis using reagent water spiked with a known amount of analytes of interest. Results should be within ± 20%. Outlying recoveries may indicate loss of analyte due to digestion procedures or laboratory contamination. If an LCS is found to be out of the specified limits, recalibrate and reanalyze. If the LCS remains out of the specified limits, redigestion of the entire batch should occur if the recovery is less than 80%. If the LCS recovery is greater than 120% redigest all positive results (greater than the MRL).

10.10. MRL standard- A standard at or near the MRL is analyzed at the beginning and end of each analytical run but not before the ICV. There are no limits in the 6010B method, but the CAS guideline used is +/- 50% of the true value. If the limits are not met the analysis is stopped and the instrument is recalibrated.

10.11. Interference Check Samples- The ICSA and ICSAB need to be run consecutively at the beginning and end of each analytical run. Results from the ICSA solution shall be monitored for false positive detections of analytes not present in the mix. The analyte recoveries for the AB solution must fall within 20% of the true value otherwise the run must be stopped, recalibrated and reanalyzed unless analytes are not detected in the associated samples or interferent elements are not present.

10.12. Serial Dilution Test If the analyte concentration is sufficiently high (minimally, a factor of 50 times above the IDL), an analysis of a 1:5 dilution should agree within ± 10% of the original determination. If not, a chemical or physical interference effect should be suspected and data may be flagged accordingly.

10.13. Post Digestion Spike Addition: Typically if a matrix spike does not yield acceptable results, a post-digestion spike may be added to a portion of a prepared sample, or its dilution, and should be recovered to within 75% to 125% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the IDL. If the spike is not recovered within the specified limits, a matrix effect has been confirmed.

10.14. Instrument Performance

- InterElement Correction Factors (IEC) are analyzed annually, or as needed.
- Linear Ranges (LR) are run biannually and must be ±5% of true value.
- Instrument Detection Limits (IDL) are analyzed quarterly, or as needed.
- Method Detection Limits (MDL) are analyzed annually.

11. REFERENCES

- *Test Methods For Evaluating Solid Waste, Physical/Chemical Methods.* USEPA SW-846, 3rd Edition, December 1996.
- *Methods For the Determination of Metals in Environmental Samples Supplement I.* USEPA/600/R-94/111, May 1994.
- 40 CFR Part136 Appendix B
- NELAC 2002 Standard

Metals Instrument Analysis Training Plan

Procedure:_____

SOP:_____ Revision_____ Date _____

Trainee:_____

1. Read SOP Trainer:___ Trainee:___ Date:___

2. Demonstrated understanding of the scientific basis of the analysis including:
-the chemical and physical principals behind the measurement by the instrument

Trainer:___ Trainee:___ Date:___

3. Demonstrated familiarity with related SOPs

-ADM-BATCHSEQ	-ADM-PCAL	-ADM-SIGFIG
-ADM-DATAENTRY	-ADM-DIL	-ADM-SPSR
-ADM-MDL	-ADM-DREV	-ADM-TRANDOC

Trainer:___ Trainee:___ Date:___

4. Observe performance of SOP
-standard and reagent prep and documentation - including pipet used
-instrument power up and warm-up
-instrument set-up, daily maintenance and checks
-use and loading of autosampler
-sample analysis including:
  -calibration
  -sample dilution
  -software command of instrument
  -use of QC samples and QC criteria
  -common troubleshooting
-instrument logbook use
-data reduction, reporting, and review

Trainer:___ Trainee:___ Date:___

5. I have read, understood and agree to perform the most recent version of the SOP:

Signature _____ Date _____

6. Perform SOP with supervision
- including all items in 4

Trainer:___ Trainee ___ Date:___

7. Independent performance of the SOP
-all of the items listed in 4
-IDC (4 mid-range standards performed before client samples are analyzed)
-attach IDC certificate, raw data, and summary spreadsheet.

Trainer:___ Trainee:___ Date:___

TABLE 1

Analyte	*MRL Water*	***MRL Soil***	*Typical IDL*
	mg/L	***ug/g***	***ug/L***
Silver	0.010	1.00	0.632
Aluminum	0.100	10.0	6.57
Arsenic	0.0100	50.0	6.89
Boron	0.200	20.0	37.3
Barium	0.0200	2.00	12.2
Beryllium	0.0050	0.500	0.26
Calcium	0.500	50.0	167
Cadmium	0.0050	0.500	0.489
Cobalt	0.0500	5.00	3.03
Chromium	0.0100	1.0	1.81
Copper	0.0200	2.00	3.02
Iron	0.100	5.00	44.1
Potassium	2.00	100	857
Lithium	0.200	20.0	23.9
Magnesium	0.500	50.0	124
Manganese	0.0100	1.0	1.78
Molybdenum	0.0250	2.50	3.08
Sodium	0.500	50.0	193
Nickel	0.0400	4.00	3.92
Lead	0.00500	5.00	1.29
Antimony	0.0600	10.0	3.72
Selenium	0.00500	50.0	12.5
Silicon	1.00	100	68.7
Strontium	0.100	10.0	5.38
Tin	0.500	100	15.8
Titanium	0.0500	5.00	3.15
Thallium	0.0100	30.0	7.77
Vanadium	0.0500	5.00	2.74
Zinc	0.0200	1.0	2.47

Table 2

Recommended Wavelengths and Instrument Specifications

Suggested wavelengths are listed below:

Analyte	Wavelength
Ag Silver	328.068
Al Aluminum	308.215
B Boron	249.773
Ba Barium	233.527
Be Beryillium	234.861
Ca Calcium	430.253
Cd Cadmium	226.502
Co Cobalt	228.616
Cr Chromium	267.716
Cu Copper	324.754
Fe Iron	238.863
Li Lithium	610.364
Mg Magnisium	279.079
Mn Manganese	257.610
Mo Molybdenum	202.030
Na Sodium	330.237
Ni Nickel	231.604
Pb Lead	220.353
Sb Antimony	206.833
Si Silicon	252.851
Sn Tin	189.933
Sr Strontium	421.552
Ti Titanium	334.941
V Vanadium	292.402
Zn Zinc	206.191
Y Yittrium	371.030

Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. Because of differences among various makes and models of spectrometers, specific instrument operating conditions cannot be provided. The instrument operating conditions herein are recommended based upon manufacturer's instrument manuals.

Table 3
Operating Conditions

Current Method Operating Conditions are as follows, these conditions may vary to optimize the instrument for different analyses:

Parameter	Radial Plasma	Axial Plasma
Resolution	Fixed	Fixed
Purge Gas Flow	Normal	Normal
Read Time (min/max sec.)	5/20	5/50
Replicates	2	2
Plasma (L/min)	15	15
Aux. (L/min)	0.5	0.3
Nebulizer Flow (L/min)	0.72	0.56
Power (watts)	1300	1450
Viewing Height (mm)	15	15

APPENDIX I

PREPARATION PROCEDURES FOR STANDARDS AND QC

RADIAL OPTIMA #1 CALIBRATION STANDARD #1 (Standard is prepared weekly or as necessary)

	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
PQL Std 1	AL		200	0.100	100	0.200	2%HNO3		A				
	BE		5			0.0050	5%HCl		B				
	CO		50			0.0500			C				
	MG		5000			5.00			D				
	SE		5			BELOW			E				
	V		50			0.0500			F				
	SB		60			0.0600			G				
	CD		5			0.0050			H				
	CU		25			0.0250			I				
	MN		15			0.0150			J				
	AG		10			0.0100			K				
	ZN		20			0.0200			L				
	AS		10			BELOW			M				
	CA		5000			5.00			N				
	FE		100			0.100			O				
	NI		40			0.0400			P				
	NA		5000			5.00			Q				
	BA		200			0.200			R				
	CR		10			0.0100			S				
	PB		5			BELOW			T				
	K		5000			5.00			U				
	TL		10			BELOW			V				
PQL Std 2	B		200	0.100		0.200			W				
	MO		25			0.0250			X				
	SN		500			0.500			Y				
	TI		50			0.0500			Z				
Single std	PB	1/10-	100	0.050		0.055			AA				
	AS		1000	0.010		0.110			BB				
	SE		1000	0.010		0.105			CC				
	TL		1000	0.010		0.110			DD				
	SR		1000	0.010		0.100			EE				

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RADIAL OPTIMA #1- CALIBRATION STANDARD #3 / HLCCV1 (Standard is prepared weekly or as necessary)
(CALIBRATION STANDARD #2 IS A 1/5 DILUTION OF THIS STANDARD)

	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
Cal Std 1	CA		5000	4.00	200	100	2%HNO3		A				
	MG		5000			100	5%HCl		B				
	K		5000			100			C				
	NA		5000			100			D				
Cal Std 2	AG		100	2.00		1.00			E				
	CR		100			1.00			F				
	MN		150			1.50			G				
	NI		400			4.00			H				
	ZN		200			2.00			I				
Cal Std 3	AL		2000	2.00		20.0			J				
	BA		2000			20.0			K				
	BE		50			0.500			L				
	CO		500			5.00			M				
	CU		250			2.50			N				
	FE		1000			10.0			O				
	V		500			5.00			P				
Cal Std 4	AS		100	8.00		4.00			Q				
	CD		50			2.00			R				
	PB		50			2.00			S				
	SE		50			2.00			T				
	TL		100			4.00			U				
Single Metals	SB		1000	2.00		10.0			V				
	SN		1000	2.00		10.0			W				
	B		1000	1.00		5.00			X				
	MO		1000	1.00		5.00			Y				
	TI		1000	1.00		5.00			Z				
	SR		1000	1.00		5.00			AA				

RADIAL OPTIMA #1 ICV/CCV STANDARD (Standard is prepared daily.)

	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot #	Pipet ID
Cal Std 1	CA		5000	2.00	200	50.0	2%HNO3		A			
	MG		5000			50.0	5%HCl		B			
	K		5000			50.0			C			
	NA		5000			50.0			D			
Cal Std 2	AG		100	1.00		0.500			E			
	CR		100			0.500			F			
	MN		150			0.750			G			
	NI		400			2.00			H			
	ZN		200			1.00			I			
Cal Std 3	AL		2000	1.00		10.0			J			
	BA		2000			10.0			K			
	BE		50			0.250			L			
	CO		500			2.50			M			
	CU		250			1.25			N			
	FE		1000			5.00			O			
	V		500			2.50			P			
Cal Std 4	AS		100	4.00		2.00			Q			
	CD		50			1.00			R			
	PB		50			1.00			S			
	SE		50			1.00			T			
	TL		100			2.00			U			
Single Elements	SB		1000	1.00		5.00			V			
	SN		1000	1.00		5.00			W			
	B		1000	0.500		2.50			X			
	MO		1000	0.500		2.50			Y			
	TI		1000	0.500		2.50			Z			
	SR		1000	0.500		2.50			AA			

RADIAL OPTIMA #1 - HLCCV2 (Standard is prepared weekly or as necessary.)

	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
Cal Std 2	AG		100	2.00	100	2.00	2%HNO3		A				
	CR		100			2.00	5%HCl		B				
	MN		150			3.00			C				
	NI		400			8.00			D				
	ZN		200			4.00			E				
Cal Std 3	AL		2000	2.00		40.0			F				
	BA		2000			40.0			G				
	BE		50			1.00			H				
	CO		500			10.0			I				
	CU		250			5.00			J				
	FE		1000			20.0			K				
	V		500			10.0			L				
Single Metals	MO		1000	1.00		10.0			M				
	PB		1000	~~0.800~~	1.00	10.0			N				
	TI		1000	1.00		10.0			O				
				CLW18b2					P				
									Q				
									R				
									S				
									T				
									U				
									V				
									W				
									X				
									Y				
									Z				

RADIAL OPTIMA #1 CRI STANDARD

Element	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	ID Letter	Nitric Acid Lot #	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
CRDL STD		Multi	0.500	500	Multi	5% HCL 2%HNO3		A				
AG		20			0.0200			B				
AS		20			BELOW			C				
								D				
BE		10			0.0100							
CD		10			0.0100			E				
CR		20			0.0200			F				
CO		100			0.100			G				
CU		50			0.0500			H				
MN		30			0.0300			I				
NI		80			0.0800			J				
PB		6			BELOW			K				
SB		120			0.120			L				
SE		10			BELOW			M				
TL		20			BELOW			N				
V		100			0.100			O				
ZN		40			0.0400			P				
AS		1000	0.050		0.120			Q				
PB		1000	0.050		0.106			R				
SE		1000	0.050		0.110			S				
TL		1000	0.050		0.120			T				

RADIAL OPTIMA #1 ICSAB STANDARD

Element	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	ID Letter	Nitric Acid Lot #	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
Int. A Sol'n		Multi	100	1000	Multi			A				
AL		5000			500			B				
CA		5000			500			C				
FE		2000			200			D				
MG		5000			500			E				
Int. B Sol'n		Multi	10.0		Multi			F				
AG		100			1.00			G				
BA		50			0.500			H				
BE		50			0.500			I				
CD		100			1.00			J				
CO		50			0.500			K				
CR		50			0.500			L				
CU		50			0.500			M				
MN		50			0.500			N				
NI		100			1.00			O				
PB		100			1.00			P				
V		50			0.500			Q				
ZN		100			1.00			R				
								S				
								T				
								U				

RADIAL OPTIMA #1 MRL STANDARD

	Element	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	ID Letter	Nitric Acid Lot #	Hydrochloric Acid Lot #	Exp. Date	Pipet ID
Cal #1	Ca		5000	0.20	1000	1.00	5% HCL		A				
	K		5000			1.00	2%HNO3		B				
	Mg		5000			1.00			C				
	Na		5000			1.00			D				
Cal #2	Cr		100	0.10		0.0100			E				
	Ag		100			0.0100			F				
	Mn		150			0.0150			G				
	Zn		200			0.0200			H				
	Ni		400			0.0400			I				
Cal #3	Al		2000	0.10		0.200			J				
	Ba		2000			0.200			K				
	Fe		1000			0.100			L				
	Co		500			0.050			M				
	V		500			0.050			N				
	Cu		250			0.025			O				
	Be		50			0.00500			P				
Cal #4	Cd		50	0.10		0.0050			Q				
	As , Tl		100			BELOW			R				
	Pb , Se		50			BELOW			S				
PQL #2	B		200	1.00		0.200			T				
	Mo		25			0.0250			U				
	Sn		500			0.500			V				
	Tl		50			0.050			W				
Single Stds	Sb		1000	0.060		0.060			X				
	Sr		1000	0.100		0.100			Y				
	Tl		1000	0.300		0.310			Z				
	As		1000	0.500		0.510							
	Se		1000	0.500		0.505							
	Pb		1000	0.050		0.055							

AXIAL OPTIMA #2 CALIBRATION STANDARD #1 (Standard is prepared weekly or as necessary)

	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
PQL Std 1	AL		200	0.100	100	0.200	2%HNO3		A				
	BE		5			0.0050	5%HCl		B				
	CO		50			0.0500			C				
	MG		5000			5.00			D				
	SE		5			BELOW			E				
	V		50			0.0500			F				
	SB		60			0.0600			G				
	CD		5			BELOW			H				
	CU		25			0.0250			I				
	MN		15			0.0150			J				
	AG		10			0.0100			K				
	ZN		20			0.0200			L				
	AS		10			BELOW			M				
	CA		5000			5.00			N				
	FE		100			0.100			O				
	NI		40			0.0400			P				
	NA		5000			5.00			Q				
	BA		200			0.200			R				
	CR		10			0.0100			S				
	PB		5			BELOW			T				
	K		5000			5.00			U				
	TL		10			BELOW			V				
Cal Std 4	AS		100	0.010		0.0200			W				
	CD		50			0.0100			X				
	SE		50			0.0100			Y				
	PB		50			0.0100			Z				
	TL		100			0.0200			AA				
PQL Std 2	B		200	0.100		0.200			BB				
	MO		25			0.0250			CC				
	SN		500			0.500			DD				
	TI		50			0.0500			EE				

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AXIAL OPTIMA #2- CALIBRATION STANDARD #3 / HLCCV1 (Standard is prepared weekly or as necessary)
(CALIBRATION STANDARD #2 IS A 1/5 DILUTION OF THIS STANDARD)

	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
Cal Std 1	CA		5000	2.00	200	50.0	2%HNO3		A				
	MG		5000			50.0	5%HCl		B				
	K		5000			50.0			C				
	NA		5000			50.0			D				
Cal Std 2	AG		100	2.00		1.00			E				
	CR		100			1.00			F				
	MN		150			1.50			G				
	NI		400			4.00			H				
	ZN		200			2.00			I				
Cal Std 3	AL		2000	2.00		20.0			J				
	BA		2000			20.0			K				
	BE		50			0.500			L				
	CO		500			5.00			M				
	CU		250			2.50			N				
	FE		1000			10.0			O				
	V		500			5.00			P				
Cal Std 4	AS		100	4.00		2.00			Q				
	CD		50			1.00			R				
	PB		50			1.00			S				
	SE		50			1.00			T				
	TL		100			2.00			U				
Single Metals	SB		1000	2.00		10.0			V				
	SN		1000	2.00		10.0			W				
	B		1000	1.00		5.00			X				
	MO		1000	1.00		5.00			Y				
	TI		1000	1.00		5.00			Z				

AXIAL OPTIMA #2 ICV/CCV STANDARD (Standard is prepared daily.)

	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot #	Pipet ID
Cal Std 1	CA		5000	1.00	200	25.0	2%HNO3		A			
	MG		5000			25.0	5%HCl		B			
	K		5000			25.0			C			
	NA		5000			25.0			D			
Cal Std 2	AG		100	1.00		0.500			E			
	CR		100			0.500			F			
	MN		150			0.750			G			
	NI		400			2.00			H			
	ZN		200			1.00			I			
Cal Std 3	AL		2000	1.00		10.0			J			
	BA		2000			10.0			K			
	BE		50			0.250			L			
	CO		500			2.50			M			
	CU		250			1.25			N			
	FE		1000			5.00			O			
	V		500			2.50			P			
Cal Std 4	AS		100	2.00		1.00			Q			
	CD		50			0.500			R			
	PB		50			0.500			S			
	SE		50			0.500			T			
	TL		100			1.00			U			
Single Elements	SB		1000	1.00		5.00			V			
	SN		1000	1.00		5.00			W			
	B		1000	0.500		2.50			X			
	MO		1000	0.500		2.50			Y			
	TI		1000	0.500		2.50			Z			

AXIAL OPTIMA #2- HLCCV2 (Standard is prepared weekly or as necessary)

	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
Cal Std 2	AG		100	2.00	100	2.00	2%HNO3		A				
	CR		100			2.00	5%HCl		B				
	MN		150			3.00			C				
	NI		400			8.00			D				
	ZN		200			4.00			E				
Cal Std 3	AL		2000	2.00		40.0			F				
	BA		*2000*			40.0			G				
	BE		50			1.00			H				
	CO		500			10.0			I				
	CU		250			5.00			J				
	FE		1000			20.0			K				
	V		500			10.0			L				
Cal Std 4	AS		100	4.00		4.00			M				
	CD		50			2.00			N				
	PB		50			below			O				
	SE		50			2.00			P				
	TL		100			4.00			Q				
Single Metals	MO		1000	1.00		10.0			R				
	PB		1000	0.800		10.0			S				
									T				
									U				
									V				
									W				
									X				
									Y				
									Z				

AXIAL OPTIMA #2 CRI STANDARD

Element	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	ID Letter	Nitric Acid Lot #	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
CRDL STD		Multi	0.500	500	Multi	5% HCL 2%HNO3		A				
AG		20			0.0200			B				
AS		20			0.0200			C				
BE		10			0.0100			D				
CD		10			0.0100			E				
CR		20			0.0200			F				
CO		100			0.100			G				
CU		50			0.0500			H				
MN		30			0.0300			I				
NI		80			0.0800			J				
PB		6			0.00600			K				
SB		120			0.120			L				
SE		10			0.0100			M				
TL		20			0.0200			N				
V		100			0.100			O				
ZN		40			0.0400			P				
								Q				

ICSA STANDARD

Element	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	ID Letter	Nitric Acid Lot #	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
Int. A Sol'n		Multi	100	1000	Multi	5% HCL		A				
AL		5000			500	2%HNO3		B				
CA		5000			500			C				
FE		2000			200			D				
MG		5000			500			E				
								F				
								G				
								H				
								I				
								J				
								K				
								L				
								M				
								N				
								O				
								P				
								Q				
								R				
								S				
								T				
								U				
								V				

AXIAL OPTIMA #2 ICSAB STANDARD

Element	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	ID Letter	Nitric Acid Lot #	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
Int. A Sol'n		Multi	100	1000	Multi			A				
AL		5000			500			B				
CA		5000			500			C				
FE		2000			200			D				
MG		5000			500			E				
Int. B Sol'n		Multi	10.0		Multi			F				
AG		20			0.200			G				
BA		50			0.500			H				
BE		50			0.500			I				
CD		100			1.00			J				
CO		50			0.500			K				
CR		50			0.500			L				
CU		50			0.500			M				
MN		50			0.500			N				
NI		100			1.00			O				
PB		5			0.0500			P				
V		50			0.500			Q				
ZN		100			1.00			R				
AS		10			0.100			S				
SB		60			0.600			T				
SE		5			0.0500			U				
TL		10			0.100			V				

OPTIMA INTERNAL STANDARD

Element	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	ID Letter	Nitric Acid Lot #	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
Y		1000	50.0	500	100	2% HNO3		A				
Cs		1000	50.0	500	100	5% HCL		B				
								C				
								D				
								E				
								F				
								G				
								H				
								I				
								J				
								K				
								L				
								M				
								N				
								O				
								P				
								Q				
								R				
								S				

AXIAL OPTIMA #2 MRL STANDARD

	Element	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	ID Letter	Nitric Acid Lot #	Hydrochloric Acid Lot #	Exp. Date	Pipet ID
Cal	Ca		5000	0.20	1000	1.00	5% HCL		A				
#1	K		5000			1.00	2%HNO3		B				
	Mg		5000			1.00			C				
	Na		5000			1.00			D				
Cal	Cr		100	0.10		0.0100			E				
#2	Ag		100			0.0100			F				
	Mn		150			0.0150			G				
	Zn		200			0.0200			H				
	Ni		400			0.0400			I				
Cal	Al		2000	0.10		0.200			J				
#3	Ba		2000			0.200			K				
	Fe		1000			0.100			L				
	Co		500			0.050			M				
	V		500			0.050			N				
	Cu		250			0.025			O				
	Be		50			0.00500			P				
Cal	Cd		50	0.20		0.0100			Q				
#4	As , Tl		100			0.0200			R				
	Pb , Se		50			0.0100			S				
PQL	B		200	1.00		0.200			T				
#2	Mo		25			0.0250			U				
	Sn		500			0.500			V				
	Tl		50			0.050			W				
Single Stds	Sb		1000	0.060		0.060			X				
									Y				
									Z				

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MISCELLANEOUS STANDARDS

Type Or Std	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot#	Expiration Date	Pipet ID
Cal Std	MAL	Li Si Sr						SD 9/21/04	A	M178005SW	M178005SW	9/27/04	M13/M17
	Li	M178005SY	1000	0.050	500	0.100	2% HNO_3 5% HCl	SD 9/28/04	B	M178005SW	M178005SW	10/4/04	M13/M15
	Si	M178005SX	1000	0.500		01.00			C				
	Sr	M178005SN	1000	0.050		0.100			D				
									E				
Cal 3	HLCCV				200		2% HNO_3 5% HCl	SD 9/21/04	F	M178005SW	M178005SW	9/27/04	M18
	Li	M178005SY	1000	2.00		10.0		SD 9/28/04	G	M178005SW	M178005SW	10/4/04	M18
	Si	M178005SX	1000	2.00		10.0			H				
	Sr	M178005SN	1000	1.00		5.00			I				
									J				
HLCCV2					100		2% HNO_3 5% HCl	SD 9/21/04	K	M178005SW	M178005SW	9/27/04	M18
	Li	M178005SY	1000	2.00		20.0			L				
	Si	M178005SX	1000	2.00		20.0			M				
	Sr	M178005SN	1000	1.00		10.0			N				
									O				
ICV/CCV					200		2% HNO_3 5% HCl	SD 9/21/04	P	M178005SW	M178005SW	9/27/04	M18/M13
	Li	M178005SW	1000	1.00		5.00		SD 9/28/04	Q	M178005SW	M178005SW	9/28/04	M18/M13
	Si	M178005SV	1000	1.00		5.00		SD 9/28/04	R	M178005SW	M178005SW	9/25/04	M18/M13
	Sr	M178005SV	1000	0.500		2.50		SD 9/27/04	S	M178005SW	M178005SW	9/28/04	M18/M13
								SD 9/28/04	T	M178005SW	M178005SW	9/29/04	M18/M13
									U				
									V				
									W				

STANDARD OPERATING PROCEDURE

for

DETERMINATION OF MERCURY IN SOLID OR SEMISOLID WASTE BY COLD VAPOR ATOMIC ABSORPTION SPECTROMETRY FOR INDIANA PINES SITE

SOP No.: MET-7471APines

Revision: 0

September 23, 2004

Approved by:	Supervisor	Date: 9/23/04
	QA Coordinator	Date: 9/23/04
	Laboratory Director	Date: 9/23/04

One Mustard St. Suite 250
Rochester, NY 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: _____ Date: _____
Initials: _____ Date: _____
Initials: _____ Date: _____

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1. SCOPE AND APPLICABILITY

This SOP uses EPA SW-846 Method 7471A to determine the concentration of mercury in soils, sediments, bottom deposits and sludge-type materials. The range of the method is 0.2 to 10 ug/L. The range may be extended above or below the normal range by increasing or decreasing the sample size. This SOP was modified specifically for the Indiana Pines site project.

2. SUMMARY OF METHOD

A known portion of a soil sample is transferred to a hot block cup. It is digested in diluted potassium permanganate solution and oxidized for thirty minutes at 95°C. Mercury in the digested water sample is reduced with stannous chloride to elemental mercury and measured by the conventional cold vapor atomic absorption technique.

3. DEFINITIONS

3.1. **Calibration Blank** - A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to auto-zero the instrument.

3.2. **Calibration Standard** - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3. **Laboratory Duplicates** - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of duplicate sample indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4. **Laboratory Control Sample (LCS)** - An aliquot of an ERA soil sample with a known concentration. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

3.5. **Matrix Spike (MS)** - An aliquot of an environmental sample to which a known quantity of the method analyte is added in the laboratory. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.6. **Preparation Blank (PB)** - An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The PB is used to determine if the method analyte or other interferences are present in the laboratory environment, reagents, or apparatus.

3.7. **Linear Dynamic Range (LDR)** - The concentration range over which the instrument response to an analyte is linear.

3.8. **Method Detection Limit (MDL)** - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

3.9. **Standard Addition** - The addition of a known amount of analyte to the sample in order to determine the relative response of the detector to an analyte within the sample matrix. The relative response is then used to assess either an operative matrix effect or the sample analyte concentration.

3.10. **Batch** - Unit of samples prepared together on the same day, not to exceed 20 samples.

4. HEALTH AND SAFETY WARNINGS

The toxicity and carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. Normal accepted laboratory safety practices should be followed during reagent preparation and instrument operation. Always wear safety glasses or full-face shield for eye protection when working with these reagents.

All contact with mercury should be avoided. Mercury vapor is especially toxic, causing severe respiratory tract damage. Chronic exposure to mercury through any route can produce central nervous system damage. May cause muscle tremors, personality and behavior changes, memory loss, metallic taste, loosening of the teeth, digestive disorders, skin rashes, brain damage and kidney damage. Can cause skin allergies and accumulate in the body. Repeated skin contact can cause the skin to turn gray in color. A suspected reproductive hazard; may damage the developing fetus and decrease fertility in males and females.

5. CAUTIONS

- Because of the extreme sensitivity of the analytical procedure and the presence of mercury in a laboratory environment, care must be taken to avoid extraneous contamination. Sampling devices, sample containers and plastic items should be determined to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contamination from airborne mercury vapor.

- Samples with high organic content may required additional permanganate. Shake and add additional permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Ensure that equal amounts of permanganate are added to all samples, standards and blanks

6. INTERFERENCES

6.1. Interferences have been reported for soils containing sulfide, chloride, copper and tellurium. Organic compounds, which have broad band UV absorbance (around 253.7 nm), are confirmed interferences. The concentration levels for interferants are difficult to define.

6.2. Low level mercury sample preparation, digestion, and analysis may be subject to environmental contamination if preformed in areas with high ambient backgrounds where mercury was previously employed as an analytical reagent in analyses such as chemical oxygen demand (COD).

7. PERSONNEL QUALIFICATIONS

At a minimum, personnel must have attained at least a 2-year degree in any subject and have successfully completed an Initial Demonstration of Capability after training using the Training Plan Form (found on the CAS Intranet). Training and Demonstration of Capability are in accordance with NELAC 2002 Standard.

8. EQUIPMENT AND SUPPLIES

8.1. Perkin Elmer FIMS - Atomic Absorption Spectrophotometer equipped with a vapor generator, quartz absorption cell and mercury hollow cathode lamp.

8.2. 50mL hot block cups and caps

8.3. 100 mL B-Cups and caps

8.4. Hot Block capable of maintaining a digestion temperature of 90-95°C.

8.5. Pipettes and graduated cylinders.

8.6. Mercury stock solution (1,000 mg/L) - Purchased. Store at room temperature. Dispose per manufacturer's expiration date.

8.7. Intermediate Stock Solution (10 mg/L) - Prepare a 1/100 dilution of the 1000mg/L Stock Solution in a volumetric flask and dilute with DI water. Acidify with 0.5 ml of concentrated HNO_3. Store at room temperature for up to 1 week.

8.8. Working Solution (100 µg/L) - Prepare a 1/100 dilution of the 10mg/L Intermediate Stock Solution in a volumetric flask and dilute with DI water. Acidify with 0.5 ml of concentrated HNO_3. Prepare fresh each day analysis is performed.

8.9. Calibration Standards - Prepare 0, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0 ug/L calibration curve. Transfer 0, 0.1, 0.25, 0.5, 1.0, 2.5, 5.0 mL aliquots of the 100 µg/L working solution to a series of labeled hotblock cups. Add the appropriate amount of reagent water to bring each cup to a final volume of 5 ml. Add 5 ml of aqua regia. Loosely cap each cup. Prepare 2 blank standards to ensure sufficient volume for the analysis. The CRDL standard is prepared as the 0.2 standard.

8.10. ASTM Type II water

8.11. Concentrated Nitric Acid – Metals Grade, purchased commercially. Expires as per manufacturer's indications.

8.12. Concentrated Sulfuric Acid – Metals Grade, purchased commercially. Expires as per manufacturer's indications.

8.13. Aqua regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

8.14. 5% w/v Potassium Permanganate Solution - Dissolve 50 g of $KMnO_4$ in 1 L of reagent water. Store at room temperature for up to 6 months.

8.15. 12% w/v Sodium chloride-hydroxylamine chloride solution - Dissolve 120 g of NaCl and 120 g of hydroxylamine hydrochloride ($NH_2OH*HCl$) in 1 L of reagent water. (Hydroxylamine sulfate $(NH_2OH)_2$ H_2SO_4 may be used in place of hydroxylamine hydrochloride.) Store at room temperature for up to 6 months.

8.16. 1.1% Stannous chloride + 3% HCl solution - Add 11.0 g of $SnCl_2*2H_2O$ to 1 L of 3% HCl. Prepare daily.

8.17. The calibration blanks (ICB and CCB), prepared daily, must contain all reagents in the same concentrations and in the same volume as used in preparing the calibration solutions.

8.18. The preparation blank (PB) is prepared in the same manner as the calibration blank and is carried through the entire preparation scheme with each batch of samples to be analyzed.

8.19. With each batch of samples to be analyzed, prepare a laboratory control sample (LCS) by weighing a 0.60g portion of an ERA soil standard and place in the bottom of a 50 mL hotblock cup. The LCS must be carried through the entire sample preparation scheme.

8.20. Initial / Continuing Calibration Verification Standard (ICV/CCV) 3.0 ug/L - Prepare an intermediate stock solution and working solution of 10 mg/L and 100 µg/L using a different stock source than the calibration standards. Transfer 1.5 ml of 100 µg/L solution (prepared daily) to a 50 ml hotblock cup. Add 3.5 ml of reagent water and 5 ml of aqua regia. Prepare 2 CCVs to ensure sufficient volume for the analysis.

8.21. The matrix spike sample (MS) is prepared by fortifying a 0.6g sample with 0.5 ml of 100 µg/L CCV standard in a hotblock cup. Carry through the entire digestion and instrument procedure as a routine sample.

9. PROCEDURE

9.1. Calibration and Standardization

Calibration Standards for the initial calibration must be prepared with each daily analysis. A blank and 5 standards is required. The correlation coefficient for each calibration must ≥0.995.

9.2. Sample Collection

Samples are to be collected in purchased, certified clean glass or plastic sample jars.

9.3. Sample Handling and Preservation

9.3.1. Maintain at 0-6°C from receipt until analysis.

9.3.2. Digested and analyze samples within 28 days of collection. Once digested, samples are analyzed as soon as possible.

9.3.3. Sample handling, storage, and custody procedures are in compliance with NELAC 2002 Standard.

9.4. Sample Preparation

9.4.1. Weigh 0.6g portion of a representative sample (approx. 0.2g portions from three areas of the sample) and place in the bottom of a hot block cup. Add 5 ml of reagent water and 5 ml of aqua regia. Loosely cap the sample cup.

9.4.2. Heat in the hotblock for 2 minutes at 95°C. Cool, then add 25 ml of reagent water and 15 ml of 5% potassium permanganate solution. Mix thoroughly and place in the hotblock for 30 minutes at 95°C.

9.4.3. *Note: Samples with high organic content may required additional permanganate. Shake and add additional permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Ensure that equal amounts of permanganate are added to all samples, standards and blanks.*

9.4.4. Cool and add 3.0 ml of 12% sodium chloride/hydroxylamine hydrochloride solution. Add 25 ml of reagent water and the samples are now ready to be analyzed. The stannous chloride solution is added automatically by the vapor generator.

9.5. Sample Analysis

9.5.1. Analyze the standards and samples using the Perkin Elmer Flow Injection Mercury System. See Operations Manual for details.

9.5.2. Sample concentrations exceeding the Linear Range require sample dilution. Dilutions should be performed so that the instrument concentration will fall in the mid-range of the calibration curve.

9.6. Troubleshooting

All maintenance activities are recorded in a maintenance logbook kept for each instrument. CAS staff performs most routine maintenance and troubleshooting. Other maintenance or repairs may, or may not require factory service, depending upon the nature of the task. Typical preventive maintenance measures include, but are not limited to, the following items:

- Check gases and tubing, daily
- Check optic tubes and filter membrane for moisture before analysis

9.7. Data Acquisition, Calculations, and Data Reduction Requirements

Calculations:

From the prepared calibration curve compute sample values by comparing response with the standard curve. Calculate the mercury concentration in the sample in mg/Kg by using the formula:

mg/Kg = Vol. (ml)/sample Wt(g) x 1mg/1000ug x 1L/1000ml x 1000g/1Kg x C x dilution

C = concentration of Hg in digestate, in ug/L

9.8. Computer Hardware and Software

- Personal Computer running Perkin Elmer AA Winlab for Window v.2.50
- Metals Analytical Review and Reporting System (MARRS) v.3.2.44
- StarLIMS v.6.11.a

10. DATA AND RECORDS MANAGEMENT

10.1. **Repsonsibilities** - It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

10.2. **Data Flow** – Samples are entered by the Project Manager into StarLIMS on a Personal Computer running on a Novell Network. On the day that the samples are received the samples appear on a daily log printed from this computer system. The Metals Prep analyst prepares a benchsheet, digests the samples and turns the samples and digest sheet over to the ICP analyst. The samples are analyzed for metals of interest using AA software. The results are transferred to MARRS (for reporting package work) and StarLIMS for validation, reporting, and invoicing.

10.3. **Data Review** – Data will be reviewed by the instrument analyst and a qualified peer using a data review checklist (attached).

11. QUALITY CONTROL AND QUALITY ASSURANCE

11.1. Preparation Blanks must be analyzed at least once per batch of 20 or fewer samples. PB values must not exceed the MRL (method reporting limit). If the PB is out of control, fresh aliquots of the samples must be prepared and analyzed again for affected analytes after the source of the contamination has been corrected and acceptable PB values have been obtained.

11.2. Laboratory Control Samples assess laboratory performance against the required control limits. The control limit range is specific for each lot and is recorded on a certificate from the manufacturer. If the recovery of mercury falls outside the required control limits, the analysis is judged to be out of control, and the source of the problem should be identified and resolved before continuing analysis. Redigestion and analysis is required until acceptable LCS recovery is performed.

11.3. Calibration Verification Standards must immediately follow each calibration, after every tenth sample, and at the end of the sample run. Initial Calibration Verification must verify that the instrument is within ±10%. Continuing Calibration Verification standards must confirm the calibration within ±10% throughout the analyses. If the recovery of mercury falls outside the required control limits, the analysis is judged to be out of control, and the source of the problem should be identified and resolved before continuing analysis. Reanalysis of any sample(s) associated with the outlying ICV or CCV standards is required. All samples must be bracketed with acceptable ICV and CCV standards.

11.4. Sample Matrix Accuracy and Precision are assessed based upon MS and Duplicated performance. Refer to Appendix C of the Quality Assurance Manual for frequency and QC criteria per method of analysis. If the MS is out of control and the LCS is in control, assume matrix interference and flag the associated data.

11.5. Method Detection Limit (MDL) - A mercury MDL must be determined annually using 7 replicates of a fortified blank solution at a concentration of 2-3 times the estimated detection limit. Practical Quantitation Limits (PQLs) are calculated from the MDL by multiplying the MDL by a factor of at least 3. The PQLs are generally used as CAS Reporting Limits. To determine the MDL, refer to 40 CFR Part 136 Appendix B.

12. REFERENCES

- *Test Methods For Evaluating Solid Waste, Physical/Chemical Methods*. USEPA SW-846, 3rd Edition, September 1994.
- *Methods For the Determination of Metals in Environmental Samples Supplement I.* USEPA/600/R-94/111, May 1994
- EPA Contract Laboratory Program, Statement of Work for Inorganic Analysis, SOW No. ILM04.0.
- Analytical Services Protocol (ASP), New York State Department of Environmental Conservation, December 1995.
- 40 CFR Part 136 Appendix B
- NELAC 2002 Standard.

Columbia Analytical Services

Analysis For: Hg EPA Method: 7470 / 7471 / 245.1 / 245.5 Analyst: _____

Temp: In___/ Out___ Report: Routine / ASP / Pkg.5 Date Prepped: _____

Time In: _____ File Name: _____ Date Analyzed: _____

Time Out: _____

	Client / Submission #	Sample Number	Initial Wgt/Volume (g/ml)	Final Volume (ml)		Client / Submission #	Sample Number	Initial Wgt/Volume (g/ml)	Final Volume (ml)
1					31				
2					32				
3					33				
4					34				
5					35				
6					36				
7					37				
8					38				
9					39				
10					40				
11					41				
12					42				
13					43				
14					44				
15					45				
16					46				
17					47				
18					48				
19					49				
20							ICB	100ml DI Water	100
21							Std 0	100ml DI Water	100
22							Std 0.2*	0.2ml of 0.1ppm	100
23							Std 0.5*	0.5ml of 0.1ppm	100
24							Std 1.0*	1.0ml of 0.1ppm	100
25							Std 2.0*	2.0ml of 0.1ppm	100
26							Std 5.0*	5.0ml of 0.1ppm	100
27							Std 10.0*	10.0ml of 0.1ppm	100
28							ICV/CCV**	3.0ml of 0.1ppm	100
29							LCS/MMS**	1.0ml of 0.1ppm	100
30							CRDL*	0.2ml of 0.1ppm	100

Lot # of Reagents Used:

HNO3: _____ H2SO4: _____ HCL: _____ K2S2O8: _____ KMnO4: _____

SnCl2: _____ NaCl: _____ NH2OH-HCL: _____ LCSS CAS Lot#: _____

LCSS ERA Lot#: _____

*Source Standard: (Vendor/Lot #)_____ **ICV Standard: (Vendor/Lot #)_____

*(10ppm stock Lot#: _____) **(10ppm stock Lot#: _____)

*(0.1ppm working std Lot#: _____) **(0.1ppm working std Lot#: _____)

Comments/Problems: _____

Batch Name: _____ _____

Metals Instrument Analysis Training Plan

Procedure:_____

SOP:_____ Revision:_____ Date:_____

Trainee:_____

1. Read SOP Trainer:____ Trainee:____ Date:____

2. Demonstrated understanding of the scientific basis of the analysis including:
-the chemical and physical principals behind the measurement by the instrument

Trainer:____ Trainee:____ Date:____

3. Demonstrated familiarity with related SOPs

-ADM-BATCHSEQ	-ADM-PCAL	-ADM-SIGFIG
-ADM-DATAENTRY	-ADM-DIL	-ADM-SPSR
-ADM-MDL	-ADM-DREV	-ADM-TRANDOC

Trainer:____ Trainee:____ Date:____

4. Observe performance of SOP
-standard and reagent prep and documentation – including pipet used
-instrument power up and warm-up
-instrument set-up, daily maintenance and checks
-use and loading of autosampler
-sample analysis including:
    -calibration
    -sample dilution
    -software command of instrument
    -use of QC samples and QC criteria
    -common troubleshooting
-instrument logbook use
-data reduction, reporting, and review

Trainer:____ Trainee:____ Date:____

5. I have read, understood and agree to perform the most recent version of the SOP:

Signature:_____ Date:_____

6. Perform SOP with supervision
- including all items in 4.

Trainer:____ Trainee:____ Date:____

7. Independent performance of the SOP
-all of the item listed in 4
-IDC (4 mid-range standards performed before client samples are analyzed)
-attach IDC certificate, raw data, and summary spreadsheet.

Trainer:____ Trainee:____ Date:____

Columbia Analytical Services
An Employee-Owned Company

METALS DEPARTMENT
DATA QUALITY CHECKLIST

Data File:_____ Run Date:_____ Instrument:_____

Methods Used: ICP- 200.7 // 6010B // ASP/CLP // NIOSH
GFAA- EPA 200 Series // SW846 // ASP/CLP
CVAA- EPA 200 Series // SW846 // ASP/CLP

Batch ID / Metals Reviewed:_____

_____

Yes	No	NA			Yes	No	NA
O	O	O	1.	**Holding Times met method requirements?** ICP / GFAA- 6 months from sampling to analysis Hg- 28 days from sampling to analysis (26 days from VTSR)	O	O	O
O	O	O	2.	**ICAL met method requirements?** Correlation Coefficient > or = 0.995 ICP High Check = 95-105%	O	O	O
O	O	O	3.	**ICV acceptable?** ICP: 200.7 = 95-105% ; NIOSH / 6010B / ASP/CLP = 90-110% GFAA: EPA 200 Series / SW846 / ASP/CLP = 90-110% Hg: EPA 200 Series = 95-105% ; SW846 / ASP/CLP = 90-110%	O	O	O
O	O	O	4.	**CCVs acceptable? Analyzed per 10 samples?** ICP: 200.7 / 6010B / ASP/CLP / NIOSH = 90-110% GFAA: EPA 200 Series = 90-110% ; SW846 / ASP/CLP = 80-120% Hg: EPA 200 Series = 90-110% ; SW846 / ASP/CLP = 80-120%	O	O	O
O	O	O	5.	**CCBs acceptable? Analyzed per 10 samples?** Concentration < RL	O	O	O
O	O	O	6.	**Method Blank results <RL?**	O	O	O
O	O	O	7.	**LCS recoveries within QC limits?** ICP: 200.7 = 85-115% ; 6010B / ASP/CLP / NIOSH = 80-120% GFAA: EPA 200 Series = 85-115% ; SW846 / ASP/CLP = 80-120% Hg: EPA 200 Series = 85-115% ; SW846 / ASP/CLP = 80-120% LCSS (soil) Certificate of Analysis QC limits per manufacturer	O	O	O
O	O	O	8.	**All sample concentrations within LR?**	O	O	O
O	O	O	9.	***MS* recoveries within QC limits?** ICP: 200.7 = 70-130% ; 6010B / ASP/CLP = 75-125% GFAA: EPA 200 Series / SW846 / ASP/CLP = 75-125% Hg: EPA 200 Series = 70-130% ; SW846 / ASP/CLP = 75-125%	O	O	O
O	O	O	10.	**Duplicate RPD within QC limits?** 20% for RPD shall be used for samples > or = 5 times the RL. RL shall be used for samples < 5 times the RL.	O	O	O
O	O	O	11.	**Is GFAA Post Digest Spike within 85-115%?**	O	O	O
O	O	O	12.	**Dilution factors verified and calculated correctly?**	O	O	O
O	O	O	13.	**Bench Sheet complete, initials, date, and time:**	O	O	O
O	O	O		•Are standards and reagents traceable?	O	O	O
O	O	O		•Is unused space on the sheet crossed out?	O	O	O

Analyst:_____ Peer Review:_____
Date:_____ Date:_____

COMMENTS:
**Comments must be provided for any items noted above as "No"

STANDARD OPERATING PROCEDURE

TOTAL SULFUR FOR ION CHROMATOGRAPHY FOR INDIANA PINES SITE

MET-ICSPINES
Revision 0
September 23, 2004

Approved By:

Supervisor	9/23/04 Date
QA Manager	9/23/04 Date
Laboratory Manager	9/23/04 Date

COLUMBIA ANALYTICAL SERVICES, INC.
1 Mustard Street, Suite 250
Rochester, NY 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: _____ Date: _____
Initials: _____ Date: _____
Initials: _____ Date: _____

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Will Not Be Updated

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Table of Contents

1. SCOPE AND APPLICABILITY

This procedure is used to determine the concentration of oxidizable sulfur in a sample using peroxide digestion and ion chromatography. This SOP describes the sample preparation step for the analysis and refers to the determinative procedure used for ion chromatography. The procedure is applicable to most sample matrices including water, wastewater, soils, and miscellaneous solids. The PQL for soils is 200 mg/Kg. This SOP was modified specifically for the Indiana Pines site project.

2. SUMMARY OF METHOD

A portion of the sample is digested using a heated peroxide solution. The resulting digestate is filtered and analyzed for sulfate using ion chromatography. The sulfate result is converted to concentration of sulfur.

3. DEFINITIONS

3.1. Laboratory Control Sample (LCS): A laboratory blank that has been fortified with target analyte and used to determine that the analysis is in control.

3.2. Matrix Spike (MS) Analysis - In the matrix spike analysis, a predetermined quantity of target analyte is added to a sample matrix prior to sample preparation and analysis. The percent recovery is calculated. The MS is used to evaluate the effects of the sample matrix on the method used for the analysis

3.3. Duplicate Sample (DUP) - A laboratory duplicate. The duplicate sample is a separate field sample aliquot that is processed in an identical manner as the sample proper. The relative percent difference between the samples is calculated and used to assess analytical precision.

3.4. Method Blank / Preparation Blank (MB) - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The blank is carried through the entire analytical procedure.

3.5. Batch – Up to 20 samples of the same matrix digested together on the same day.

4. HEALTH AND SAFETY WARNINGS

The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical and sample should be treated as a potential health hazard. Exposure should be reduced to the lowest possible level. The laboratory maintains a compilation of Material Safety Data Sheets in binders the conference room. Always wear safety glasses or a shield for eye protection, and protective clothing, and observe proper mixing when working with these reagents.

5. CAUTIONS

Boiling samples to dryness may cause combustion

6. INTERFERENCES

Samples impervious to peroxide digestion will yield results of low bias. Samples with high organic content may require additional digestions.

7. PERSONNEL QUALIFICATIONS

At a minimum, personnel must have attained at least a 2-year degree in a science-related field and have successfully completed an Initial Demonstration of Capability and the Training Plan Form (attached). Training and Demonstration of Capability are in accordance with NELAC 2002 standard.

8. EQUIPMENT AND SUPPLIES

8.1. 50ml Digestion Vessel for Hot Block

8.2. 250 mL glass beaker and ribbed watch glasses

8.3. Hotplate capable of maintaining a digestion temperature of 90-95°C.

8.4. Hot Block Digestor- Environmental Express

8.5. Filter Mate 2u filter paper and plunger for Environmental Express Digestion Vessel.

8.6. Dionex Ion Chromatograph Series 4000i, as described in GEN-300.0 SOP.

8.7. 10 N Sodium Hydroxide (NaOH): Dissolve 400g sodium hydroxide in distilled water, cool and dilute to 1 liter. Store at room temperature for up to 1 year.

8.8. 30% peroxide; purchased solution. Store at room temperature. Expires upon manufacturer's indications or in 1 year, whichever is sooner.

8.9. Laboratory D.I. water

8.10. Granular sodium sulfite, Na_2SO_3, anhydrous FW=126.04. 254390 mg/Kg (25.4%) sulfur. To be used for the LCS and for spiking the MS.

9. PROCEDURE

9.1. Sample Collection

9.1.1. Samples are to be collected in purchased, precleaned, certified sample containers – (plastic, glass, etc). Samples are to be cooled upon collection and shipment to lab.

9.1.2. The amount of sample collected should be 3 times the analytical aliquot, at a *minimum.*

9.2. Sample Handling and Preservation

9.2.1. Maintain samples at 0-6 °C upon receipt until analysis.

9.2.2. No specific holding time applies.

9.2.3. For further sample handling, storage, and custody procedures, see SMO-GEN.

9.3. Sample Preparation

9.3.1. Aqueous samples: Measure a 50 ml sample aliquot into a digestion vessel. Record the volume.

9.3.2. Soil samples: weigh out 0.5-5g of sample into a digestion vessel. Record the weight.

9.3.3. Add 2 drops of 10 N NaOH to each vessel, or until the sample is basic in nature.

9.3.4. Add appropriate standard to matrix spike and LCS aliquots.

9.3.5. Add 3 mL 30% peroxide to each vessel.

9.3.6. Bring each vessel to 50 ml with D.I. water.

9.3.7. Place digestion vessel in hotblock digester OR transfer contents of digestion vessel to a beaker and place on a hotplate.

9.3.8. Digest each sample until digestate is clear, or three times. Bring the volume of the digestate to ~ 5 - 10 mL each time taking care to not evaporate the samples to dryness. BOILING SAMPLE TO DRYNESS MAY CAUSE COMBUSTION.

9.3.9. Allow samples to cool. Bring soil and water samples to a final volume of 20.0 mL in the digestion vessel. Record the final volume. If particulates are present in the sample, filter using 2u FilterMate filter for Environmental Express digestion vessels. If one sample is filtered, the entire batch is to be filtered, including the MB and LCS.

9.3.10. Give the batch of samples and a copy of the digest sheet to Wetchem for analysis. Document custody transfer.

9.4. Sample Analysis

The extract is analyzed for sulfate by ion chromatography (IC) using SOP GEN-300. Refer to that SOP for specific analysis instructions.

9.5. Troubleshooting and Preventive Maintenance – Wipe down all hoods in the Metals Prep Lab once a week with DI water.

9.6. Data Acquisition, Calculations, and Data Reduction Requirements

9.6.1. The PeakNet software will multiply the solution result by any dilution made at the IC and by the final volume. Divide by the initial volume or weight.

9.6.2. The IC sulfate result will be multiplied by 0.3338 to obtain the concentration of the sulfur (S is 33.38% of SO_4 by atomic weight).

10. DATA AND RECORDS MANAGEMENT

10.1. **Responsibilities** – It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

10.2. **Data Flow** – Samples are entered by the Project Manager into StarLIMS v.6.11.a on a Personal Computer running on a Novell Network. On the day that the samples are received the samples appear on a daily log printed from this computer system. The Metals Prep analyst prepares a benchsheet (attached), digests the samples and turns the samples and digest sheet over to the IC analyst. The samples are analyzed for sulfate using Dionex PeakNet 5 Chromatography software and the results are transferred into the StarLIMS computer system for final calculation, validation, reporting, and invoicing.

10.3. **Data Review** - Data will be reviewed by the IC analyst and a qualified peer using a Data Review Checklist (attached to GEN-300) and validated by a supervisor.

11. QUALITY CONTROL AND QUALITY ASSURANCE

11.1. **Method Blank-**

11.1.1. Frequency - Prepare one method blank per batch of 20 samples.

11.1.2. Acceptance Criteria – The result of the method blank must be less than the reporting limit. If there is method blank contamination, samples which have results less than the reporting limit may be reported.

11.1.3. Corrective Action - If there is method blank contamination, attempt to find the source of the contamination, correct the problem, and re-digest the batch (with the exception of the samples accepted as above).

11.2. **LCS –**

11.2.1. Frequency – one per batch of 20 or fewer samples.

11.2.2. Acceptance criteria – The result of the LCS must be within 80-120% of the true value.

11.2.3. Corrective action – If the LCS is out of control limits, find and correct the problem and re-digest the batch.

11.3. **Matrix Spike –**

11.3.1. Frequency – one per batch of 20 or fewer samples of the same matrix.

11.3.2. Acceptance criteria – The result of the MS should be within 70-130% of the true value.

11.3.3. Corrective Action – If the MS is out of control limits, and the LCS is compliant, assume matrix interference and report. If the MS is out of control and the LCS is out of control, find the problem and redigest the batch.

11.4. IC QC Requirements are outlined in Section 12 of GEN-300.

12. REFERENCES

NELAC, 2002 Standard
CAS SOP for Ion Chromatography, GEN-300.

CAS - Rochester,NY: Total Sulfur for IC Digestion Log

Report Type: Routine // 6 // ASP // Pkg5

Analyst:_____ Date:_____

Prep Method: Total Sulfur for IC by Method 300

Digest: Initial // Redigest Of:_____

Spike Witness / Lot Approval: _____

Batch ID: _____

Batch Temp: _____

	Submission / Order #	pH	Initial Vol. / Wt. (ml / g)	Final Vol(ml)	Initial Color / Clarity	Final Color / Clarity	Analyte	Spike Added Vol(ml)
1							Total Sulfur/Sulfate	
2								
3								
4								
5								
6								
7								
8								
9								
10								
11								
12								
13								
14								
15								
16								
17								
18								
19								
20								
21								
22								
23								
24								
25								
26								

Spiking Standards / Reagent Lot Numbers:

10 N Sodium Hydroxide (NaOH): _____

30 % Peroxide: _____

Sodium Sulfite (Na2SO4):_____

Color / Clarity Key:
Color: C = Colorless ; Y = Yellow ; B = Brown ; G = Grey
BL = Black
Clarity: CDY = Cloudy ; CLR = Clear ; OP = Opaque
Texture: F = Fine ; M = Medium ; C = Coarse ; NA = Non Aqueous

COMMENTS: _____

Metals Digestion Training Plan

Procedure:_____

SOP:_____ *Revision:*_____ *Date:*_____

Trainee:_____

1. Read SOP Trainer:____ Trainee:____ Date:____

2. Demonstrated familiarity with related SOPs
   -ADM-BATCHSEQ -ADM-PCAL -ADM-SIGFIG
   -ADM-DATAENTRY -ADM-SPSR -ADM-MDL
   -ADM-TRANDOC
   Trainer:____ Trainee:____ Date:____

3. Observe performance of SOP
   -standard and reagent prep and documentation – including pipet use and balance use and calibration, if applicable
   -digestion unit set-up
   -sample prep and reagent and spike addition
   -holding times
   -benchsheet/logbook use
   -analytical sequence, batch QC required
   -time and temperature needed to digest sample, if applicable
   -preventive maintenance and other troubleshooting
   -digestate filtering and dilution
   -digestate labelling and storage
   Trainer:____ Trainee:____ Date:____

4. I have read, understood and agree to perform the most recent version of the SOP:
   Signature:_____ Date:_____

5. Perform SOP with supervision
   - including all items in 4.
   Trainer:____ Trainee:____ Date:____

6. Independent performance of the SOP
   -all of the item listed in 4
   -IDC (4 mid-range standards performed before client samples are analyzed)
   -attach IDC certificate, raw data, and summary spreadsheet.
   Trainer:____ Trainee:____ Date:____