APPENDIX C

SOIL PROCESSING STANDARD OPERATING PROCEDURE

LSB ROUTINE APPROVED
SEPTEMBER 6, 2000

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MINISTRY OF ENVIRONMENT
LABORATORY SERVICES BRANCH
QUALITY MANAGEMENT UNIT

APPROVAL FORM FOR RELEASE OF ANALYTICAL METHOD FOR ROUTINE USE

METHOD TITLE: THE DETERMINATION OF TRACE METALS IN VEGETATION BY THE SPECTRO INDUCTIVELY-COUPLED PLASMA-OPTICAL EMISSION SPECTROMETER (ICP-OES)

COMPLETE METHOD CATALOGUE CODE: HMARVEG-E3065

DATE OF LAST REVISION: JUNE 12, 1997

REVISIONS REQUIRED FOR THIS REVIEW?: Y

SECTION: SPECTROSCOPY SECTION

TECHNICAL CONTACT: JIM HOWDEN

AUTHOR(S): LIZ PASTOREK, revised by JIM HOWDEN in 2000.

METHOD REFERENCED UNDER MOE REGULATIONS/GUIDELINES?: Y_____ N __X__

CHECKED BY: _____George Steinke_______

• **DESCRIPTION:**
SLUDGE UTILIZATION:
MISA:
SITE CLEAN-UP:
COMPOST:
OTHER:

SUPERVISOR APPROVAL:____________________________ **DATE:**___________

MANAGER APPROVAL:____Rusty Moody_______________ **DATE:**___September 6, 2000

QM UNIT APPROVAL:__George Steinke________________ **DATE:**___September 6, 2000

*** The approval of this document is valid for two years at which time it will be subject to review to determine if any updates or modifications are warranted.***

NOTE: Equivalent suppliers to those stated in the method are acceptable. Reference to a particular brand does not constitute an endorsement by the Ontario Ministry of the Environment

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THE DETERMINATION OF TRACE METALS IN VEGETATION BY THE SPECTRO ICP-OES

1.0 SUMMARY

This method is used for the routine analysis of vegetation materials for 18 elements. Results are reported for aluminum, barium, beryllium, boron, calcium, cadmium, cobalt, chromium, copper, iron, magnesium, manganese, molybdenum, nickel, lead, strontium, vanadium and zinc.
Metals are analyzed in vegetation because of the potential toxic effects certain elements have on plants, animals and humans. Toxic elements that are absorbed by plants can work their way up the food chain through animals to humans.

As well, the presence of certain elements can be an indication of local emission sources. The presence of low levels of essential elements can be an indication of a lack in the soil of necessary nutrition.

1.1 Principle of Method

The samples of dried, ground "washed" or "unwashed" terrestrial vegetation, dried ground mossbags or freeze-dried ground aquatic vegetation are weighed out and ashed. The ash is digested with a mixed hot acid mixture and the resultant solution is analyzed for 18 metals using the Spectro Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES).

The option of "washed" or "unwashed" is designed to provide some measure of determining whether the metals of interest are surface deposits or are incorporated within the plant tissue. Ashing followed by aqua regia digestion removes organic matter which would otherwise interfere in the subsequent analysis. The ICP provides the high temperature conditions required for atomic speciation necessary for the accurate determination of metal concentrations by emission spectrometry.

ICP-OES is a widely used technique for the multi-element analysis of environmental samples. Solutions of vegetation materials are aspirated into an argon plasma which is a high energy source (approximately 8000°C). The plasma desolvates the aerosol, leaving salt particles for vaporization and atomization. The atoms move from a ground state into an excited state. When the atoms return to a lower energy state, photons are emitted at specific wavelengths. A spectrum is thus obtained. Each emitted wavelength is proportional to the concentration of the particular element in the sample solution and is measured by an optical spectrometer. The spectrum is separated into component wavelengths by a diffraction grating and a photomultiplier detector measures the intensity of the light. The intensity of each emitted wavelength is proportional to the concentration of the particular element in solution.

The instrument is calibrated for each element using a set of prepared standards of known analyte concentration. The instrument response to the standards are measured and a calibration curve produced.

1.1.1 Relationship to Other Methods.

As a result of the speed of analysis, comparable or superior detection limits and relative freedom of interferences, ICP-OES has replaced Atomic Absorption Spectrophotometry (AAS) as the method of choice for multi-element analysis. Unlike AAS, many elements may be determined simultaneously. The high temperature of the plasma makes the method free of the chemical and ionization interferences present in AAS.

eliminating the need for suppressants and releasing agents. It is also less susceptible to ionization interferences and generally has better detection limits than Direct Current Plasma-Optical Emission Spectrometry (DCP-OES) (see Reference 1.7.1).

Spectral interferences or overlap does occur in ICP-OES and corrections based on the sample matrix are usually required. This problem is not generally encountered in AAS. For this reason, when a multi-element capability is not required, AAS is often the method of choice.

1.2 Parameters Measured

Eighteen parameters are measured routinely by ICP-OES.

Parameter	Parameter
Aluminium	Iron
Boron	Lead
Barium	Magnesium
Beryllium	Manganese
Cadmium	Molybdenum
Calcium	Nickel
Chromium	Strontium
Cobalt	Vanadium
Copper	Zinc

The LIMS Product Code is MET3065.

1.3 Sample Matrices

Vegetation, terrestrial and aquatic (VE) and mossbags (VM) matrices are analyzed using this method.

1.4 Sample Requirements

1.4.1 Specifications.

1.4.1.1 Terrestrial Vegetation and Mossbag Samples.

Vegetation and mossbag samples are collected and prepared for analysis by the Ministry of Environment, Standards Development Branch, Phytotoxicology Section. No preservative is required. The sample is dried at 80°C, disaggregated and mechanically ground to pass through a 1.0 mm screen. The sample is placed in a glass jar with a plastic lid and submitted to the Laboratory Services Branch.

The jars must be recapped immediately after removing the sample aliquot for analysis. During storage the lids must be secure to prevent absorption of moisture as results are based on the sample weight as received. A minimum of 20 g of sample is required.

There is an indefinite holding time for these samples, once dried and stored at ambient temperature.

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1.4.1.2 Aquatic Vegetation

Aquatic vegetation samples are collected and prepared for analysis by the Ministry of Environment, Environmental Monitoring and Reporting Branch or Standards Development Branch. The sample is freeze-dried and mechanically ground to pass through a 1.0 mm screen. A minimum of 5 g of sample is submitted in a glass vial and submitted to the LSB.

There is an indefinite holding time for these samples, once freeze-dried and stored at ambient temperature.

1.4.2 Contingencies.

An extra jar of sample is usually retained by the processing laboratory. In the event of insufficient sample, the originator must resample.

If sample size is limited, a list of analytical priority should be included. If any sample is not analyzed, a LIMS Remark Code is entered to explain the absence of the result. Examples of LIMS Remark Codes are:

CODE	EXPLANATION
NDUA	No Data: Unsuitable for Analysis
NDIS	No Data: Insufficient Sample

Some results will be entered with a LIMS Remark Code to further explain the numeric result. Examples of this type of LIMS Remark Code are:

CODE	EXPLANATION
UNH	Unreliable: Sample Not Homogeneous
UIC	Unreliable: Improper Container

1.5 Shortcomings

1.5.1 Interferences.

Spectral overlap is the main source of determinate error in ICP-OES. This occurs when some of the light emitted by one element has a wavelength within the bandpass of the exit slit of another element. An enhanced signal for the analyte will be measured. This enhancement is offset by applying an inter-element correction factor (IEC) or by finding an alternate wavelength at which to measure the light emitted by the analyte. Large IEC factors should be avoided if possible, as they may result in a deterioration of detection limits and accuracy. Analyte wavelengths used are chosen to avoid optical interference from major elements occurring in the samples (Ca, and Mg) and from base metals (Cr, Cu, Fe, Ti, V and Zn).

The IEC factors used on the Spectro are shown in Appendix IV under SPECTROIEC. They correct for the spectral interferences

1.5.2 Biases.

[illegible]

Scattered light and molecular emission of light from the plasma itself produces a background emission which enhances the

Standard Operating Procedure for Processing of Soil Samples Prior to Analyses

Author:	_Debbie Terry/Jane Thrush______	Version:	_1.1_______
Signature:	_Debbie Terry/Jane Thrush______	Date:	__April 17, 2000_
Authorized By:	_George Crawford________________________________		
Name:	__George Crawford__________________________________		
Title:	__Manager, Ecological Standards and Toxicology Section________		
Date:	__April 17, 2000______________________________		

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1 SCOPE

The following protocol is followed by the Ecological Standards and Toxicology Section of Standards Development Branch for drying of soil samples before analyses. This SOP is in support of the following PCLS Section methods: E3012, E3096, E3137, E3138, E3139, E3142, E3263, E3327 and E3328. This SOP is also in support of Spectroscopy Section methods: E3073, E3075, E3215, E3059, E3245 and General Chemistry and Microbiology Section methods: E3005, E3013, E3015 and E3116.

2 OBJECTIVE

To ensure that all soil samples have been dried, sieved and ground in a consistent manner to ensure homogeneity of the samples prior to analysis.

3 TEXT

NOTE: All non-disposable labwares are soaked in tap water, scrubbed with Alconox, rinsed with tap water and a final rinse of pure water, then air-dried between samples to prevent cross-contamination.

Soil samples are usually processed by the Ministry of the Environment, Standards Development Branch, Ecological Standards and Toxicology Section.

3.1 Labwares

3.1.1 Spatula, rubber.
3.1.2 Brush, paint, small (1 inch).
3.1.3 Labels, adhesive.
3.1.4 Pen, marker, permanent.
3.1.5 Bottle, wash, polyethylene.
3.1.6 Kimwipes.
3.1.7 Scoop.
3.1.8 Bag, garbage.
3.1.9 Mask, dust, (3M 8710).
3.1.10 Gloves, disposable.
3.1.11 Dishes, drying (disposable weigh dishes, 120 x 120 mm).
3.1.12 Jars, glass with plastic lids, 125 mL.
3.1.13 Boxes, cardboard (with capacity to hold 24-125 mL jars).

3.2 Reagents

3.2.1 Water, pure.

3.3 Equipment

3.3.1 Mortar and pestle, procelain or agate.
3.3.2 Sieve, brass, 2mm (10 mesh ASTM), 8 inch diameter with bottom pan.
3.3.3 Sieve, brass, <355 µm, (45 mesh ASTM), 8 inch diameter with bottom pan.
3.3.4 Grinder, Retsch, (model RMU), with agate mortar or equivalent.
3.3.5 Fan, 3 speed (optional).

3.4 Procedure

Soil Processing

3.4.1 After soil (SO) type samples are received from Field Investigators, the samples are logged into PIMS (Phytotoxicology Information Management System) and recorded in the Processing log.

3.4.2 The entire contents of each sample bag is spread out on clean, plastic trays, making sure to break the large lumps of soil. The assigned field number is clipped to the tray. This does not apply to samples collected for organic analysis.

3.4.3 The trays are placed in closed shelving cupboards. The soil is allowed to dry at room temperature for a minimum of 48 hours or until no moisture remains. The soil may be turned periodically to aid in the drying process.

NOTE: Wear a dust mask and gloves when handling soil samples.

3.4.4 Under the fumehood, the entire sample is desegregated using a wooden mallet and any twigs, rocks, stones are removed and discarded.

3.4.5 The entire sample is sieved through a Number 10 mesh, (2.0MM sieve) to obtain a soil fraction. Any material not passing through the sieve is discarded.

3.4.6 If pH or conductivity is requested transfer sufficient sample for analysis of the <2.00 mm sample into a glass jar labelled with the field sample number. Place the jars in cardboard storage boxes. Label the outside of the box with the sample numbers and year.

3.4.7 After throughly mixing the sieved sample, a sub-aliquot of < 2.0 mm fraction is taken and the excess sample is discarded.

3.4.8 The sub-sample is further desegregated using a mortar and pestle, or by a mechanical grinder. The **entire** sub-sample is ground until it passes through a Number 45 mesh (355 μm sieve)

3.4.9 Operation of Grinder.

3.4.9.1 Ensure that the agate motor is rotated until locked in position.

3.4.9.2 Place plastic ring over the motor (do not operate grinder without this ring in place).

3.4.9.3 Close lid and tighten latch.

3.4.9.4 Turn timer **ON** for approximately 5 minutes.

3.4.9.5 When grinder has stopped, loosen the latch, open lid and remove mortar.

3.4.9.6 Sieve sample through a Number 45 mesh, (355μm sieve).

3.4.10 Transfer the <355 μm sample into a 125 mL glass jar labelled with the field sample sticker, place in cardboard box. Label the outside of the box with the field numbers and year.

3.5 Cleaning

3.5.1 Clean sieve by inverting over garbage pail and tapping lightly. Use a paint brush to remove sample trapped in the sieve holes by brushing lightly with a paint brush so the particles are pushed back through the mesh. Wipe sieve pan with a Kimwipe. Rinse the mortar and pestle with Pure Water and dry with Kimwipes between samples.

4 PARTS REVISED:

4.1 April 2000
Format change to conform to LSBSOP.001
SOP reviewed and reauthorized.

5 REFERENCES:

6 REFERENCED SUPPLEMENTS:

Lakefield Research was granted formal certification by the Standards Council of Canada (SCC) and the Canadian Association of Environmental Analytical Laboratories (CAEAL), in January 1994. In October 1995, the Standards Council of Canada issued Lakefield Research Analytical Services accreditation at the ISO/IEC Guide 25 level for various inorganic and organic parameters.

ISO/IEC Guide 25 is an internationally accepted standard for laboratory operation that covers all aspects of a laboratory's operation. Guide 25 accreditation is available worldwide. The Guide 25 designation automatically signifies that the laboratory has been judged by an independent panel of skilled auditors to be conducting its business at an internationally acceptable level and that the laboratory has *proven* its proficiency with the accredited methods by participating in regular formal proficiency programs. Guide 25 is also dynamic. The auditing criteria for laboratories has evolved over twenty years and will continue to change to take into account new technologies, new management philosophies, new analytical requirements and new challenges to data integrity.

Laboratories seeking accreditation have two choices, they can seek registration to ISO/IEC 9002, an international quality management standard, or they can apply for accreditation under Guide 25. Guide 25 provides a specific assessment of a laboratory's technical capabilities. ISO/IEC 9002 provides a generic system for quality management applicable to any type or size of organization. Guide 25 addresses both quality management and the technical aspects of operating a testing laboratory. For example, Guide 25 includes requirements for the technical competence of personnel, test and calibration procedures and proficiency testing. The calibration and testing activities of Guide 25 accredited laboratories comply with the relevant requirements of the ISO/IEC 9000 series standards. However, accreditation to the ISO/IEC 9000 series standards will not automatically qualify a laboratory for accreditation under Guide 25. ISO/IEC 17025, a proposed new standard is even more explicit. ISO/IEC 17025 will replace Guide 25 early in 2000 and will allow laboratories to establish a single quality system to satisfy the requirements of both ISO/IEC 9000 and ISO/IEC 17025.

The quality assurance system at Lakefield consists of a documented quality system. All appropriate documentation (quality manual, methods, written instructions, standard operating procedures, and data approval criteria) is in place. As required, the Quality Control Co-ordinator is independent of the production area of the laboratory and reports directly to the Manager.

Quality control procedures are method specific and include duplicate samples, spiked blanks, spiked replicates, reagent/instrument blanks, preparation control samples, certified reference material analysis, and instrument control samples, as appropriate for the individual methods. Matrix matching of reference materials to samples is always attempted. Frequency of insertion of control samples is method specific and follows legislated guidelines. Specific MISA or EPA protocols are followed for all environmentally mandated tests. Of the total samples analyzed at Lakefield Research, a minimum of 20% is quality control and often that percent is exceeded.

Lakefield Research is committed to delivering high quality sample analysis. Methods and method detection limits are reviewed and revalidated annually in order to confirm that data quality objectives are being met and maintained. Lakefield Research also participates in many formal and informal proficiency testing programs. In addition, the laboratory is involved in many informal programs as well as being an active participant in the certification programs for new reference materials with CANMET, NRC, ROCKLABS, NIST, etc.

Lakefield Research Analytical Services strives to be in the forefront of providing quality work. In February of 1998 Lakefield Research was the first commercial analytical lab to be evaluated at ISO/IEC Guide 25 for various mining and mineralogical parameters.

Lakefield Research has been inspected and approved by the Ontario Ministry of the Environment as a MISA analytical facility. Similarly, the Standards Council of Canada and CAEAL audit the Lakefield Research quality control/quality assurance program on a routine basis. Copies of the current scope of testing and accreditation documentation are available upon request. All methods are currently summarized in mini-methods that are available on request and any method specific questions can be addressed at any time. If you have any further questions regarding quality control in the laboratory, please do not hesitate to contact me.

Sincerely,

Diane Wingett
Quality Control Co-ordinator
Phone: 705-652-2006
E-mail: dwingett@lakefield.com

METHOD SUMMARY

METHOD 9-2-37 Preparation of Sewage Sludges and Soils for the Determination of Various Metals Using the MARS 5 MAW2 Microwave Oven

1. **Parameter(s) measured, unit(s):**
   Various Metals (g/t)

2. **Typical sample size:**
   Dry samples: 0.5000 – 0.5050 g
   Wet samples: 10mL

3. **Type of sample applicable (media):**
   Sewage, sludges, and soils.

4. **Sample preparation technique used:**
   Mix the sample thoroughly to ensure that a homogeneous subsample is taken.

5. **Sample preservation required and holding time:**
   N/A

6. **Method of analysis used:**
   - Weigh 0.5000-0.5050 g or pipette 10 mL of sample into a Teflon sleeve.
   - Add 5 mL each of concentrated HNO_3 and HCl
   - Place the vessels in the microwave carousel. Place in microwave and start first heating cycle.
   - Allow vessels to cool to <60°C (~ approx. 45 min.).
   - Pour contents into 50 mL volumetric flask and dilute to volume with deionized water.
   - Analyze by ICP-OES
   - Calculate Final Concentration (g/t)

7. **Data reduction by:**
   Computer, on line, data fed to the Laboratory Information Management System with secure audit trail.

8. **Accreditation:**
   Standards Council of Canada in partnership with the Canadian Association of Environmental Laboratories (CAEAL) at ISO/IEC Guide 25 standards.