Standard Operating Procedure for:

Using the Inductively Coupled Plasma – Optical Emissions Spectroscopy (ICP-OES) Instrument for the Determination of Trace Metal Concentration in Water, Sediment, or Organic Samples
(ICP metals.doc)

Missouri State University

and

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Table of Contents

1 Identification of the method

Operation of the ICP Varian Model 150AX to determine trace metal concentration of water, sediment, or organic samples.

2 Applicable matrix or matrices

This instrument and procedure can be used for the analysis of natural samples.

3 Detection limit

Detection limits depend on the metal, matrix, interferences, and operating conditions, and must be determined experimentally.

4 Scope of method

These procedures allow Missouri State University (MSU) laboratory personnel to use the ICP Varian Model 150AX, which permits effective multielemental determination of metals. The procedures in this method are applicable for the following elements: aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, calcium, chromium, cobalt, copper, iron, lead, lithium, magnesium, manganese, molybdenum, nickel, potassium, selenium, silica, silver, sodium, strontium, thallium, vanadium, and zinc. MSU projects generally focus on arsenic, cadmium, copper, zinc, and lead. Detailed instruction for the preparation of those standards is in Section 11 of OEWRI Standard Operating Procedures regarding water, sediment, and organic media. The preparation of additional standards will be necessary If other elements are of interest.

5 Summary of method

The procedures follow Standard Method 3120B and guidelines provided by the manufacturer. A radio frequency field is inductively coupled to ionized argon gas by a water-cooled coil. This coil surrounds a quartz “torch” that supports and confines plasma that carries a sample aerosol. When the sample aerosol is injected directly into the ICP its atoms are subjected to 6000 to 8000°K, exciting and in some cases ionizing them. The atomic and/or ionic emission spectra are then measured for intensity using a photomultiplier at wavelengths specific for the elements of interest.

6 Definitions

6.1 Duplicate - Two samples taken at the same time and place under identical circumstances and that are treated identically throughout field and laboratory procedures. Analysis of field duplicates indicates the precision associated with sample collection, preservation, and storage.

6.2 Replicate - The division of one sample into 2 samples for separate analysis. A replicate is made primarily to assess precision associated with analytical procedures.

6.3 Field blank - Prepared by filling a sample container with DDI while in the laboratory. The trip blank is taken to the field and exposed to the exact conditions of the samples collected, but is not opened or used in any other way. Trip blanks are used to determine contamination error associated with container cleanliness and sample handling and shipment.

6.4 Rinsate blank - Prepared by using analyte-free water in decontaminated equipment or instrumentation, such as collection or filtering apparatus, to determine residual contamination from that equipment or instrumentation. Consult with the project manager to determine what equipment or instrumentation requires a rinsate blank.

6.5 DDI water – Deionized water further purified by a Barnstead Cartridge Deionization Nanopure II System that pretreats, exchanges ions, and removes organics.

6.6 Standards – Prepared with known concentrations of each metal of concern and corresponding acids and reagents to mirror the matrix.

6.7 Blank – Prepared by using DDI water and corresponding acids and reagents to mirror the matrix. This blank is used to regulate ICP-OES drift and must be less than the MDL.

6.8 Method detection limit (MDL) -- The lowest level at which an analyte can be detected with 99 percent confidence that the analyte concentration is greater than zero. The MDL is normally determined as three times the standard deviation of the blank measurements.

7 Interferences

7.1 Spectral interference occurs when light emission from spectral sources other than the element of interest is overlapped and increases signal intensity. Spectral interference can be avoided by selecting alternate analytical wavelengths, choosing background correction positions, or using empirically determined correction factors with the computer software.

7.2 Nonspectral interferences include physical and chemical interferences. Physical interferences are associated with the nebulization and transport of the sample. If a sample contains more than 10% by volume acid or more than 1500mg of dissolved solids/L viscosity and surface tension properties of the sample. Simple dilution can cure physical interferences. Dissolved solids also contribute to salt buildup on the tip of the nebulizer. Changes in argon quality and quantity can decrease the interference. Chemical interferences are caused by molecular compound formation, ionization, thermochemical effects during vaporization and atomization. The use of matrix matched standards or spikes lessen the influences of both physical and chemical interferences.

8 Health and safety

8.1 Protect from water borne illness by wearing protective gloves while filtering undigested water samples, avoid touching eyes, nose and mouth and washing hands frequently with soap and water.

8.2 Calibration standards contain high concentrations of metals and concentrated acids so exposure should be as low as reasonably achievable. Wear protective gloves and eye protection and prevent any contact with skin or lungs. These

chemicals have the potential to be highly toxic or hazardous: cadmium granules, ammonium hydroxide, sodium hydroxide, phosphoric acid, sulfanilamide, and hydrochloric acid. For details consult the MSDS located in Temple 125.

8.3 Wear appropriate clothing for a chemical laboratory: close toed shoes, limited jewelry, lab coat, hair out face, etc. Protect eyes and hands with appropriate goggles and gloves.

9 Personnel qualifications

All laboratory technicians have a working knowledge of laboratory housekeeping, sample handling and labeling, analytical procedures, and health and safety protocols. Missouri State University (MSU) laboratory personnel who have written Standard Operating Procedures for the instrumentation used and who provide consistent oversight of the laboratories have trained all laboratory technicians. All projects involving the use of laboratory instrumentation are under the supervision of a project manager.

10 Equipment and supplies

10.1 ICP Varian Model 150AX unit
10.2 True samples
10.3 All duplicates, replicates, blanks, and standards
10.4 Additional blank to flush the system between standards and samples
10.5 Safety materials: eye goggles, gloves, etc.
10.6 Laboratory Notebook, Pen

11 Reagents and standards

All reagents and standards will be prepared using the standard operating procedures appropriate for the media of interest. Reagents and standards for trace metal analyses will be stored in the trace metal cabinet or other trace metal free environments. All reagents and standards will be sealed and transferred to the room containing the instrument before analysis and will be removed from the room upon completion of analysis.

12 Sample collection, preservation, shipment and storage

12.1 Samples are not collected using this procedure, consult with the project manager for specific sample collection, preservation, and storage procedures. Consult with the project manager to determine what rinsate blanks should be collected during time of sample collection.

12.2 Samples are not shipped off of the MSU campus, but are sealed and transferred upstairs to the room with the instrument before analysis and returned to a trace metal free environment upon completion of the analysis. Samples will be disposed of only after the project manager reviews data derived from the samples.

12.3 All samples to be analyzed for trace metal concentration will be stored in the trace metal cabinet or other trace metal free environment.

13 Quality control

13.1 All standards, replicates, and blanks should be prepared at the same time, covered during nonuse and transport, and used immediately to prevent contamination.

13.2 Only trace metal apparatus will be used during trace metal determinations and will be taken from and stored in the trace metal cabinet only.

13.3 All glassware and bottles used during trace metal determinations will be pre-washed and stored appropriately to prevent contamination.

13.4 All data including quality control data will be maintained and available for reference and inspection by the project manager during and after the analyses.

13.5 A duplicate should be prepared for every tenth sample and processed and analyzed as a true sample.

13.6 The instrument should be recalibrated after every twentieth sample, or whenever the control or blank fall out of range.

13.7 The control and blank should be analyzed after every fifth sample.

13.8 Deionized water will be used to flush the system between standards and samples.

13.9 Data derived from analyses will be monitored by the analyst. When the calibration blank concentration exceeds the detection limit, carryover is occurring. Repeat rinsing until proper calibration blank concentrations are obtained and inform the project manager.

13.10 Data derived from analysis will be monitored. Use the control standard to check for instrument drift. When the control or standard produces concentrations that deviate by more than ±10%, drift is occurring. Recalibrate and reanalyze all of the samples analyzed after the last acceptable instrument check to insure quality. If evidence of drift persists, terminate sample analysis and inform the project manager.

13 Calibration and standardization

Refer to the manual ICP Varian Model 150AX for unit calibration and consult with a project manager for any questions regarding the ICP. Startup and calibration procedures are detailed in section 15 of this SOP.

15 Procedure

15.1 Startup and calibration

a. Open the water circulator and flip the switch up to the on position.

b. Turn exhaust fan 2 to the on position.

c. Reattach peristaltic pump tubing to the pump head and apply tension to the tubing.

d. Turn on monitor.

e. Turn on plasma power with switch located on the left portion of the instrument.

f. Press F10 to bring up the method index.

g. Press shift F12 to ignite the plasma torch. If torch does not light, try again.

i. Select option 22 from the main menu and select “Grating” from the options at the bottom of the page. This measures emission from an internal mercury lamp to calibrate the system. The grating calibration is satisfactory if the values in the “DP” column (Difference from Previous) are all less than 10, with the exception of the first value, which may exceed 10.

j. Switch to the methods page, and highlight “RapidRun” at the bottom of the page.

k. Enter the number corresponding to the desired method.

l. Check the instrumentation parameters, which should be as follows:

Stabilization Time	30s
Plasma Power	1.00kW
Plasma	15.0L/min
Auxiliary	1.50L/min
Pump Speed	15.0rpm
Nebulizer	200kPa

m. Wavelengths for each element should be set at:

	As	Cu	Zn	Pb	Cd
Wavelength (nm)	188.979	327.396	213.856	220.353	228.802

n. Place the bottle with the high standard in it on the platform on the “X” to load the standard.

o. Wipe the sampling tube and Insert it into the bottle ensuring that the tube does not lie on the bottom of the bottle.

p. Press Std. Select standard 1 from the options at the bottom of the page. The keyboard spacebar will toggle between the different standards.

q. Allow the first calibration standard solution to reach the pump before pressing the run key (F5, with the green arrow) on the keyboard to the right of instrument. Aspirate or "run" the standard until the system has completed scans of all elements.

r. As the liquid is drawn into the instrument check for any solution leaks from tubing as well as air bubbles during the periods of wavelength scanning.

s. When the instrument has completed the run, remove the tube from the bottle, wipe it clean, and insert it into the DDI water bottle or separate bottle containing the calibration blank near the platform.

t. Repeat the prior three steps for each additional calibration standard.

u. Rinse the instrument for at least 45 seconds between standard, calibration blank, or sample runs to decrease the likelihood of cross contamination from the previous solution.

v. Place the bottle with the calibration blank in it on the platform on the "X" to load the calibration blank.

x. Insert the tube into the bottle ensuring that the tube does not lie on the bottom of the bottle.

y. Select "Blank" from the options at the bottom of the page and run.

z. Rerun the calibration blank, but this time using the "sAmple" option. Label this as "Blank check 1". Values should be less than detection limits.

aa. Note that after calibration (or recalibration), the calibration calculations are not completed until the first sample is run. When the blank is rerun as a sample, calibration results will be calculated and printed. Inspect these to make sure that all calibrations appear satisfactory.

bb. Load and run the control check solution to check calibration. Values should be within $\pm$ 10% of the expected values. If not, recalibrate the instrument.

15.2 Sample Analyses

a. Run all samples inserting the calibration blank and control after every five samples. Use "sample" option to run samples, controls, etc. When "Sample" is selected, type in the identification information for the sample.

b. Check each measurement for the calibration blank and check standard. All values for the calibration blank should be below the desired detection

limit, and all values for the check standard should be within ±10% of the expected values.

c. Rinse the instrument for at least 45 seconds between standard, calibration blank, and sample runs to decrease the likelihood of cross contamination from the previous solution.

d. Label the ICP printout during sample analyses to identify the calibration blank and control. Run field blanks, trip blanks, rinsate blanks, method blanks, duplicates, replicates, and true samples as samples through the ICP. Refer to sampling scheme to identify blanks, duplicates and replicates after the ICP analysis is complete. Only label the calibration blank and control on the ICP printout.

15.3 Instrument Shutdown

a. After all samples have been analyzed, return the tube to the DDI water bottle near the platform and allow DDI water to run through the instrument.

b. Turn off the torch by pressing the shift F12 key.

c. Turn off the plasma power by switching off the RF switch on the front left side of the instrument.

d. Turn off the monitor.

e. Turn off exhaust fan 2.

f. Turn of the water circulator.

g. Relax tension from the peristaltic tubing and disconnect the tubing from the pump head.

16 Data acquisition, calculations, and reporting

16.1 Calculation of water sample concentrations, corrected for dilution: For samples for which dilution was required, the concentration in the original water sample is calculated using equation 1.

a. Equation 1: $C_{sample} = C_{analysis} \times (10.0\ mL / V_{aliquot})$

$V_{aliquot}$

b. Where: C_{sample} is the concentration in the original water sample,
$C_{analysis}$ is the concentration of the solution as determined in (16.1),
and $V_{aliquot}$ is the volume of the aliquot diluted to 10 mL in (15.2.b).

c. If additional dilution was carried out (e.g., for samples with $A_{220} > 2.0$), include an additional correction factor.

16.2 Reporting results: Results should be reported to 0.001 mg/L precision.

16.3 The evaluation of MDL and precision require calculation of standard deviation. Standard deviations should be calculated as indicated below, where n = number of samples, x = concentration in each sample. Note: This is the sample standard deviation calculated by the STDEV function in Microsoft Excel.

$$s = \left(\frac{\sum x^2 - \frac{\left(\sum x\right)^2}{n}}{n-1} \right)^{1/2}$$

16.4 Field method corrections: Subtract the values of the field blank, trip blank, and rinsate or equipment blank from each sample value to correct for field or equipment contamination.

16.5 Laboratory method corrections: Subtract the value of the method blank from each sample value to correct for reagent or method contamination.

16.6 Instrument corrections: Subtract the value of an adjacent calibration blank from each sample value to make a baseline drift correction. Both negative and positive values should be used.

17 Computer hardware and software

The ICP Varian Model 150AX unit is preprogrammed with methods used for MSU laboratory analyses. Refer to the ICP Varian Model 150AX unit manual for unit hardware and software information and consult with a project manager for any questions regarding the ICP.

18 Method performance

Refer to Method 3120B Table 3120:II for generally expected precision and bias regression equations. Desired precision and accuracy should be within ±20%.

19 Pollution prevention

All wastes from these procedures shall be collected and disposed of according to existing waste policies within the MSU College of Natural and Applied Sciences.

20 Data assessment and acceptable criteria for quality control measures

20.1 Data assessment and acceptable criteria could fluctuate based on the media being analyzed. The project manager will establish acceptable criteria and will assess all data collected.

20.2 The analyst should review all data for correctness (e.g., calculations).

20.3 Precision values are calculated for pairs of duplicate analyses. Record the precision values as a percent on the bench sheet. The desired precision is ± 20%.

20.4 The completed bench sheet is reviewed by the analyst's supervisor or the OEWRI QA coordinator.

21 Corrective actions for out-of-control or unacceptable data

21.1 If a precision value exceeds 20% then the analyst should note that the data are associated with an out-of-control duplicate analysis in the data report given to the QA/QC manager. The upper control limit (UCL) = 20%.

21.2 If a blank value exceeds the detection limit then the analyst should include that information in the data report given to the QA/QC manager.

21.3 If there is sufficient volume of sample remaining for all samples, the batch may be re-analyzed. Quality control data from the first run must be recorded.

21.4 If data are unacceptable for any reason, the analyst should review their analytical technique prior to conducting this analysis again.

22 Waste management

Samples should be collected as waste in an appropriate labeled container.

23 References

Standard Methods for the Examination of Water and Wastewater. 1995. 19th Edition. APHA, AWWA, WEF Publishers.

24 Tables, diagrams, flowcharts and validation data

There are no tables, diagrams, flowcharts or validation data for this method