

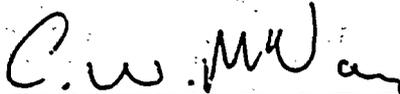
WEST VALLEY NUCLEAR SERVICES CO., INC.

ACM-AA-2003, Rev. 1
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ANALYTICAL CHEMISTRY METHOD
ANALYTICAL AND PROCESS CHEMISTRY

Metals (Atomic Absorption Method [Hydride])

Approved By:



C. W. McVay, Manager
Analytical and Process Chemistry

Part I

1.0 PURPOSE

1.1 To establish an analytical method for the determination of metals on aqueous samples by atomic absorption (hydride).

2.0 APPLICATION

2.1 Metals in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in surface waters, domestic and industrial wastes, and saline waters.

2.2 Detection limits and optimum ranges of the metals will vary depending on the element and model atomic absorption spectrophotometer. WVNS will be using an Instrumentation Laboratory Video 22. See the I. L. manual for sensitivities of each individual metal.

3.0 DISCUSSIONS

3.1 Atomic absorption spectroscopy is well suited for the determination of trace metals in water samples. It is a rapid method, relatively free from interferences and excellent sensitivity for most elements. Utilizing the hydride generator attachment provides the capability of analyzing arsenic, selenium, and mercury from a few ppb to higher concentrations.

3.2 Sample Handling and Preservation

3.2.1 Aqueous samples are made acidic by adding 1 percent nitric acid at the time of collection. If possible the analysis is done immediately, otherwise the sample is stored at approximately 4°C until it can be tested. This is especially important for environmental samples.

3.2.1.1 For the determination of total metals, the sample is digested as per Standard Method 302.D nitric acid digestion. Mix sample and transfer a suitable volume (50 mL) to a 100 mL beaker. Add 5 mL concentrated HNO₃. Bring to a slow boil and evaporate on a hot plate to the lowest volume possible (about 15 to 20 mL) before precipitation or salting-out occurs. Add 5 mL concentrated HNO₃, cover with a watch glass, and heat to obtain a gentle refluxing action. Continue heating and adding concentrated HNO₃ as necessary until digestion is complete, as shown by a light-colored, clear solution.

3.2.1.2 Add 1 to 2 mL concentrated HNO₃ and warm slightly to dissolve any remaining residue. Wash down beaker walls and watch glass with distilled water. Transfer to a 50 mL volumetric flask with two 5 mL portions of water, adding these rinsings to the volumetric flask. Cool, dilute to mark, and mix thoroughly. Take portions of this solution for required metal determinations.

3.2.2 Solids Samples

Solid samples must first be digested before they can be analyzed on the spectrophotometer. Microwave dissolution of solid samples is discussed in ACM-MICRO-1901. Fusion dissolution of samples can be done in a number of ways, using a number of different fusion agents, such as: Potassium Hydroxide, Sodium Carbonate, and Rubidium Oxide. Fusion of samples can be found with their applicable method.

3.2.3 Slurry Samples

Slurry samples can be handled in much the same way as solid samples. See ACM-MICRO-1901 for more specific techniques.

3.3 Procedure for Analyzing Metals

3.3.1 Follow instrument manual for all parameters on each metal determination.

3.4 Preparation of Standards

Standard calibration solutions are prepared by diluting a manufacturer's certified stock metal solutions at the time of analysis. Standards made from in-house reagents may also be made as long as another standard is available to compare with. For best results, calibration standards should be prepared fresh each time an analysis is to be made and discarded after use. Prepare a blank and calibration standards in graduated amounts in the appropriate range. The acid strength of the calibration standards should be similarly adjusted to the sample acid strength. Beginning with the blank, aspirate the solutions and record the readings. Repeat the operation with both the calibration standards and the samples a sufficient number of times to secure a reliable average reading for each solution. Stock metal solutions are good for one year.

3.5 DEFINITION OF TERMS

3.5.1 Sensitivity is the concentration in milligrams of metal per liter that produces an absorption of 1 percent.

3.5.2 Detection Limit is defined as the concentration that produces absorption equivalent to twice the magnitude of the fluctuation in the background (zero absorption).

3.5.3 Total Metals is the concentration of metals determined on a sample following vigorous digestion.

3.5.4 AA is an abbreviation for Atomic Absorption

3.5.5 AAS is an abbreviation for Atomic Absorption Spectrophotometer.

3.5.6 PPB is a unit of concentration expressed as Parts Per Billion.

3.5.7 PPM is a unit of concentration expressed as Parts Per Million.

4.0 REFERENCES

4.1 Standard Methods for the Examination of Water and Waste Water, 16th Edition.

- 4.2 EPA, "Methods for Chemical Analysis of Water and Waste,"
EPA-600/4-77-020
- 4.3 Atomic Absorption Methods Manual, Instrumentation Laboratory

Part II

5.0 EQUIPMENT

NOTE: All calibrated equipment is controlled per ACP 7.1

- 5.1 Atomic Absorption Spectrophotometer: Instrumentation Laboratory
Video 22 with vapor generating apparatus.
- 5.2 Hot plate.
- 5.3 Hood: To ventilate acid fumes when digesting the sample.
- 5.4 Exhaust hood to ventilate gas fumes from AA unit when burner head
is in operation.
- 5.5 Assorted beakers and volumetric flasks.
- 5.6 Pipets capable of delivering 5 μ l - 10 mL accurately.

6.0 REAGENTS AND STANDARDS

NOTE: All reagents and standards are prepared per ACP 8.1 and have a
shelf life of one year unless otherwise stated.

- 6.1 Deionized distilled water
- 6.2 Nitric acid - concentrated - reagent grade.
- 6.3 Hydrochloric acid - concentrated reagent grade.
- 6.4 Hydrofluoric acid - concentrated reagent grade.
- 6.5 Hydrogen Peroxide (30 percent)
- 6.6 Reagent grade sodium borohydrate
- 6.7 Reagent grade stannous chloride
- 6.8 Reagent grade Sodium Hydroxide
- 6.9 Stock metal solutions from 1,000 ppm solutions.

- 6.10 Standard metal solutions: Prepare a series of standards of the metal, by dilution of the appropriate stock solution, to cover the concentration range desired.
- 6.11 Fuel and oxidant: Commercial grade acetylene is generally acceptable. Plant-supplied instrument air (not oxygen).

7.0 SAFETY PRECAUTIONS

- 7.1 All sample digesting techniques must be done in ventilated fume hoods.
- 7.2 When using AAS, always turn on fuel last and turn off fuel first, after AAS drainage is verified. Failure to do this may result in a flashback.
- 7.3 AAS drainage is verified.
- 7.4 Safety glasses required while working in the laboratory.
- 7.5 Follow standard laboratory safety precautions (ACP 7.2).

8.0 RECORDS

- 8.1 All measurement data and sample identification shall be recorded on the worksheet (Attachment A). The final result shall be recorded on the analytical request form.

9.0 CALIBRATION AND CONTROL

Consistently accurate results requires careful quality control checks of the various components involved in the test per ACP 8.2.

- 9.1 Quality Control charts will be established for all elements tested. A portion of the QC test solution will be run during each group of samples. If the deviation exceeds 3σ , the samples will be retested.
- 9.2 Stock solutions and QC test solutions are either purchased from a reputable source, such as SPEX or J. T. Baker or prepared from high-purity (>99.9 percent) metals and metal compounds in the laboratory. All reagents used must be of at least analytical grade quality. Refer to ACP 7.1, Section 5.9.2 for proper labeling and shelf life.
- 9.3 Calibration solutions are prepared by taking aliquots of the stock solutions and diluting them with 5 percent nitric acid. The concentration range may extend past the linear portion of the curve to the limits acceptable by the instrumental software.

- 9.4 The instrument is calibrated using the prepared solutions over the range of interest.
- 9.5 Prior to calibration, the instrument is optimized. A standard is then run using the absorbance mode and the value is compared to the "book value." This is found in the manufacturer's procedure book. If the value obtained is less than 70 percent of what is expected, then the AA is reoptimized. When the instrument response cannot be brought within 70 percent of this listed sensitivity, a problem exists with the determination.
1. Check the standard solutions for correct concentrations.
 2. Troubleshoot instrumental parameters.
 3. Obtain service, if necessary.

Samples may be run if a calibration curve is obtainable over the range of interest.

10.0 GENERAL PROCEDURE FOR ANALYSIS BY ATOMIC ABSORPTION

- 10.1 After choosing the correct hollow cathode lamp for the desired metal, install in the instrument and roughly set the wavelength dial according to manufacturer's specifications.
- 10.2 Set slit width according to manufacturer's suggested setting for the element being analyzed.
- 10.3 Turn on instrument, apply to the hollow cathode lamp the current suggested by the manufacturer and let instrument warm up until energy source stabilizes, generally about 5 to 10 minutes. Adjust background correction to proper level, if needed.
- 10.4 Readjust current as necessary after warm-up.
- 10.5 Optimize wavelength by adjusting wavelength dial until maximum energy gain is obtained. Align lamp to give the maximum energy reading.
- 10.6 Align cell attachment until optimum energy gain is achieved. Follow 10.1.20 to 10.1.23 for analysis.
- 10.7 For hydride generator analysis, make all necessary connections to generator, turn on argon gas, turn on hydride generator and prime pump with sodium borohydrate solution, for the analysis of arsenic and selenium or stannous chloride solution for the analysis of mercury.
- 10.8 Adjust all controls on the hydride generator to desired settings, according to manufacturer's specifications.

10.9 The instrument is now ready to operate.

10.10 When analyses are completed, shut off hydride generator and argon gas making sure the gas line is bled.

11.0 CALCULATION

11.1 Direct determination: Read the metal value in mg/L from the calibration curve or directly from the readout system of the instrument.

mg/L metal in sample = (mg/L of metal in the aliquot) x D

where D = $\frac{\text{mL of aliquot} + \text{mL of deionized distilled water}}{\text{mL of aliquot}}$

12.0 ATTACHMENT

> 12.1 Attachment A - Atomic Absorption Worksheet (Hydride)

ATTACHMENT A

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ATOMIC ABSORPTION WORKSHEET

>
SAMPLE NAME _____ LOG NUMBER _____

SPECIAL INSTRUCTIONS _____

Instruments Used: Instrumentation Laboratory Video 22 AA/AE Spectrophotometer
Serial, #1356

SAMPLE ID									
ELEMENT									
<u>QC VALVE</u>									
QC MEAN									
STD 1									
ABS									
STD 2									
ABS									
STD 3									
ABS									
ALIUQOT (Ml)									
VOLUME									
ALIQUOT									
ABSORBANCE									
SAMPLE (PPB)									

ANALYST _____ DATE _____

APPROVED _____ DATE _____