

## METHOD 7760A

### CADMIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

#### 1.0 SCOPE AND APPLICATION

1.1 Method 7760 is an atomic absorption procedure approved for determining the concentration of silver (CAS Registry Number 7440-22-4) in wastes, mobility procedure extracts, soils, and ground water. All samples must be subjected to an appropriate dissolution step prior to analysis.

#### 2.0 SUMMARY OF METHOD

2.1 Prior to analysis by Method 7760, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to the acid-digestion procedure described in this method.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into an air/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the silver concentration. Background correction must be employed for all analyses.

2.3 The typical detection limit for this method is 0.01 mg/L; typical sensitivity is 0.06 mg/L.

#### 3.0 INTERFERENCES

3.1 Background correction is required because nonspecific absorption and light scattering may occur at the analytical wavelength.

3.2 Silver nitrate solutions are light-sensitive and have the tendency to plate out on container walls. Thus silver standards should be stored in brown bottles.

3.3 Silver chloride is insoluble; therefore, hydrochloric acid should be avoided unless the silver is already in solution as a chloride complex.

3.4 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

#### 4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer: Single- or dual-channel, single- or double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Silver hollow cathode lamp.

- 4.3 Strip-chart recorder (optional).
- 4.4 Graduated cylinder or equivalent.
- 4.5 Hot plate or equivalent - adjustable and capable of maintaining a temperature of 90-95°C.
- 4.6 Ribbed watchglasses or equivalent.

## 5.0 REAGENTS

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

5.2 Reagent Water. Reagent water is interference free. All references to water in the method refer to reagent water unless otherwise specified.

5.3 Nitric Acid (concentrated),  $\text{HNO}_3$ .

5.4 Ammonium Hydroxide (concentrated),  $\text{NH}_4\text{OH}$ .

5.5 Silver Stock Standard Solution (1,000 mg/L),  $\text{AgNO}_3$ . Dissolve 0.7874 g anhydrous silver nitrate in water. Add 5 mL  $\text{HNO}_3$  and bring to volume in a 500-mL volumetric flask (1 mL = 1 mg Ag). Alternatively, procure a certified aqueous standard from a supplier and verify by comparison with a second standard.

5.6 Silver working standards - These standards should be prepared from silver stock solution to be used as calibration standards at the time of analysis. These standards should be prepared with nitric acid and at the same concentrations as the analytical solution.

5.7 Iodine solution (1N). Dissolve 20 g potassium iodide (KI), in 50 mL of water. Add 12.7 g iodine ( $\text{I}_2$ ) and dilute to 100 mL. Store in a brown bottle.

5.8 Cyanogen iodide solution. Add 4.0 mL ammonium hydroxide, 6.5 g potassium cyanide (KCN), and 5.0 mL of iodine solution to 50 mL of water. Mix and dilute to 100 mL with water. Do not keep longer than 2 weeks.

**CAUTION:** This reagent cannot be mixed with any acid solutions because toxic hydrogen cyanide will be produced.

5.9 Air.

5.10 Acetylene.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a  $\text{pH} < 2$  with nitric acid.

6.4 When possible, standards and samples should be stored in the dark and in brown bottles.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

## 7.0 PROCEDURE

7.1 Sample preparation - Aqueous samples should be prepared according to Steps 7.2 and 7.3. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

### 7.2 Preparation of aqueous samples

7.2.1 Transfer a representative aliquot of the well-mixed sample to a beaker and add 3 mL of concentrated  $\text{HNO}_3$ . Cover the beaker with a ribbed watch glass. Place the beaker on a hot plate and cautiously evaporate to near dryness, making certain that the sample does not boil. DO NOT BAKE. Cool the beaker and add another 3-mL portion of concentrated  $\text{HNO}_3$ . Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

NOTE: If the sample contains thiosulfates, this step may result in splatter of sample out of the beaker as the sample approaches dryness. This has been reported to occur with certain photographic types of samples.

7.2.2 Continue heating, adding additional acid, as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, evaporate to near dryness and cool the beaker. Add a small quantity of  $\text{HNO}_3$  so that the final dilution contains 0.5% (v/v)  $\text{HNO}_3$  and warm the beaker to dissolve any precipitate or residue resulting from evaporation.

7.2.3 Wash down the beaker walls and watch glass with water and, when necessary, filter the sample to remove silicates and other insoluble material that could clog the nebulizer. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis.

7.3 If plating out of AgCl is suspected, the precipitate can be redissolved by adding cyanogen iodide to the sample. This can be done only after digestion and after neutralization of the sample to a pH > 7 to prevent formation of toxic cyanide under acid conditions. In this case do not adjust the sample volume to the predetermined value until the sample has been neutralized to pH > 7 and cyanogen iodide has been added. If cyanogen iodide addition to the sample is necessary, then the standards must be treated in the same manner. Cyanogen iodide must not be added to the acidified silver standards. New standards must be made, as directed in Steps 5.5 and 5.6, except that the acid addition step must be omitted. For example, to obtain a 100 mg/L working standard, transfer 10 mL of stock solution to a small beaker. Add water to make about 70 mL. Make the solution basic (pH above 7) with ammonium hydroxide. Rinse the pH meter electrodes into the solution with water. Add 1 mL cyanogen iodide and allow to stand 1 hour. Transfer quantitatively to a 100-mL volumetric flask and bring to volume with water.

CAUTION: CNI reagent can be added only after digestion to prevent formation of toxic cyanide under acidic conditions. CNI reagent must not be added to the acidified silver standards.

NOTE: Once the sample or sample aliquot has been treated with the CNI reagent and diluted per instruction, the solution has a cyanide concentration of approximately 260 mg/L. A solution of that cyanide concentration must be considered a potential hazardous waste and must be disposed of using an approved safety plan in accordance with local authority requirements. Until such time that a detailed disposal plan can be fully documented and approved, the use of the CNI reagent should be avoided.

7.4 The 328.1 nm wavelength line and background correction shall be employed.

7.5 An oxidizing air-acetylene flame shall be used.

7.6 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

## 8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

## 9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 272.1 of "Methods for Chemical Analysis of Water and Wastes."

9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

## 10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.
2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, December 1987.
3. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
4. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ATSM: Philadelphia, PA, 1985; D1193-77.

TABLE 1.  
METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Wastewater treatment sludge	3050	2.3, 1.6 mg/Kg
Emission control dust	3050	1.8, 4.2 mg/Kg

METHOD 7760A  
SILVER (ATOMIC ABSORPTION, DIRECT ASPIRATION)

