

METHOD 7741A

SELENIUM (ATOMIC ABSORPTION, GASEOUS HYDRIDE)

1.0 SCOPE AND APPLICATION

1.1 Method 7741 is an atomic absorption procedure that is approved for determining the concentration of selenium in wastes, mobility-procedure extracts, soils, and ground water, provided that the sample matrix does not contain high concentrations of chromium, copper, mercury, silver, cobalt, or molybdenum. All samples must be subjected to an appropriate dissolution step prior to analysis. Spiked samples and relevant standard reference materials are employed to determine applicability of the method to a given waste. If interferences are present the analyst should consider using Method 7740.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared according to the nitric/sulfuric acid digestion procedure described in this method. Next, the selenium in the digestate is reduced to Se(IV) with tin chloride. The Se(IV) is then converted to a volatile hydride with hydrogen produced from a zinc/HCl or sodium borohydrate/HCl reaction.

2.2 The volatile hydride is swept into an argon-hydrogen flame located in the optical path of an atomic absorption spectrophotometer; the resulting absorbance is proportional to the selenium concentration.

2.3 The typical detection limit for this method is 0.002 mg/L.

3.0 INTERFERENCES

3.1 High concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel, and silver can cause analytical interferences.

3.2 Traces of nitric acid left following the sample work-up can result in analytical interferences. Nitric acid must be distilled off the sample by heating the sample until fumes of SO_3 are observed.

3.3 Elemental selenium and many of its compounds are volatile; therefore, certain samples may be subject to losses of selenium during sample preparation.

4.0 APPARATUS AND MATERIALS

4.1 100-mL beaker.

4.2 Electric hot plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95°C.

4.3 A commercially available zinc slurry hydride generator or a generator constructed from the following material (see Figure 1):

4.3.1 Medicine dropper: Fitted into a size "0" rubber stopper capable of delivering 1.5 mL.

4.3.2 Reaction flask: 50-mL, pear-shaped, with two 14/20 necks (Scientific Glass, JM-5835).

4.3.3 Gas inlet-outlet tube: Constructed from a micro cold-finger condenser (JM-3325) by cutting the portion below the 14/20 ground-glass joint.

4.3.4 Magnetic stirrer: To homogenize the zinc slurry.

4.3.5 Polyethylene drying tube: 10-cm, filled with glass wool to prevent particulate matter from entering the burner.

4.3.6 Flow meter: Capable of measuring 1 liter/min.

4.4 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190-800 nm, and provisions for interfacing with a strip-chart recorder and simultaneous background correction.

4.5 Burner: Recommended by the particular instrument manufacturer for the argon-hydrogen flame.

4.6 Selenium hollow cathode lamp or electrodeless discharge lamp.

4.7 Strip-chart recorder (optional).

5.0 REAGENTS

5.1 Reagent water: Water should be monitored for impurities. Reagent water will be interference free. All references to water will refer to reagent water.

5.2 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If a method blank made with the acid is <MDL, the acid can be used.

5.3 Concentrated sulfuric acid: Acid should be analyzed to determine levels of impurities. If a method blank made with the acid is <MDL, the acid can be used.

5.4 Concentrated hydrochloric acid: Acid should be analyzed to determine levels of impurities. If a method blank made with the acid is <MDL, the acid can be used.

5.5 Diluent: Add 100 mL 18 N H₂SO₄ and 400 mL concentrated HCl to 400 mL reagent water and dilute to a final volume of 1 liter with reagent water.

5.6 Potassium iodide solution: Dissolve 20 g KI in 100 mL reagent water.

5.7 Stannous chloride solution: Dissolve 100 g SnCl_2 in 100 mL of concentrated HCl.

5.8 Selenium standard stock solution: 1,000 mg/L solution may be purchased, or prepared as follows: Dissolve 0.3453 g of selenious acid (assay 94.6% of H_2SeO_3) in reagent water. Add to a 200-mL volumetric flask and bring to volume (1 mL = 1 mg Se).

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 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile selenium compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

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

7.0 PROCEDURE

7.1 Sample preparation:

7.1.1 To a 50-mL aliquot of digested sample (or, in the case of extracts, a 50-mL sample) add 10 mL of concentrated HNO_3 and 12 mL of 18 N H_2SO_4 . Evaporate the sample on a hot plate until white SO_3 fumes are observed (a volume of about 20 mL). Do not let it char. If it chars, stop the digestion, cool, and add additional HNO_3 . Maintain an excess of HNO_3 (evidence of brown fumes) and do not let the solution darken because selenium may be reduced and lost. When the sample remains colorless or straw yellow during evolution of SO_3 fumes, the digestion is complete.

Caution: Venting reaction vessels should be done with caution and only under a fume hood or well ventilated area.

7.1.2 Cool the sample, add about 25 mL reagent water, and again evaporate to SO_3 fumes just to expel oxides of nitrogen. Cool. Add 40 mL concentrated HCl and bring to a volume of 100 mL with reagent water.

7.2 Prepare working standards from the standard stock solutions. The following procedures provide standards in the optimum range.

7.2.1 To prepare a working stock solution, pipet 1 mL standard stock solution (see Paragraph 5.8) into a 1-liter volumetric flask. Bring to volume with reagent water containing 1.5 mL concentrated HNO_3 /liter. The concentration of this solution is 1 mg Se/L (1 mL = 1 mg Se).

7.2.2 Prepare six working standards by transferring 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of the working stock solution (see Paragraph 7.2.1) into 100-mL volumetric flasks. Bring to volume with diluent. The concentrations of these working standards are 0, 5, 10, 15, 20, and 25 ug Se/L.

7.3 Standard additions:

7.3.1 Take the 15-, 20-, and 25-ug standards and transfer quantitatively 25 mL from each into separate 50-mL volumetric flasks. Add 10 mL of the prepared sample to each. Bring to volume with reagent water containing 1.5 mL HNO₃/liter.

7.3.2 Add 10 mL of prepared sample to a 50-mL volumetric flask. Bring to volume with reagent water containing 1.5 mL HNO₃/liter. This is the blank.

7.4 Follow the manufacturer's instructions for operating an argon-hydrogen flame. The argon-hydrogen flame is colorless; therefore, it may be useful to aspirate a low concentration of sodium to ensure that ignition has occurred.

7.5 The 196.0-nm wavelength shall be used for the analysis of selenium.

7.6 Transfer a 25-mL portion of the digested sample or standard to the reaction vessel. Add 0.5 mL SnCl₂ solution. Allow at least 10 min for the metal to be reduced to its lowest oxidation state. Attach the reaction vessel to the special gas inlet-outlet glassware. Fill the medicine dropper with 1.50 mL sodium borohydride or zinc slurry that has been kept in suspension with the magnetic stirrer. Firmly insert the stopper containing the medicine dropper into the side neck of the reaction vessel. Squeeze the bulb to introduce the zinc slurry or sodium borohydride into the sample or standard solution. The metal hydride will produce a peak almost immediately. When the recorder pen returns partway to the base line, remove the reaction vessel.

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 270.3 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 270.3.

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