

METHOD 7741

SELENIUM (ATOMIC ABSORPTION, GASEOUS HYDRIDE)

1.0 Scope and Application

1.1 Method 7741 is an atomic absorption procedure which is approved for determining the concentration of selenium in wastes, mobility procedure extracts, soils, and groundwater, 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.

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 the +4 form using tin chloride. The +4 selenium is then converted to a volatile hydride with hydrogen produced from a zinc/HCl reaction.

2.2 The volatile hydride is swept into an argon-hydrogen flame located in the optical path of an atomic absorption spectrophotometer, and 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 workup can result in analytical interferences. Nitric acid must be distilled off by heating the sample until fumes of SO₃ are observed.

3.3 Elemental selenium and many of its compounds are volatile and 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.

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 A 50-ml pear-shaped reaction flask 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 A 10-cm polyethylene drying tube filled with glass 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 having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 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.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Concentrated sulfuric acid: Acid should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.4 Concentrated hydrochloric acid: Acid should be analyzed to determine levels of impurities. If impurities are detected all analyses should be blank-corrected.

5.5 Diluent: Add 100 ml 18 N H_2SO_4 and 400 ml concentrated HCl to 400 ml Type II water and dilute to a final volume of 1 liter with Type II water.

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5.6 Potassium iodide solution: Dissolve 20 g KI in 100 ml Type II water.

5.7 Stannous chloride solution: Dissolve 100 g SnCl_2 in 100 ml of conc. HCl.

5.8 Selenium standard stock solution: 1000 mg/liter solution may be purchased, or prepared as follows. Dissolve 0.3453 g of selenious acid (assay 94.6% of H_2SeO_3) in Type II 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 Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II 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 less than 2 with nitric acid.

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

7.0 Procedure

7.1 Sample preparation

7.1.1 To a 50-g sample (or in the case of EP extracts a 50-ml sample) add 10 ml conc. 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.

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

7.2 Prepare working standards from the standard stock solutions. The following procedure provides standards in the optimum working range.

7.2.1 Pipet 1 ml stock solution into a 1-liter volumetric flask. Bring to volume with Type II water containing 1.5 ml conc. HNO_3 /liter. The concentration of this solution is 1 mg Se/liter (1 ml = 1 μg 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 selenium stock standard (see Section 5.8) into a 100-ml volumetric flasks. Bring to volume with diluent. The concentrations of these working standards are 0, 5, 10, 15, 20 and 25 μg Se/liter.

7.3 Standard additions

7.3.1 Take the 15-, 20-, and 25- μg 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 Type II water containing 1.5 ml HNO_3 /liter.

7.3.2 Add 10 ml of prepared sample to a 50-ml volumetric flask. Bring to volume with Type II water containing 1.5 ml HNO_3 per liter. This is the blank.

7.4 Follow the manufacturer's instructions for operating an argon-hydrogen flame. The argon-hydrogen flame is colorless so 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 SnCl_2 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 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 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.

7.7 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.8 Duplicates, spiked samples, and check standards should be routinely analyzed.

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7.9 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. For example, if the method of standard additions was employed, the analytical value will be one-tenth the concentration of the original sample due to dilution during preparation. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.