

METHOD 7740

SELENIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7740 is an atomic absorption procedure approved for determining the concentration of selenium 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 7740, samples must be prepared in order to convert organic forms of selenium to inorganic forms, to minimize organic interferences, and to convert samples to suitable solutions for analysis. The sample-preparation procedure varies, depending on the sample matrix. Aqueous samples are subjected to the acid-digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of lamp radiation during atomization will be proportional to the selenium concentration.

2.3 The typical detection limit for this method is 2 ug/L.

3.0 INTERFERENCES

3.1 Elemental selenium and many of its compounds are volatile; therefore, samples may be subject to losses of selenium during sample preparation. Spike samples and relevant standard reference materials should be processed to determine if the chosen dissolution method is appropriate.

3.2 Likewise, caution must be employed during the selection of temperature and times for the dry and char (ash) cycles. A nickel nitrate solution must be added to all digestates prior to analysis to minimize volatilization losses during drying and ashing.

3.3 In addition to the normal interferences experienced during graphite furnace analysis, selenium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Selenium analysis is particularly susceptible to these problems because of its low analytical wavelength (196.0 nm). Simultaneous background correction is required to avoid erroneously high results. High iron levels can give overcorrection with deuterium background. Zeeman background correction can be useful in this situation.

3.4 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at full power at regular intervals in the analytical scheme.

3.5 Selenium analysis suffers interference from chlorides (>800 mg/L) and sulfate (>200 mg/L). The addition of nickel nitrate such that the final concentration is 1% nickel will lessen this interference.

4.0 APPARATUS AND MATERIALS

4.1 250-mL Griffin beaker.

4.2 10-mL volumetric flasks.

4.3 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 simultaneous background correction and interfacing with a strip-chart recorder.

4.4 Selenium hollow cathode lamp, or electrodeless discharge lamp (EDL): EDLs provide better sensitivity for the analysis of Se.

4.5 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.6 Strip-chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis, such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

4.7 Pipets: Microliter with disposable tips. Sizes can range from 5 to 1,000 uL, as required.

5.0 REAGENTS

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

5.2 Concentrated nitric acid (HNO₃): 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. Hydrogen peroxide (30%): Oxidant should be analyzed to determine levels of impurities. If a method blank made with the oxidant is <MDL, the oxidant can be used.

5.4 Selenium standard stock solution (1,000 mg/L): Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 0.3453 g of selenious acid (actual assay 94.6% H_2SeO_3 , analytical reagent grade) or equivalent in Type II water and dilute to 200 mL.

5.5 Nickel nitrate solution (5%): Dissolve 24.780 g of ACS reagent grade $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or equivalent in Type II water and dilute to 100 mL.

5.6 Nickel nitrate solution (1%): Dilute 20 mL of the 5% nickel nitrate to 100 mL with Type II water.

5.7 Selenium working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of the analysis. Withdraw appropriate aliquots of the stock solution, add 1 mL of concentrated HNO_3 , 2 mL of 30% H_2O_2 , and 2 mL of the 5% nickel nitrate solution. Dilute to 100 mL with Type II water.

5.8 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.9 Hydrogen: Suitable for instrumental analysis.

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 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 <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: Aqueous samples should be prepared in the manner described in Steps 7.1.1 to 7.1.3. Sludge-type samples should be prepared according to Method 3050. 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.

7.1.1 Transfer 100 mL of well-mixed sample to a 250-mL Griffin beaker; add 2 mL of 30% H_2O_2 and sufficient concentrated HNO_3 to result in an acid concentration of 1% (v/v). Heat for 1 hr at 95°C or until the volume is slightly less than 50 mL.

7.1.2 Cool and bring back to 50 mL with Type II water.

7.1.3 Pipet 5 mL of this digested solution into a 10-mL volumetric flask, add 1 mL of the 1% nickel nitrate solution, and dilute to 10 mL with Type II water. The sample is now ready for injection into the furnace.

7.2 The 196.0-nm wavelength line and a background correction system must be employed. Follow the manufacturer's suggestions for all other spectrophotometer parameters.

7.3 Furnace parameters suggested by the manufacturer should be employed as guidelines. Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.4 Inject a measured μL -aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

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

7.6 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.7 Duplicates, spiked samples, and check standards should be analyzed every 20 samples.

7.8 Calculate metal concentrations: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account.

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 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the entire sample preparation and analytical process.

8.7 The method of standard additions (see Method 7000, Section 8.7) 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.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 270.2 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

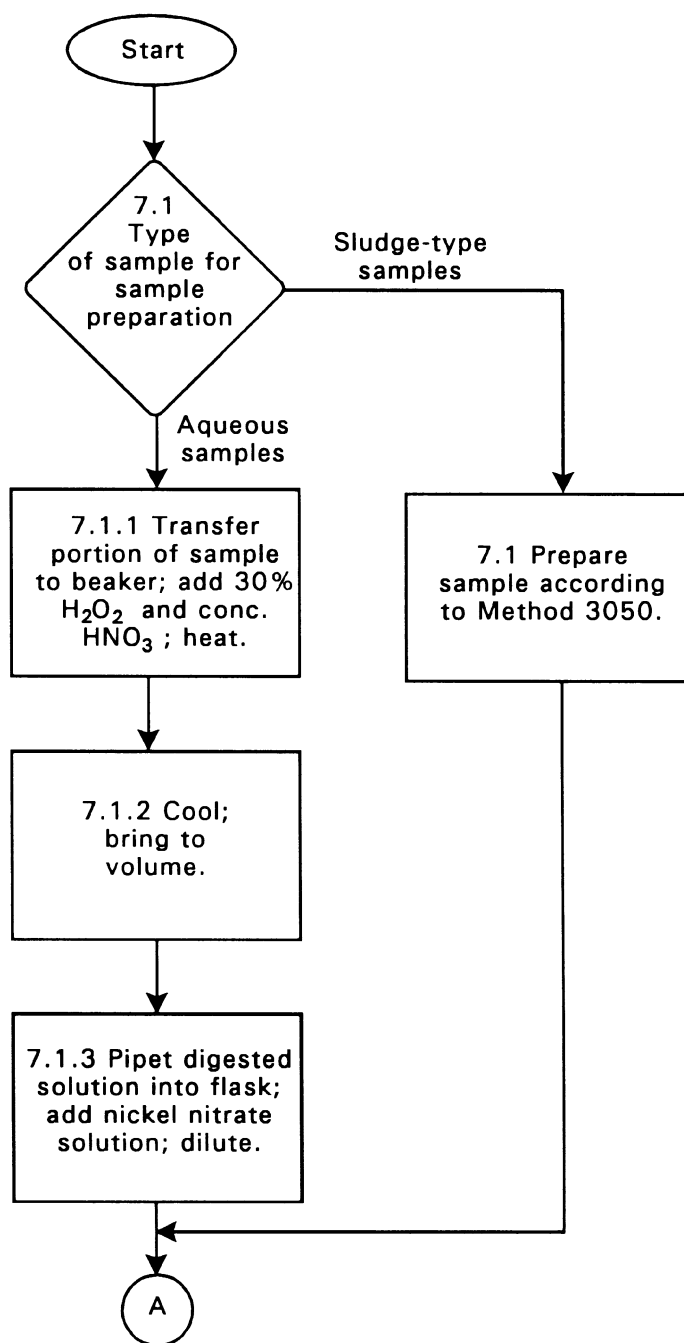
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 270.2.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Emission control dust	3050	14, 11 ug/g

METHOD 7740
SELENIUM (ATOMIC ABSORPTION, FURNACE METHOD)



METHOD 7740
SELENIUM (ATOMIC ABSORPTION, FURNACE METHOD)
(Continued)

