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100 Barr Harbor Dr., West Conshohocken, PA 19428
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Standard Test Methods for Selenium in Water[1]

This standard is issued under the fixed designation D 3859; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These test methods cover the determination of dissolved and total recoverable selenium in most waters and wastewaters. Both test methods utilize atomic absorption procedures, as follows:

	Sections
Test Method A—Gaseous Hydride AAS[2]	7 to 15
Test Method B—Graphite Furnace AAS	16 to 24

1.2 These test methods are applicable to both inorganic and organic forms of dissolved selenium. They are applicable also to particulate forms of the element, provided that they are solubilized in the appropriate acid digestion step. However, certain selenium-containing heavy metallic sediments may not undergo digestion.

1.3 These test methods are most applicable within the following ranges:

Test Method A	1 to 20 µg/L
Test Method B	2 to 100 µg/L

These ranges may be extended (with a corresponding loss in precision) by decreasing the sample size or diluting the original sample, but concentrations much greater than the upper limits are more conveniently determined by flame atomic absorption spectrometry.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Note 2 and Note 3.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[3]

D 1193 Specification for Reagent Water[3]

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D–19 on Water[3]

D 3370 Practices for Sampling Water from Closed Conduits[3]

D 3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry[3]

D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents[3]

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in these test methods, refer to Terminology D 1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *total recoverable selenium*—an arbitrary analytical term relating to the recoverable forms of selenium that are determinable by the digestion procedures included in these test methods.

4. Significance and Use

4.1 In most natural waters selenium concentrations seldom exceed 10 µg/L. However, the runoff from certain types of seleniferous soils at various times of the year can produce concentrations as high as several hundred micrograms per litre. Additionally, industrial contamination can be a significant source of selenium in rivers and streams.

4.2 High concentrations of selenium in drinking water have been suspected of being toxic to animal life. Selenium is a priority pollutant and all public water agencies are required to monitor its concentration.

4.3 These test methods determine the dominant species of selenium reportedly found in most natural and wastewaters, including selenities, selenates, and organo-selenium compounds.

5. Purity of 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.[4] Other grades may be used, provided it is ascertained that the reagent is of sufficiently high

[1] These test methods are under the jurisdiction of ASTM Committee D-19 on Water and are the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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[2] Lansford, M., McPherson, E. M., and Fishman, M. J., *Atomic Absorption Newsletter*, Vol 13(4), 1974, pp. 103–105. Pollack, E. N., and West, S. J., *Atomic Absorption Newsletter*, Vol 12(1), 1973, pp. 6–8.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

purity to permit its use without lessening the accuracy of the determination.

5.2 *Purity of Water*— Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Specification D 1193, Type I. Other reagent water types may be used provided it is first ascertained that the water is of sufficiently high purity to permit its use without adversely affecting the bias and precision of the test method. Type II water was specified at the time of round robin testing of this test method.

6. Sampling

6.1 Collect the samples in accordance with Practices D 3370. Take the samples in acid-washed TFE-fluorocarbon or glass bottles. Other types of bottles may be used for sampling, but should be checked for selenium absorption. The holding time for the samples may be calculated in accordance with Practice D 4841.

6.2 When determining only dissolved selenium, filter the sample through a 0.45-µm membrane filter as soon as possible after sampling. Add HNO_3 to the filtrate to bring the pH to <2.0.

6.3 When determining total recoverable selenium, add HNO_3 to the unfiltered sample to a pH of <2.0.

TEST METHOD A—GASEOUS HYDRIDE AAS

7. Scope

7.1 This test method covers the determination of dissolved and total recoverable selenium in the range from 1 to 20 µg/L. The range may be extended by decreasing the sample size or diluting the original sample.

7.2 This test method has been used successfully with reagent water, natural water, wastewater, and brines. The information on precision may not apply to waters of other matrices.

8. Summary of Test Method

8.1 The determination consists of the conversion of selenium in its various forms to gaseous selenium hydride (hydrogen selenide), with the subsequent analysis of the gas by flame AAS.

8.1.1 The conversion consists of (*a*) decomposition and oxidation to selenium (VI), (*b*) reduction to selenium (IV), and (*c*) final reduction to selenium hydride.

8.1.2 The absorbance is determined at 196.0 nm in a hydrogen-argon (air-entrained) flame.

8.2 Sample concentrations are obtained directly from a simple concentration versus absorbance calibration curve.

8.3 Total recoverable selenium is determined by treating the entire sample as the procedure indicates, and the dissolved selenium is determined by treating the filtrate after the sample is filtered through a 0.45-µm membrane filter.

9. Interferences

9.1 Mercury and arsenic at concentrations greater than 500 µg/L and greater than 100 µg/L, respectively, may inhibit the formation of selenium hydride.

10. Apparatus

10.1 An apparatus similar to that depicted in Fig. 1, with the components specified in 10.2-10.4.8, is recommended for this test method.[5]

10.2 *Atomic Absorption Spectrophotometer*—The instruments shall consist of an atomizer and burner, suitable pressure and flow regulation devices capable of maintaining constant diluent and fuel pressure for the duration of the test, a selenium lamp, an optical system capable of isolating the desired wavelength, an adjustable slit, a photomultiplier tube or other photosensitive devices such as a light measuring and amplifying device, and a readout mechanism for indicating the amount of absorbed radiation. A background corrector may be used, but is not absolutely essential.

10.2.1 *Selenium Electrodeless Discharge Lamp*—The sensitivity of selenium to atomic absorption spectroscopy is generally improved with this lamp, although some hollow-cathode lamps produce equivalent results. The intensity and stability of the lamp shall be adequate to determine selenium in the range from 1 to 20 µg/L.

10.2.2 *Recorder or Digital Readout, or Both*—Any multi-range, variable-speed recorder, or digital readout accessory that is compatible with the atomic absorption detection system, is suitable.

10.2.3 The manufacturer's instructions are to be followed for all instrument parameters.

10.3 *Gas System*:

10.3.1 See 11.14 for materials for the gas system.

10.3.2 *Pressure-Reducing Valves*—Pressure-reducing valves shall be capable of maintaining argon pressure at 40 psig (275 kPa) and hydrogen pressure at 20 psig (138 kPa).

10.4 *Additional Equipment*:

10.4.1 *Flask Header*—The flask header shall consist of a three-hole rubber stopper into which is inserted:

10.4.1.1 A sintered-glass aeration tube for the argon sweep gas,

10.4.1.2 A small gas chromatographic-type septum (5 to 10 mm in diameter), for injection of the borohydride solution, and

10.4.1.3 A glass outlet tube for the reaction gases to exit.

NOTE 1—Instead of the gas chromatographic-type septum, a more secure seal may be obtained by using a glass tube with a septum cap. These items are commercially available on an individual basis. A different header may be used if proven reliable.

10.4.2 *Fittings and Adapters*—Stainless steel fittings and adapters shall be used to install the reaction-flask header in series with the auxiliary oxidant line and the burner. Plastic or other metals may be substituted if proven acceptable.

10.4.3 *Tubing*—Any commercially available plastic tubing that is not susceptible to attack by hydrochloric acid, selenium hydride, or other gases from the reaction mixture is acceptable. Poly(vinyl chloride) tubing has been found acceptable.

10.4.4 *Gas-Flow Regulator*—A suitable in-line gas-flow valve shall be used to adjust the flow of argon to the reaction-flask header.

10.4.5 *Water Trap (optional)*—Any commercially available glass trap suitable to prevent carryover moisture from going to the burner is acceptable.

[5] A static system, such as one using a balloon, has been found satisfactory for this purpose. See McFarren, E. F., "New, Simplified Method for Metal Analysis," *Journal of American Water Works Association*, Vol 64, 1972, p. 28.

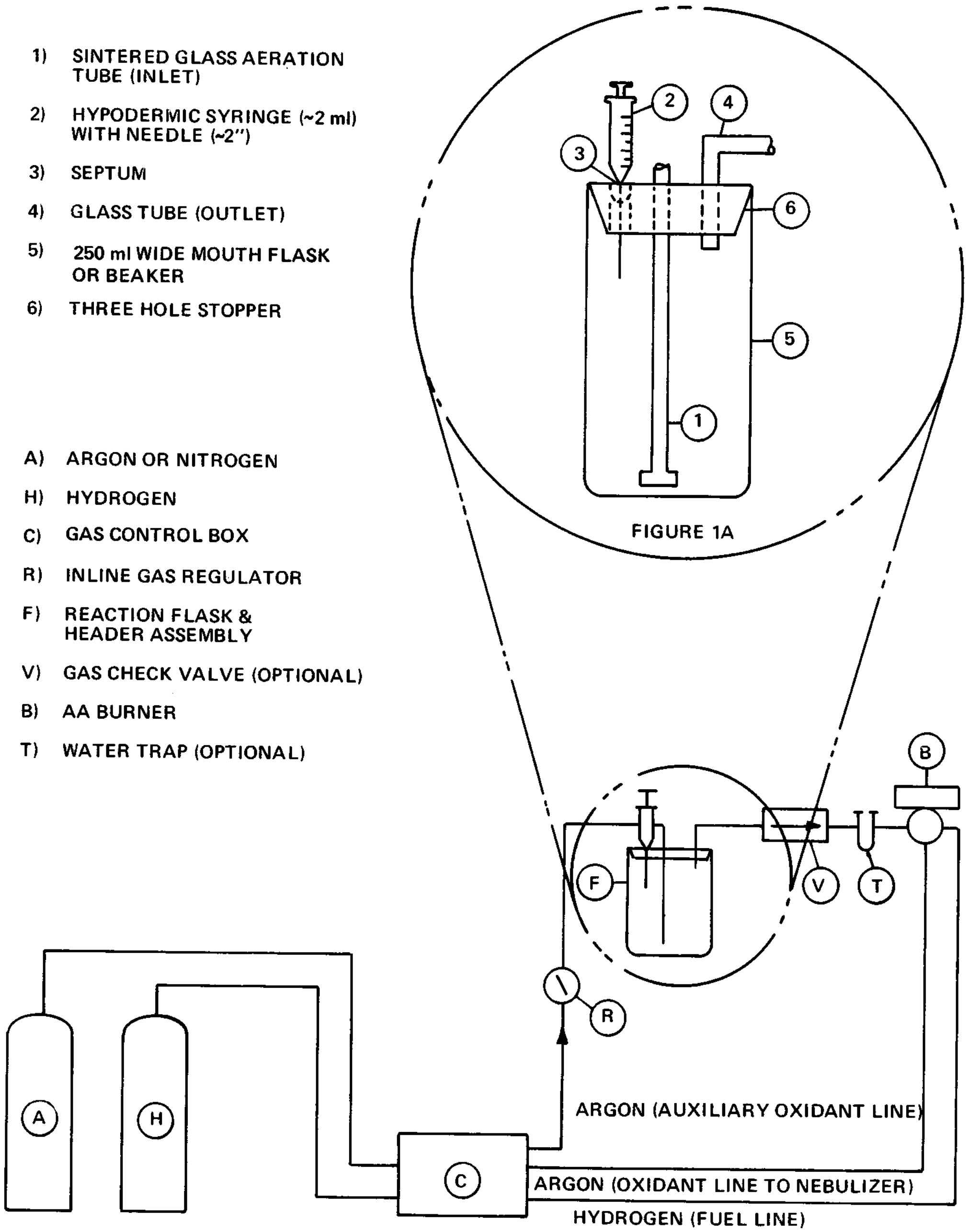

FIG. 1 Apparatus for Selenium Determination

10.4.6 *One-Way Gas Check Valve (optional)*—A one-way check valve can be installed in series with the water trap and burner to prevent hydrogen from back flowing to the generating flask whenever samples are changed. However, precautionary measures could generally preclude the use of this device, since only when the flask header is removed for prolonged periods would there be significant hydrogen back flow.

10.4.7 *Reaction Flasks*, 250-mL spoutless beakers, or their equivalent, with graduations may be used. Conical and restricted neck flasks do not perform as reliably as spoutless beakers.

10.4.8 *Hypodermic Syringe*, 2-mL capacity with a 50-mm needle.

11. Reagents and Materials

11.1 *Calcium Chloride Solution* (30 g/L)—Dissolve 30 g of calcium chloride ($CaCl_2 \cdot 2H_2O$) in water and dilute to 1 L.

11.2 *Hydrochloric Acid* (sp gr 1.19), concentrated hydrochloric acid (HCl).

11.3 *Hydrochloric Acid* (1 + 1)—Add 1 volume of HCl (sp gr 1.19) to 1 volume of water.

11.4 *Hydrochloric Acid* (1 + 99)—Add 1 volume of HCl (sp gr 1.19) to 99 volumes of water.

11.5 *Methyl Orange Indicator Solution* (25 mg/100 mL)—Dissolve 25 mg of methyl orange in 100 mL of water.

11.6 *Nitric Acid* (sp gr 1.42), concentrated nitric acid (HNO_3).

11.7 *Nitric Acid* (1 + 99)—Add 1 volume of HNO_3 (sp gr 1.42) to 99 volumes of water.

11.8 *Potassium Permanganate Solution* (0.3 g/L)— Dissolve 0.3 g of potassium permanganate ($KMnO_4$) in water and dilute to 1 L.

11.9 *Selenium Solution, Stock* (1.00 mL = 1.00 mg selenium)—Accurately weigh 1.000 g of gray elemental selenium and place in a small beaker. Add 5 mL of HNO_3 (sp gr 1.42). Warm until the reaction is complete, then cautiously evaporate to dryness. Redissolve with HCl (1 + 99) and dilute to 1 L with the same acid solution.

11.9.1 Alternatively, certified selenium stock solutions are commercially available through chemical supply vendors and may be used.

11.10 *Selenium Solution, Intermediate* (1.00 mL = 10 µg selenium)—Dilute 5 mL of the selenium stock solution to 500 mL with HCl (1 + 99).

11.11 *Selenium Solution, Standard* (1.00 mL = 0.10 µg selenium)—Dilute 10 mL of the selenium intermediate solution to 1000 mL with HCl (1 + 99). Prepare fresh daily and store in a TFE-fluorocarbon or other acceptable container.

11.12 *Sodium Borohydride Solution* (4 g/100 mL)— Dissolve 4 g of sodium borohydride ($NaBH_4$) and 2 g of sodium hydroxide in water and dilute to 100 mL. Prepare fresh weekly.

NOTE 2—**Warning:** Sodium borohydride reacts strongly with acids.

11.13 *Sodium Hydroxide Solution* (4 g/L)—Dissolve 4 g of sodium hydroxide (NaOH) in water and dilute to 1 L.

11.14 *Gases*:

11.14.1 *Argon* (nitrogen may be used in place of argon)—Standard, commercially available argon is the usual diluent.

11.14.2 *Hydrogen*—Standard, commercially available hydrogen is the usual fuel.

12. Standardization

12.1 Transfer 0.0, 0.5, 1.0, 2.0, 5.0, and 10.0-mL portions of the standard selenium solution (1.0 mL = 0.10 µg Se) to freshly washed 250-mL reaction flasks. Adjust the volume to 50 mL with water.

12.2 Proceed as directed in 13.3-13.15.

12.3 Prepare a calibration curve by plotting absorbance (or recorder scale readings) versus micrograms of selenium on linear graph paper. Alternatively, if provided with this capability, calibrate the spectrophotometer to output micrograms of selenium directly.

13. Procedure

13.1 It is emphasized that careful control of pH, oxidant concentration, temperature, and time are imperative if accurate and precise selenium determinations are to be obtained.

13.2 For each sample, transfer 50 mL or less (to contain not more than 1.0 µg selenium) to a freshly washed 250-mL reaction flask. Make up to 50 mL with water if necessary.

13.3 To each sample, standard, and blank, add a few drops of methyl orange solution, 0.5 mL of $CaCl_2$ solution and three or four boiling stones.

13.4 Adjust the pH to the red end point of methyl orange (pH = 3.1) with HCl (1 + 99) or NaOH solution (4 g/L). Add 0.5 mL of HCl (1 + 99) in excess. A pH meter may be used in place of the indicator if the sample is sufficiently discolored to affect the methyl orange end point.

13.5 Add potassium permanganate solution dropwise (about 3 drops) to maintain the purple tint indicating excess $KMnO_4$. Boil the solution on a hotplate, carefully maintaining the purple tint until the volume is reduced to about 25 mL. Add 2 mL of NaOH solution (4 g/L) and concentrate the solutions to dryness, being careful not to overheat the residue.

13.6 Cool and add 15 mL of concentrated HCl (sp gr 1.19). Heat on a hot water or steam bath for 20 min. Do not boil. This step reduces the selenium (VI) to selenium (IV).

13.7 Cool and add HCl (1 + 1) to adjust the volume to 50 mL. Hold these solutions until all samples and standards are brought to this stage.

13.8 Set the atomic absorption instrument parameters in accordance with the manufacturer's instructions. Typical settings are as follows:

Grating	ultraviolet
Wavelength	196.0 nm
Burner	triple-slot or equivalent
Radiation Source	selenium electrodeless discharge lamp or equivalent
Slit	2.0 nm
Flame	hydrogen-argon (nitrogen may be used in place of argon)

13.9 If the gas control box is not equipped with separate controls for argon and hydrogen, simply connect the oxidant inlet line for the control box to the argon tank regulator and connect the fuel inlet line for the control box to the hydrogen tank regulator. The oxidant controls will then control the argon diluent gas and the fuel controls will control the hydrogen gas. To preclude the possibility of accidentally mixing the hydrogen fuel with the air oxidant normally used with atomic absorption spectroscopy, shut off all sources of air oxidant to the system. Set the tank pressures, the burner control box pressures, and the flow rates in accordance with the manufacturer's instructions for argon and hydrogen.

13.10 Center the burner about 5 mm below the optical light path. Ignite the flame. Since the flame does not give off visible light, optical flame sensors must be bypassed, but the presence of the low-temperature flame may be verified by aspirating tap water, which contains soluble salts that impart color to the flame. Optimize the burner position to give maximum absorbance while aspirating the intermediate selenium standard (1.0 mL = 10 µg selenium).

13.11 Interrupt the auxiliary oxidant line at the burner connection and attach the gas lines, the flask header, and the associated equipment. Connect in series, in this order, the auxiliary oxidant line, the in-line gas flow regulator, and the header aeration tube. Then connect the header outlet tube, the water trap (optional), the one-way check valve (optional), and the auxiliary oxidant inlet. Use minimum lengths of tubing to minimize dilution of the selenium hydride. Attach a reaction flask containing 50 mL of water to the flask header. With argon flowing through the system, adjust the in-line flow regulator to permit a maximum flow of the argon sweep gas to the reaction flask, with negligible solution carryover into the outlet line. The set-up is then complete.

13.12 If a recorder is used, adjust the span so that an absorbance of 0.500 from the spectrophotometer reads full scale on the recorder.

13.13 Rinse the reaction flask and header with water and introduce the blank, sample, or standard into the reaction flask. Replace the header and secure to form a tight seal. Allow the system to stabilize and prepare to record the peak absorbance or the total absorbance.

13.14 The precision of this test method is highly dependent on the use of a consistently reproduced technique in this final step. Inject the 2-mL hypodermic needle through the septum and quickly add 2.0 mL $NaBH_4$ solution (4 g/100 mL) to the sample. The H_2Se evolution will peak within a few seconds, but will trail off for up to 30 s afterward. After the H_2Se is swept from the system, remove the header and rinse well with water.

NOTE 3—**Warning:** Selenium hydride is toxic to certain organs of the body. Avoid inhalation.

13.15 Treat each succeeding sample, blank, and standard in a like manner.

14. Calculation

14.1 Determine the weight of selenium in each sample by referring to 12.3. Calculate the concentration of selenium in the sample in micrograms per litre, using Eq 1:

$$\text{Selenium } \mu g/L = (1000/V) \times W \tag{1}$$

where:
V = volume of sample, mL, and
W = weight of selenium in sample, µg.

15. Precision and Bias [6]

15.1 The overall and single-operator precision of this test method within its designated range for reagent water and nonreagent water varies with the quantity being measured in accordance with Table 1. These values were established for four laboratories, using six operators over three consecutive days. The nonreagent waters included natural, waste, and brine waters.

15.1.1 The overall precision for reagent water varies linearly with the quantity being measured, and it may be expressed mathematically using Eq 2:

$$S_t = 0.146X + 0.49 \tag{2}$$

where:
S_t = overall precision, µg/L, and
X = concentration of selenium, µg/L.

15.2 The bias of this test method determined from recoveries of known amounts of selenium from selenium dioxide and selenium triphenylchloride in a series of prepared standards are given in Table 2.

15.3 The information on precision and bias may not apply to other wastewaters.

15.4 Precision and bias of this test method conform to Practice D 2777–77, which was in place at the time of collaborative testing. Under the allowances made in 1.5 of Practice D 2777–86, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D–19 test methods.

TEST METHOD B—GRAPHITE FURNACE AAS

16. Scope

16.1 This test method includes the determination of dissolved and total recoverable selenium in the range from 2 to 100 µg/L. The range may be extended by decreasing the sample size or diluting the original sample.

16.2 This test method has been used successfully with reagent water, waste treatment plant effluent, tap water, well water, and treated wood plant effluent. The information on precision may not apply to waters of other matrices.

17. Summary of Test Method

17.1 Selenium is determined by a method of graphite furnace AAS, expanded to include background correction and matrix modification, with concentrations determined by a method of standard additions.

17.1.1 The sample, modifier, and standard are placed in the furnace where they are dried, charred (ashed or pyrolyzed), and atomized—the absorbance being determined during atomization. The analysis is repeated for at least two different standard levels for each determination.

17.1.2 The analytical concentration is calculated as functions of the sample absorbance (unspiked) and the absorbance/concentration slope established for the analyte by the method of standard additions.

17.2 A general guide for the application of this procedure is given in Practice D 3919.

17.3 Dissolved selenium is determined on a filtered sample with no pretreatment. Total recoverable selenium is normally

[6] Supporting data are available from ASTM Headquarters. Request RR: D19-1056.

TABLE 1 Overall (S_T) and Single-Operator (S_O) Interlaboratory Precision for Selenium by Gaseous Hydride AAS, Test Method A

Concentration (X), µg/L	S_T	S_O
	Reagent Water	
2.79	0.95	0.72
8.50	1.62	1.44
17.89	2.98	1.71
	Natural Water	
2.69	0.69	0.78
8.56	1.70	1.63
18.35	2.13	1.67

TABLE 2 Recovery and Bias Data, Test Method A (Gaseous Hydride AAS)

Amount Added, µg/L	Amount Found, µg/L	Recovery, %	Bias, %	Statistically Significant at 95 % Confidence Level
		Reagent Water (Type II)		
3	2.8	93	−7	no
8	8.5	106	+ 6	no
17	17.9	105	+ 5	no
		Nonreagent Water (Natural, Waste, and Brine)		
3	2.7	90	−10	no
8	8.6	107	+ 7	no
17	18.4	108	+ 8	yes

determined following acid digestion and filtration. The filtration is omitted only if suspended material is not present.

18. Interferences

18.1 For a complete discussion of general interferences, refer to Practice D 3919.

18.2 The determination of selenium by graphite furnace AAS is especially susceptible to enhancement or suppression interferences. In the determination of 50 µg/L selenium in 5% HCl, copper, germanium, nickel, antimony, tellurium, titanium, and tungsten at 10 mg/L elevate the analytical response by 50 to 150 %. Chromium, iron, mercury, molybdenum, vanadium, and erbium elevate the response by 150 to 300 %. On the other hand, sulfate and phosphate (and, to a lesser degree, nitrate and chloride) suppress the evolvement of selenium during atomization.[7,8]

18.2.1 In the procedure specified, the magnitude of these interferences is reduced by matrix modification through the addition of nickel. The nickel also acts to increase the sensitivity of this test method and to permit the use of higher charring temperatures.[7,9,10]

18.2.2 Residual chemical interferences are compensated for by a method of standard additions, unless such interferences are known to be absent.

18.3 Background interferences are also frequently encountered in the determination of selenium. Unless known to be absent, they are eliminated by means of automatic simultaneous background correction or by means of background correction at an appropriate nonabsorbing spectral line.

18.4 Spectral interferences are not frequently encountered, but for selenium determined at 196.0 nm, such an interference is known to be caused by moderate concentrations of iron. The interference is eliminated by performing the analysis at a wavelength free of such interference.

19. Apparatus

19.1 *Atomic Absorption Spectrophotometer*, for use at about 196.0 nm. (Other wavelengths will be used if they are determined to be both necessary and suitable.)

19.1.1 The optical system, photosensitive device and amplifier, and readout mechanism are to be comparable to those specified in 10.2. A capability for automatic simultaneous background correction will be highly advantageous.

19.1.2 *Selenium Light Source*—A single element hollow-cathode lamp is satisfactory. Multielement lamps (if they do not provide for spectral interferences) and electrodeless discharge lamps may also be used.

19.2 *Graphite Furnace*, compatible with spectrophotometer, with temperature programmer, capable of reaching temperatures sufficient to atomize selenium. Ideally, the temperature programmer should have considerable flexibility so that the analyst can alter the time-at-temperature profile extensively to provide assurances that the profile is satisfactory for the analytical requirements and appropriate for the samples.

19.2.1 *Graphite Tubes*, standard, compatible with furnace device.

NOTE 4—Metal furnaces have reportedly been used successfully in place of graphite furnaces. However, no round-robin data are presently available using these furnaces.

19.3 *Pipets*, microlitre with disposable tips, as required.

19.4 *Strip Chart Recorder*, with full-scale response time of 0.2 s or less. The recorder is recommended so that there will be a permanent record of the analysis and so that problems with the analysis may be easily recognized. Electronic peak-measuring devices may be used but are generally less satisfactory.

20. Reagents and Materials

20.1 *Hydrogen Peroxide* (30%).

20.2 *Nickel Solution* (1 mL = 2.0 mg nickel)—Dissolve 9.9 g of nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$) in reagent water and dilute to 1 L.

20.3 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3).

20.4 *Nitric Acid* (1 + 1)—Add 1 volume of HNO_3 (sp gr 1.42) to 1 volume of water.

20.5 *Nitric Acid* (1 + 499)—Add 1 volume of HNO_3 (sp gr 1.42) to 499 volumes of water.

20.6 *Selenium Solution, Stock* (1.00 mL = 1.00 mg selenium)—Accurately weigh 1.000 g of gray elemental selenium and place in a small beaker. Add 5 mL of HNO_3 (sp gr 1.42). Warm until the reaction is complete, then cautiously evaporate to dryness. Redissolve with HNO_3 (1 + 499) and dilute to 1 L with the same acid solution.

20.6.1 Alternatively, certified selenium stock solutions are commercially available through chemical supply vendors and may be used.

20.7 *Selenium Solution, Intermediate* (1.00 mL = 10 µg selenium)—Dilute 5 mL of the selenium stock solution to 500 mL with HNO_3 (1 + 499).

20.8 *Selenium Solution, Standard* (1.00 mL = 0.10 µg selenium)—Dilute 10 mL of the selenium intermediate solution to 1000 mL with HNO_3 (1 + 499). Prepare fresh daily and store in a TFE-fluorocarbon or other acceptable container.

20.9 *Argon*, standard, welders grade. Nitrogen and hydrogen may also be used if recommended by the instrument manufacturer.

21. Standardization

21.1 Initially set the instrument in accordance with the manufacturer's specifications. Follow the general instructions provided in Practice D 3919, being sure to utilize automatic simultaneous background correction if available.

21.2 Prepare a calibration curve using a blank and a series of standards in the appropriate concentration range in accordance with the general instructions, but with the following modifications:

21.2.1 For each standard and blank, inject into the furnace a sample volume which is no greater than one-half the maximum recommended volume for the furnace. Additionally, inject an aliquot of nickel solution (1.0 mL = 2.0 mg nickel) and an aliquot of reagent water, each equal to one-half the sample volume. The distribution of standard, matrix modifier, and

[7] *Analytical Chemistry*, Vol 47, No. 3, March 1975, p. 428.

[8] *Atomic Absorption Newsletter*, Vol 15, No. 2, March–April 1976, p. 29.

[9] *Atomic Absorption Newsletter*, Vol 14, No. 5, September–October 1975, p. 127.

[10] *Atomic Absorption Newsletter*, Vol 14, No. 5, September–October 1975, p. 109.

water will then be identical to the distribution of sample, matrix modifier, and water or standard addition for the samples.

21.2.2 Utilize the calibration curve to establish the linear concentration range for the test method and to estimate the concentration of the analyte in the samples. Determine the analytical concentration precisely, however, by the method of standard additions.

22. Procedure

22.1 Clean all glassware by rinsing first with HNO_3 (1 + 1) and then with reagent water. If possible, soak the glassware overnight in HNO_3 (1 + 1).

22.2 Measure 100.0 mL of the well-mixed sample into a 125-mL beaker or flask. For total recoverable selenium, add 5 mL of 30% H_2O_2 and 5 mL of HNO_3 (sp gr 1.42). For dissolved selenium, proceed with 22.5.

22.3 Heat the sample at 95°C on a steam bath or hotplate in a well-ventilated fume hood until the volume has been reduced to 15 to 20 mL, making sure that the samples do not boil.

22.4 Cool and filter the sample through a suitable filter, such as fine-textured, acid washed, ashless paper, into a 100-mL volumetric flask. Wash the filter paper 2 or 3 times with reagent water and bring to volume. If suspended material is not present, the filtration may be omitted.

22.5 Inject measured aliquots of sample, nickel nitrate (1.0 mL = 2.0 mg nickel), and reagent water into the furnace, using the volumes specified in 21.2.1.

22.6 In the absence of automatic simultaneous background correction, additionally determine the absorbance at an appropriate nonabsorbing line. (The mercury line at 194.2 nm is usually satisfactory for determinations at 196.0 nm.) Calculate the background-corrected absorbance as the difference between the absorbance determined at the analytical line and the absorbance determined at the nonabsorbing line.

22.7 Carefully observe the absorbance peak assumed to be due to the analyte. With respect to shape and position, it must be identical to that derived for the standards, and it must be completely resolved from other peaks.

22.7.1 If not, modify the time-at-temperature program in accordance with the manufacturer's instructions, to provide for identical and interference-free behavior of the analyte, and reestablish the calibration curve.

22.8 Estimate the concentration of selenium in the sample by reference to the analytical curve. If the apparent concentration is greater than about 40% of the highest linear concentration, dilute the sample so that the concentration falls near that value and analyze the sample again.

22.9 Using either the original sample or the diluted sample, as appropriate, repeat the analysis, but substitute the highest linear selenium standard in place of the reagent water. This will provide for the spike verification detailed in Practice D 3919.

22.10 For the determination of selenium in many matrices, analytical verification in this manner will indicate significant enhancement or suppression effects, which must be compensated for by the method of standard additions. The standard procedure for this test method (specified in Practice D 3919) should be used unless the abbreviated method (22.10.1-22.10.5) is shown to be satisfactory.

22.10.1 In some cases, however, the procedure specified in the general practice may be substantially abbreviated. Certainly for samples where satisfactory relative precision is indicated by the reproducibility for duplicate analyses, concentrations may be determined directly from the absorbance values obtained for the original analysis and the spiking verification.

22.10.2 In such cases, the concentration of selenium in the injected sample may be calculated by the method detailed in Practice D 3919, using the equivalent concentration of the spike as the concentration of the standard addition.

22.10.3 Alternatively, the concentration may be calculated using Eq 3:

$$A \times C/(B - A) = \mu g/L \text{ Se (in injected sample)} \quad (3)$$

where:

A = absorbance of the unspiked sample,
B = absorbance of the spiked sample, and
C = equivalent concentration of the spike, sample basis, µg/L Se.

22.10.4 The precision of the abbreviated test method may be substantially enhanced by the inclusion of a third data point, which may be obtained by repeating the spiking verification procedure with a selenium standard of a concentration equal to one-half the highest linear concentration. In this way, the absorbance value for a second standard addition (equivalent to one-half the addition previously utilized) may be obtained.

22.10.5 For the three-point extrapolation, the concentration of selenium in the injected sample may be calculated by the graphic method in 22.10.2.

22.11 As to a provision for spectral interferences, this is only necessary for one of a group of samples of generally similar composition, and it is only possible for samples with apparent undiluted selenium concentrations near or greater than the highest linear concentration. For such samples, however, the absence of spectral interferences is established as follows:

22.11.1 Abiding by the specifications established for the original analysis, repeat the analysis at an alternative wavelength, using a sample concentration which is appropriate with respect to the decreased sensitivity at the secondary line.

22.11.2 Calculate the concentration of selenium so determined and the concentration originally determined in accordance to 24.1-24.3. If the values are identical within the limits of precision at the two wavelengths, the analyses are probably free of spectral interferences and may be performed at either line. If the values differ significantly, spectral interference has contributed to the higher value.

22.11.3 If these considerations indicate that the analytical wavelength should be altered, do so in accordance with the manufacturer's instructions. Prepare a calibration curve at the new conditions, and analyze the samples again.

23. Calculation

23.1 For the standard procedure, calculate the concentration of selenium in the injected sample in accordance with Practice D 3919 for the method of standard additions.

23.2 For the abbreviated procedure, the calculations for the concentration of selenium in the injected sample are given in 22.10.2 and 22.10.3.

23.3 Correct the values so obtained for all sample dilutions prior to analysis, and report the final value using Eq 4:

$$\text{Selenium, µg/L} = C \times D \tag{4}$$

where:

C = concentration in injected sample and
D = total dilution prior to injection.

24. Precision and Bias [6]

24.1 For reagent water, as established by eight laboratories, the overall precision of this test method within its designated range may be expressed using Eq 5:

$$S_t = 0.1072X + 0.54 \tag{5}$$

where:

S_t = overall precision, and
X = concentration of selenium determined, µg/L.

24.2 For waste-treatment plant effluent, tap water, well water, and treated wood plant effluent waters, as established by five laboratories, the overall precision of this test method within its designated range may be expressed using Eq 6:

$$S_t = 0.2658X - 0.03 \tag{6}$$

where:

S_t = overall precision, and
X = concentration of selenium determined, µg/L.

24.3 Because of the large number of metals analyzed in this study, the requirement for replicate tests has been waived; therefore, single-operator precision is not available.

24.4 For the same collaborative test data, the bias of this test method are given in Table 3.

24.5 The information on precision and bias may not apply to other waters.

25. Keywords

25.1 atomic absorption; furnace (Method B); hydride technique (Method A); selenium; total recoverable selenium; water

TABLE 3 Recovery and Bias Data, Test Method B (Graphite Furnace AAS)

Amount Added, µg/L	Amount Found, µg/L	Recovery, %	Bias, µg/L	Bias, %	Statistically Significant at 95 % Confidence Level
Reagent Water (Type II)					
3.0	2.5	85	−0.5	−15	no
6.0	5.4	90	−0.6	−10	no
14.0	13.2	95	−0.8	−5	no
Nonreagent Water [A]					
3.0	2.3	76	−0.7	− 24	yes
6.0	5.6	93	−0.4	− 7	no
14.0	12.6	90	−1.4	−10	no

[A] Waste treatment plant effluent, tap water, U-gas process condensate, well water, and treated wood plant effluent.