Designation: D3859 – 15

Standard Test Methods for Selenium in Water[1]

This standard is issued under the fixed designation D3859; 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, 3]	7 – 16
Test Method B—Graphite Furnace AAS	17 – 26

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—Gaseous Hydride AAS[2, 3]	1 to 20 µg/L
Test Method B—Graphite Furnace AAS	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 The values stated in SI units are to be regarded as standard. The values given in parentheses are mathematical conversions to inch-pound units that are provided for information only and are not considered standard.

1.5 *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 11.12 and 13.14.

2. Referenced Documents

2.1 *ASTM Standards:*[4]

D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3370 Practices for Sampling Water from Closed Conduits
D3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry
D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
D5673 Test Method for Elements in Water by Inductively Coupled Plasma—Mass Spectrometry
D5810 Guide for Spiking into Aqueous Samples
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in these test methods, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *total recoverable selenium, n*—a descriptive term relating to the selenium forms recovered in the acid-digestion procedure specified 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.

[1] These test methods are under the jurisdiction of ASTM Committee D19 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, No. 4, 1974, pp. 103–105.

[3] Pollack, E. N., and West, S. J., *Atomic Absorption Newsletter* , Vol 12, No. 1, 1973, pp. 6–8.

[4] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

***A Summary of Changes section appears at the end of this standard**

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.[5] Other grades may be used, provided it is ascertained that the reagent is of sufficiently high 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 D1193, 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 D3370. 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 D4841.

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 within 15 minutes of collecting the sample.

NOTE 1—Alternatively, the pH may be adjusted in the laboratory if the sample is returned within 14 days. However, acid must be added at least 24 hours before analysis to dissolve any metals that adsorb to the container walls. This could reduce hazards of working with acids in the field when appropriate.

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 (*1*) decomposition and oxidation to selenium (VI), (*2*) reduction to selenium (IV), and (*3*) 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.[6]

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 multirange, 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.

[5] *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 *Annual 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.

[6] 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.

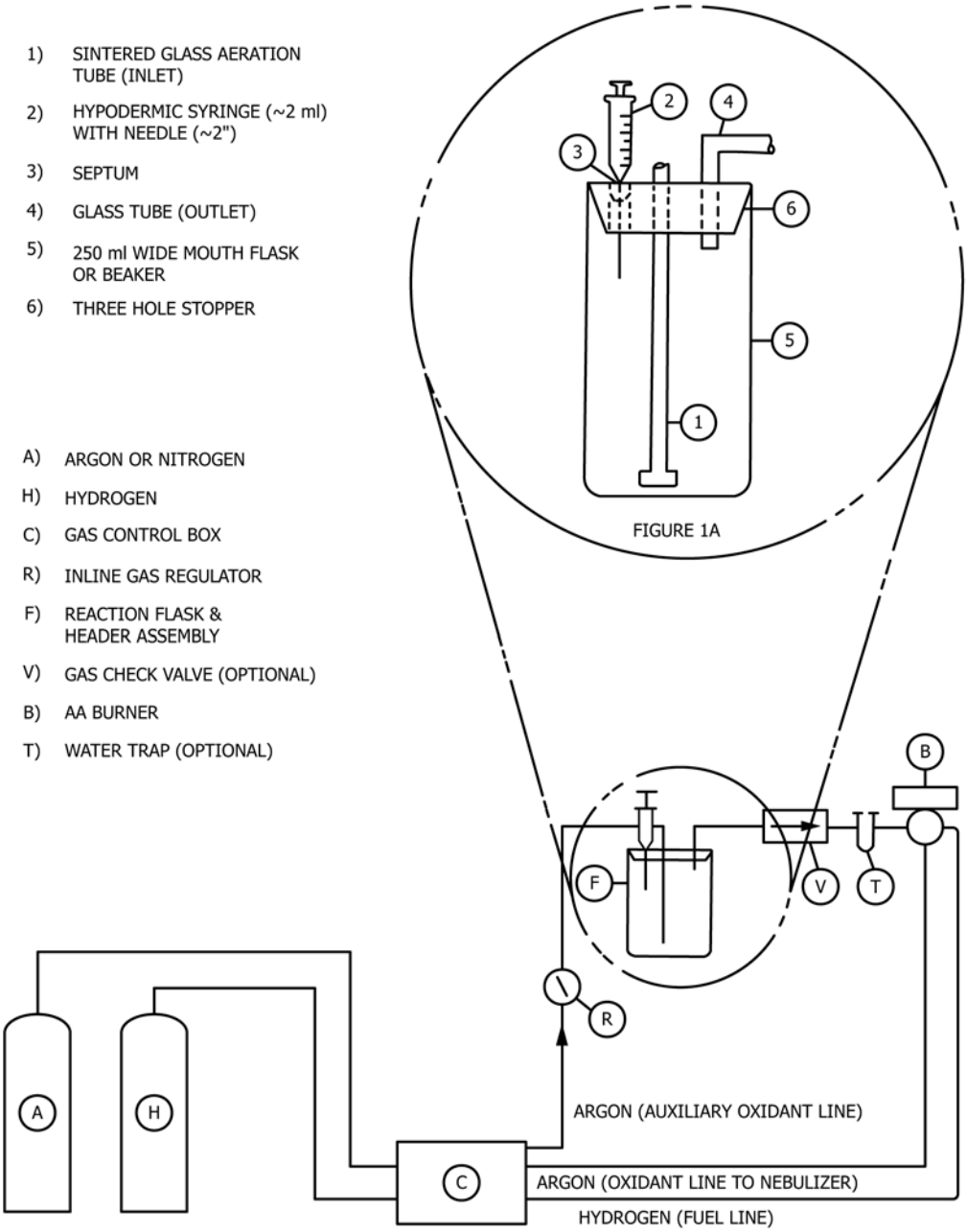

FIG. 1 Apparatus for Selenium Determination

10.3 *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 275 kPa (40 psi) and hydrogen pressure at 138 kPa (20 psi).

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 2—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.

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)—Commercially purchase or 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. Always add acid to water.

11.4 *Hydrochloric Acid* (1 + 99)—Add 1 volume of HCl (sp gr 1.19) to 99 volumes of water. Always add acid to 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 A purchased metal selenium stock solution of appropriate known purity is also acceptable.

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. To minimize waste only prepare 100 mL of the Selenium Standard Solution.

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. (**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) (11.11) to freshly washed 250-mL reaction flasks. Adjust the volume to 50 mL with water. Analyze at least six working standards containing concentrations of selenium that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument.

12.2 Proceed as directed in 13.3 – 13.15.

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

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 (11.5), 0.5 mL of $CaCl_2$ solution (11.1) 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) (11.4) or NaOH solution (4 g/L) (11.13). 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 (11.8) 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) (11.13) 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) (11.2). Heat on a hot water or steam bath for 20 min. Do not boil. This step reduces the selenium (VI) to selenium (IV).

NOTE 3—Many laboratories have found block digestion systems a useful way to digest samples for trace metals analysis. Systems typically consist of either a metal or graphite block with wells to hold digestion tubes. The block temperature controller must be able to maintain uniformity of temperature across all positions of the block. For trace metals analysis, the digestion tubes should be constructed of polypropylene and have a volume accuracy of at least 0.5 %. All lots of tubes should come with a certificate of analysis to demonstrate suitability for their intended purpose.

13.7 Cool and add HCl (1 + 1) (11.3) 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) (11.12) 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. (**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:

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

where:

1000 = 1000 mL / Litre
V = volume of sample, mL, and
W = weight of selenium in sample, µg.

15. Precision and Bias[7]

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:

[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1056. Contact ASTM Customer Service at service@astm.org.

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

$$S_t = 0.146X + 0.49 \quad (2)$$

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 This section on precision and bias conforms to Practice D2777 – 77 which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777 – 13, these precision and bias data do meet existing requirements of interlaboratory studies of Committee D19 test methods.

16. Quality Control

16.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing selenium.

16.2 *Calibration and Calibration Verification:*

16.2.1 Analyze at least six working standards containing concentrations of selenium that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument (see 12.1). The calibration correlation coefficient shall be equal to or greater than 0.990.

16.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The concentration of a mid-range standard should fall within ±15 % of the known concentration. Analyze a calibration blank to verify system cleanliness.

16.2.3 If calibration cannot be verified, recalibrate the instrument.

16.2.4 It is recommended to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) at a 10 % frequency. The results should fall within the expected precision of the method or ±15 % of the known concentration.

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

16.3 *Initial Demonstration of Laboratory Capability:*

16.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, and so forth, a precision and bias study must be performed to demonstrate laboratory capability.

16.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a midrange concentration of selenium. The matrix and chemistry of the solution should be equivalent to the solution used in the collaborative study. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps.

16.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 2. This study should be repeated until the recoveries are within the limits given in Table 1. If a concentration other than the recommended concentration is used, refer to Practice D5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

16.4 *Laboratory Control Sample (LCS):*

16.4.1 To ensure that the test method is in control, prepare and analyze a LCS containing a known concentration of selenium with each batch (laboratory-defined or twenty samples). The laboratory control samples for a large batch should cover the analytical range when possible. It is recommended, but not required to use a second source, if possible and practical for the LCS. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for a mid-range LCS shall fall within ±15 % of the known concentration.

16.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the samples in the batch must be reanalyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

16.5 *Method Blank:*

16.5.1 Analyze a reagent water test blank with each laboratory-defined batch. The concentration of selenium found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of selenium is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

16.6 *Matrix Spike (MS):*

16.6.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each laboratory-defined batch by spiking an aliquot of the sample with a known concentration of selenium and taking it through the analytical method.

16.6.2 The spike concentration plus the background concentration of selenium must not exceed the high calibration standard. The spike must produce a concentration in the spiked

sample that is 2 to 5 times the analyte concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

16.6.3 Calculate the percent recovery of the spike (P) using the following formula:

$$P = 100\left[A\left(V_s + V\right) - BV_s\right]/CV \quad (3)$$

where:

A = analyte known concentration (µg/L) in spiked sample,
B = analyte known concentration (µg/L) in unspiked sample,
C = known concentration (µg/L) of analyte in spiking solution,
V_s = volume (mL) of sample used, and
V = volume (mL) of spiking solution added.

16.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte concentration, listed in Guide D5810, Table 1. If the percent recovery is not within these limits, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

NOTE 4—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 for additional information.

16.7 *Duplicate:*

16.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each laboratory-defined batch. If the concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

16.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an F test. Refer to 6.4.4 of Practice D5847 for information on applying the F test.

16.7.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

16.8 *Independent Reference Material (IRM):*

16.8.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

TEST METHOD B—GRAPHITE FURNACE AAS

17. Scope

17.1 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.

17.2 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.

18. Summary of Test Method

18.1 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. ICP-MS may also be appropriate but at a higher instrument cost. See Test Method D5673.

18.1.1 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.

18.1.2 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.

18.2 A general guide for the application of this procedure is given in Practice D3919.

18.3 Dissolved selenium is determined on a filtered sample with no pretreatment. Total recoverable selenium is normally determined following acid digestion and filtration. The filtration is omitted only if suspended material is not present.

19. Interferences

19.1 For a complete discussion of general interferences, refer to Practice D3919.

19.2 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.[8, 9]

19.2.1 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.[8, 10, 11]

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

[8] *Analytical Chemistry*, Vol 47, No. 3, March 1975, p. 428.
[9] *Atomic Absorption Newsletter*, Vol 15, No. 2, March–April 1976, p. 29.
[10] *Atomic Absorption Newsletter*, Vol 14, No. 5, September–October 1975, p. 127.
[11] *Atomic Absorption Newsletter*, Vol 14, No. 5, September–October 1975, p. 109.

19.3 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.

19.4 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.

20. Apparatus

20.1 *Atomic Absorption Spectrophotometer,* for use at about 206.0 nm. (Other wavelengths will be used if they are determined to be both necessary and suitable.)

20.1.1 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.

20.1.2 *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.

20.2 *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.

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

NOTE 5—Metal furnaces have reportedly been used successfully in place of graphite furnaces. However, no round-robin data are presently available using these furnaces.

20.3 *Pipettes,* microlitre with disposable tips, as required.

20.4 *Data Storage and Reduction Devices, Computer- and Microprocessor-Controlled Devices, or Strip Chart Recorders,* shall be utilized for collection, storage, reduction, and problem recognition (such as drift, incomplete atomization, changes in sensitivity, etc.). Strip chart recorders shall have a full scale deflection time of 0.2 s or less to ensure accuracy.

21. Reagents and Materials

21.1 *Filter Paper*—Purchase suitable filter paper. Typically the filter papers have a pore size of 0.45-µm membrane. Material such as fine-textured, acid-washed, ashless paper, or glass fiber paper are acceptable. The user must first ascertain that the filter paper is of sufficient purity to use without adversely affecting the bias and precision of the test method.

21.2 *Hydrogen Peroxide* (30 %).

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

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

21.5 *Nitric Acid* (1 + 1)—Add 1 volume of HNO_3 (sp gr 1.42) to 1 volume of water. Always add acid to water.

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

21.7 *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.

21.7.1 A purchased metal stock solution of appropriate known purity is also acceptable.

21.8 *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).

21.9 *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. To minimize waste only prepare 100 mL of the Selenium Standard Solution.

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

22. Standardization

22.1 Initially set the instrument in accordance with the manufacturer's specifications. Follow the general instructions provided in Practice D3919, being sure to utilize automatic simultaneous background correction if available.

22.2 Analyze at least three working standards containing concentrations of selenium that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument. 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:

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

22.2.2 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.

23. Procedure

23.1 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).

23.2 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 (21.2) and 5 mL of HNO_3 (sp gr 1.42) (21.4). For dissolved selenium, proceed with 23.5.

23.3 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. (See Note 3.)

23.4 Cool and filter the sample through a suitable filter (21.1), 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.

23.5 Inject measured aliquots of sample, nickel nitrate (1.0 mL = 2.0 mg nickel) (21.3), and reagent water into the furnace, using the volumes specified in 22.2.1.

23.6 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.

23.7 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.

23.7.1 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.

23.8 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.

23.9 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 D3919.

23.10 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 D3919) should be used unless the abbreviated method (23.10.1 – 23.10.5) is shown to be satisfactory.

23.10.1 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.

23.10.2 In such cases, the concentration of selenium in the injected sample may be calculated by the method detailed in Practice D3919, using the equivalent concentration of the spike as the concentration of the standard addition.

23.10.3 Alternatively, the concentration may be calculated using Eq 4:

$$A \times C/(B - A) = \mu g/L\ Se\ (\text{in injected sample}) \quad (4)$$

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.

23.10.4 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.

23.10.5 For the three-point extrapolation, the concentration of selenium in the injected sample may be calculated by the graphic method in 23.10.2.

23.11 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:

23.11.1 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.

23.11.2 Calculate the concentration of selenium so determined and the concentration originally determined in accordance to 25.1 – 25.3. 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.

23.11.3 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.

24. Calculation

24.1 For the standard procedure, calculate the concentration of selenium in the injected sample in accordance with Practice D3919 for the method of standard additions.

24.2 For the abbreviated procedure, the calculations for the concentration of selenium in the injected sample are given in 23.10.2 and 23.10.3.

24.3 Correct the values so obtained for all sample dilutions prior to analysis, and report the final value using Eq 5:

$$\text{Selenium, } \mu g/L = C \times D \quad (5)$$

where:

C = concentration in injected sample and

D = total dilution prior to injection.

25. Precision and Bias[7]

25.1 For reagent water, as established by eight laboratories, the overall precision of this test method within its designated range may be expressed using Eq 6:

$$S_t = 0.1072X + 0.54 \quad (6)$$

where:

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

25.2 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 7:

$$S_t = 0.2658X - 0.03 \quad (7)$$

where:

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

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

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

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

25.6 This section on precision and bias conforms to Practice D2777 – 77 which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777 – 13, these precision and bias data do meet existing requirements of interlaboratory studies of Committee D19 test methods.

26. Quality Control

26.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing selenium.

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.

26.2 *Calibration and Calibration Verification:*

26.2.1 Analyze at least three working standards containing concentrations of selenium that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument (see 22.2). The calibration correlation coefficient shall be equal to or greater than 0.990.

26.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The concentration of a mid-range standard should fall within ±15 % of the known concentration. Analyze a calibration blank to verify system cleanliness.

26.2.3 If calibration cannot be verified, recalibrate the instrument.

26.2.4 It is recommended to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) at a 10 % frequency. The results should fall within the expected precision of the method or ±15 % of the known concentration.

26.3 *Initial Demonstration of Laboratory Capability:*

26.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, and so forth, a precision and bias study must be performed to demonstrate laboratory capability.

26.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a midrange concentration of selenium. The matrix and chemistry of the solution should be equivalent to the solution used in the collaborative study. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps.

26.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 3. This study should be repeated until the recoveries are within the limits given in Table 3. If a concentration other than the recommended concentration is used, refer to Practice D5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

26.4 *Laboratory Control Sample (LCS):*

26.4.1 To ensure that the test method is in control, prepare and analyze a LCS containing a known concentration of selenium with each batch laboratory-defined or twenty samples). The laboratory control samples for a large batch should cover the analytical range when possible. It is recommended, but not required to use a second source, if possible and practical for the LCS. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for a mid-range LCS shall fall within ±15 % of the known concentration.

26.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the samples in the batch must be reanalyzed, or the results must

be qualified with an indication that they do not fall within the performance criteria of the test method.

26.5 *Method Blank:*

26.5.1 Analyze a reagent water test blank with each laboratory-defined batch. The concentration of selenium found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of selenium is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

26.6 *Matrix Spike (MS):*

26.6.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each laboratory-defined batch by spiking an aliquot of the sample with a known concentration of selenium and taking it through the analytical method.

26.6.2 The spike concentration plus the background concentration of selenium must not exceed the high calibration standard. The spike must produce a concentration in the spiked sample that is 2 to 5 times the analyte concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

26.6.3 Calculate the percent recovery of the spike (P) using the following calculation:

$$P = 100\left[A\left(V_s + V\right) - BV_s\right]/CV \quad (8)$$

where:

A = analyte known concentration (µg/L) in spiked sample,

B = analyte known concentration (µg/L) in unspiked sample,

C = known concentration (µg/L) of analyte in spiking solution,

V_s = volume (mL) of sample used, and

V = volume (mL) of spiking solution added.

26.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte concentration, listed in Guide D5810, Table 1. If the percent recovery is not within these limits, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

NOTE 6—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 for additional information.

26.7 *Duplicate:*

26.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each laboratory-defined batch. If the concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

26.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an F test. Refer to 6.4.4 of Practice D5847 for information on applying the F test.

26.7.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

26.8 *Independent Reference Material (IRM):*

26.8.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

27. Keywords

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

SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D3859 – 08) that may impact the use of this standard. (Approved March 15, 2015.)

(1) Revised Section 1 to update the units of measurement statement.
(2) Revised Section 2 to include D5673.
(3) Revised Section 3.
(4) Revised Section 6 to allow for pH of the samples in the laboratory.
(5) Revised Sections 11 and 21 to allow for commercial standards and filter paper information was added.
(6) Revised Sections 12 and 22 were modified with standard and calibration information.
(7) Revised Sections 12, 12, and 23 to add reagent references.
(8) Revised Sections 12 and 23 to include note about the use of block digestion systems.
(9) Revised Sections 16 and 26.
(10) Revised Section 18 to inform the user of the possibility of using an ICP-MS.