



Designation: D 3859 – 03

## Standard Test Methods for Selenium in Water<sup>1</sup>

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 ( $\epsilon$ ) 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 <sup>2</sup>	7 to 16
Test Method B—Graphite Furnace AAS	17 to 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	1 to 20 $\mu\text{g/L}$
Test Method B	2 to 100 $\mu\text{g/L}$

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 11.12 and 13.14.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

D 1129 Terminology Relating to Water<sup>3</sup>

D 1193 Specification for Reagent Water<sup>3</sup>

D 2777 Practice for Determination of Precision and Bias of

Applicable Methods of Committee D19 on Water<sup>3</sup>

D 3370 Practices for Sampling Water from Closed Conduits<sup>3</sup>

D 3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry<sup>3</sup>

D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents<sup>3</sup>

D 5810 Guide for Spiking into Aqueous Samples<sup>3</sup>

D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis<sup>4</sup>

### 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  $\mu\text{g/L}$ . 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

<sup>1</sup> 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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<sup>2</sup> 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.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 11.02.

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

specifications are available.<sup>5</sup> 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 **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- $\mu\text{m}$  membrane filter as soon as possible after sampling. Add  $\text{HNO}_3$  to the filtrate to bring the pH to <2.0.

6.3 When determining total recoverable selenium, add  $\text{HNO}_3$  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  $\mu\text{g/L}$ . 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- $\mu\text{m}$  membrane filter.

### 9. Interferences

9.1 Mercury and arsenic at concentrations greater than 500  $\mu\text{g/L}$  and greater than 100  $\mu\text{g/L}$ , 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.<sup>6</sup>

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  $\mu\text{g/L}$ .

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

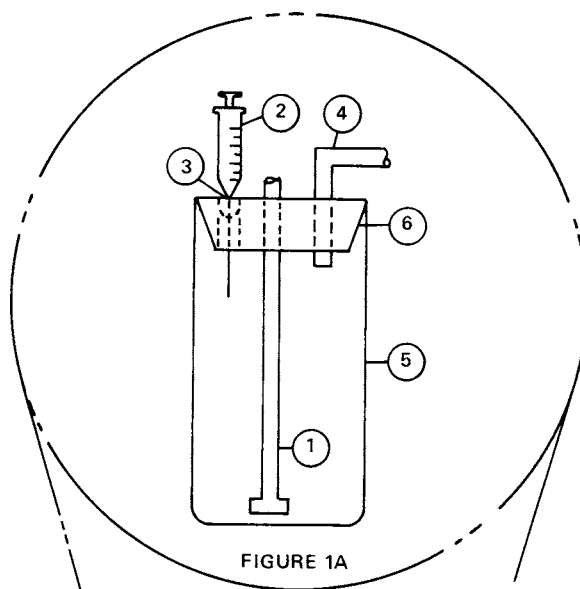
10.4.1.3 A glass outlet tube for the reaction gases to exit.

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.

<sup>5</sup> *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.

<sup>6</sup> 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.

- 1) SINTERED GLASS AERATION TUBE (INLET)
- 2) HYPODERMIC SYRINGE (~2 ml) WITH NEEDLE (~2")
- 3) SEPTUM
- 4) GLASS TUBE (OUTLET)
- 5) 250 ml WIDE MOUTH FLASK OR BEAKER
- 6) THREE HOLE STOPPER



- A) ARGON OR NITROGEN
- H) HYDROGEN
- C) GAS CONTROL BOX
- R) INLINE GAS REGULATOR
- F) REACTION FLASK & HEADER ASSEMBLY
- V) GAS CHECK VALVE (OPTIONAL)
- B) AA BURNER
- T) WATER TRAP (OPTIONAL)

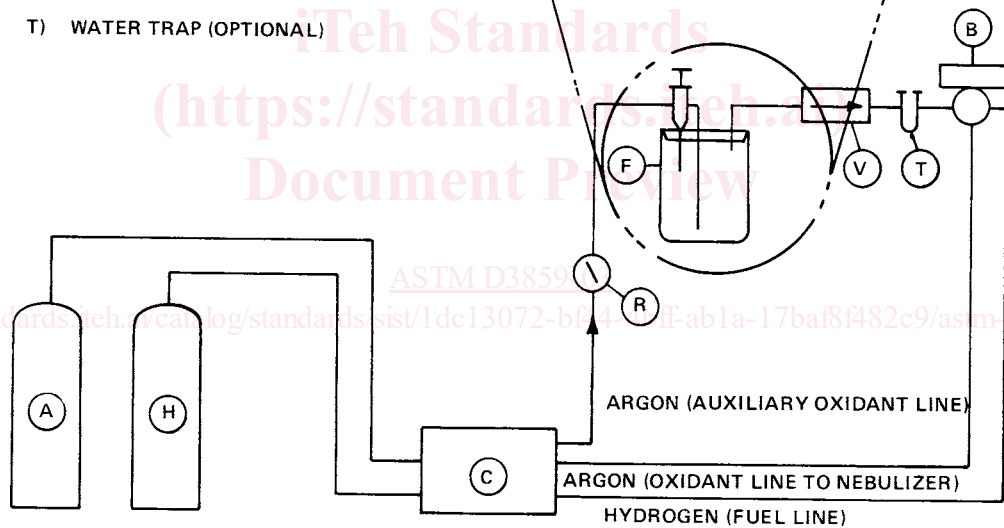


FIG. 1 Apparatus for Selenium Determination

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)*—Dissolve 30 g of calcium chloride ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) 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 ( $\text{HNO}_3$ ).

11.7 *Nitric Acid (1 + 99)*—Add 1 volume of  $\text{HNO}_3$  (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 ( $\text{KMnO}_4$ ) 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  $\text{HNO}_3$  (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  $\mu\text{g}$  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  $\mu\text{g}$  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 ( $\text{NaBH}_4$ ) 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  $\mu\text{g}$  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  $\mu\text{g}$  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  $\text{CaCl}_2$  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  $\text{KMnO}_4$ . 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  $\mu\text{g}$  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<sub>4</sub> solution (4 g/100 mL) to the sample. The H<sub>2</sub>Se evolution will peak within a few seconds, but will trail off for up to 30 s afterward. After the H<sub>2</sub>Se 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:

V = volume of sample, mL, and

W = weight of selenium in sample,  $\mu\text{g}$ .

#### 15. Precision and Bias <sup>7</sup>

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:

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

<sup>7</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report 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), $\mu\text{g/L}$	$S_T$	$S_O$
	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

where:

$S_T$  = overall precision,  $\mu\text{g/L}$ , and

X = concentration of selenium,  $\mu\text{g/L}$ .

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 D 2777 – 77 which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D 2777 – 98, 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 three working standards containing concentrations of selenium that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument. The calibration correlation coefficient shall be equal to or greater than 0.990. In addition to the initial calibration blank, a calibration blank shall be analyzed at the end of the batch run to ensure contamination was not a problem during the batch analysis.

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  $\pm 15\%$  of the known concentration.

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

Amount Added, $\mu\text{g/L}$	Amount Found, $\mu\text{g/L}$	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

16.2.3 If calibration cannot be verified, recalibrate the instrument.

### 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. The replicates may be interspersed with samples.

16.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in **Table 1**. 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, analyze a LCS containing a known concentration of selenium with each batch or ten samples. If large numbers of samples are analyzed in the batch, analyze the LCS after every ten samples. The laboratory control samples for a large batch should cover the analytical range when possible. 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  $\pm 15\%$  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 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 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:

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

where

- A = analyte concentration (mg/L) in spiked sample,
- B = analyte concentration (mg/L) in unspiked sample,
- C = concentration (mg/L) of analyte in spiking solution,
- $V_s$  = volume (mL) of sample used, and
- V = volume (mL) added with spike.

16.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte concentration, listed in Test Method D 5810, 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 2—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Test Method D 5810 for additional information.

### 16.7 Duplicate

16.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each 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 D 5847 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 88 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 D 3859 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  $\mu\text{g/L}$ . 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