

Selenium, atomic absorption spectrometric, hydride

Parameters and Codes:

Selenium, dissolved, I-1667-85 ($\mu\text{g/L}$ as Se): 01145
Selenium, total, I-3667-85 ($\mu\text{g/L}$ as Se): 01147
Selenium, suspended total, I-7667-85 ($\mu\text{g/L}$ as Se): 01146
Selenium, total-in-bottom-material, dry wt, I-5667-85 ($\mu\text{g/g}$ as Se): 01148

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least $1 \mu\text{g/L}$ of selenium. Samples containing more than $20 \mu\text{g/L}$ need to be diluted.

1.2 Suspended total selenium is calculated by subtracting dissolved selenium from total selenium.

1.3 This method may be used to analyze bottom material containing at least $1 \mu\text{g/g}$ of selenium. Usually a 100-mg sample of prepared bottom material (method P-0520) is taken for analysis. However, if the sample contains more than $20 \mu\text{g/g}$ of selenium, a smaller sample needs to be used.

1.4 Total selenium in water-suspended sediment may be determined after each sample has been thoroughly mixed by vigorous shaking and a suitable sample portion has been rapidly withdrawn from the mixture.

2. Summary of method

Organic selenium compounds, if present, are first decomposed by digestion with potassium permanganate in hot acidic solution. The solution is then made basic and evaporated to dryness in the presence of calcium chloride to prevent loss of selenate during the evaporation. Hydrochloric acid is added to the residue to reduce the selenate to selenite. Quantitative reduction without loss of selenium requires control of the temperature, time, and acid concentration. All selenium must be in the selenite form prior to its final reduction with stannous chloride in 6M hydrochloric acid solution. The selenium hydride so formed is subsequently removed from solution by aeration and swept by a flow of nitrogen into a hydrogen diffusion

flame where it is determined by atomic absorption at 196.0 nm (Freeman and Uthe, 1974; Lansford and others, 1974).

3. Interferences

3.1 Arsenic interferes by suppressing the selenium absorption if an excess of stannous chloride is used. This interference can be avoided by carefully controlling the amount of stannous chloride added. If 42 mg stannous chloride is added, as much as $150 \mu\text{g/L}$ of arsenic can be tolerated. At least this amount must be added, however, to ensure efficient reduction of selenite to the hydride.

3.2 Mercury interferes when its concentration exceeds $25 \mu\text{g/L}$.

4. Apparatus

4.1 *Atomic absorption spectrometer.*

4.2 Refer to the manufacturer's manual to optimize instrument for the following:

Grating -----	Ultraviolet
Wavelength -----	196.0 nm
Source (electrodeless discharge lamp) ---	Selenium
Burner -----	Three-slot
Fuel -----	Hydrogen
Diluent -----	Nitrogen
Carrier -----	Nitrogen

4.3 *Selenium hydride vapor analyzer* (fig. 40) consisting of —

4.3.1 *Fleaker*, 300-mL capacity, or beaker, Berzelius, 200-mL capacity.

4.3.2 *Gas dispersion tube*, coarse frit (Scientific Glass Apparatus Co. No. JG-8500 has been found satisfactory).

4.3.3 *Medicine dropper*, 2-mL capacity min.

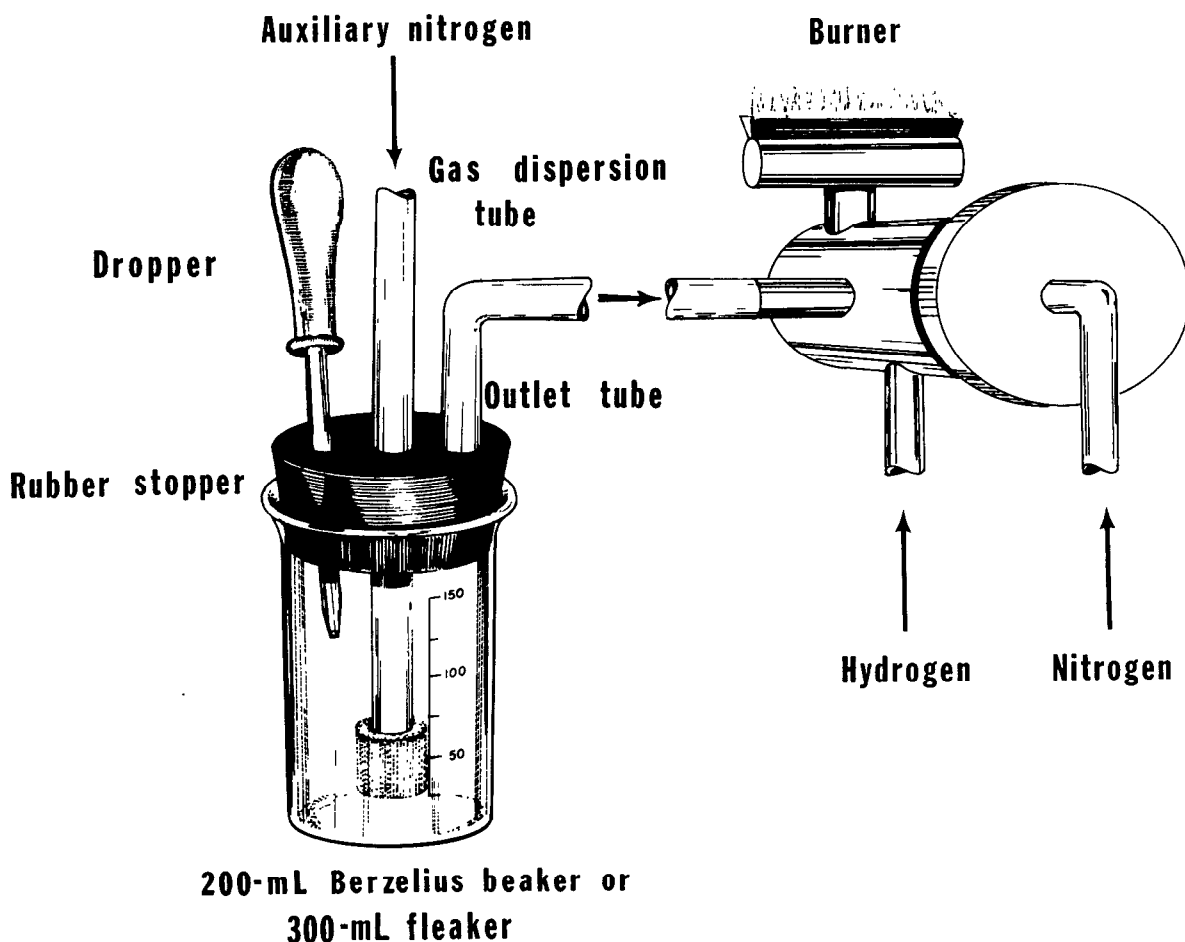


Figure 40.—Selenium hydride vapor analyzer

5. Reagents

5.1 *Ammonium chloride solution*, 250 g/L: Dissolve 250 g NH_4Cl in demineralized water and dilute to 1 L.

5.2 *Calcium chloride solution*, 22.6 g/L: Dissolve 30 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in demineralized water and dilute to 1 L.

5.3 *Hydrochloric acid*, concentrated (sp gr 1.19).

5.4 *Hydrochloric acid*, 6M: Dilute 500 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.5 *Hydrochloric acid*, 0.1M: Dilute 8 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.6 *Methyl orange indicator solution*, 50 mg/100 mL: Dissolve 50 mg methyl orange in 100 mL demineralized water.

5.7 *Potassium permanganate solution*, 0.3

g/L: Dissolve 0.3 g KMnO_4 in 1 L demineralized water.

5.8 *Selenium standard solution I*, 1.00 mL = 1.00 mg Se: Dissolve 2.3928 g Na_2SeO_4 in demineralized water. Add 1 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1000 mL with demineralized water.

5.9 *Selenium standard solution II*, 1.00 mL = 10.0 μg Se: Dilute 10.0 mL selenium standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1000 mL with demineralized water. Discard after 3 months.

5.10 *Selenium standard solution III*, 1.00 mL = 0.100 μg Se: Dilute 5.00 mL selenium standard solution II and 1 mL concentrated HNO_3 (sp gr 1.41) to 500 mL with demineralized water. Prepare fresh weekly.

5.11 *Sodium hydroxide solution*, 0.1M: Dissolve 4 g NaOH in demineralized water and dilute to 1 L.

5.12 *Stannous chloride solution*, 4.2 g/100 mL concentrated HCl: Dissolve 5 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 100 mL concentrated HCl (sp gr 1.19). This solution is unstable. Prepare fresh daily.

6. Procedure

6.1 Follow instructions in paragraph 6.1.1 for waters and water-suspended sediment mixtures and in paragraph 6.1.2 for bottom materials.

6.1.1 Pipet a volume of well-mixed sample containing less than 2.0 μg Se (100 mL max) into a 300-mL fleaker and dilute to 100 mL.

6.1.2 Weigh a portion of prepared bottom-material sample containing less than 2.0 μg Se (100 mg max); transfer to a 300-mL fleaker and add 100 mL demineralized water (NOTE 1). Stir to mix thoroughly and allow to settle.

NOTE 1. Do not use more than 100 mg of bottom material or severe bumping and loss of selenium may occur during the subsequent digestion of the sample.

6.2 Prepare, in 300-mL fleakers, a blank and sufficient standards containing from 0.1 to 2.0 μg Se by diluting 1.0- to 20.0-mL portions of selenium standard solution III. Dilute each to approx 100 mL.

6.3 To each fleaker add 1 drop methyl orange, 0.5 mL CaCl_2 solution, and a boiling chip or several glass beads.

6.4 To the fleakers containing the blank and standards, add 0.5 mL 0.1M HCl.

6.5 To the fleakers containing the samples, titrate with 0.1M HCl until the indicator shows a distinct red color and then add 0.5 mL excess (NOTE 2).

NOTE 2. If the water or water-suspended sediment samples have been acidified either at the time of collection or in the laboratory, titrate with 2M NaOH until the indicator shows a distinct yellow-orange color and then continue with paragraph 6.5. When the presence of interferences makes it impossible to adjust the pH with use of methyl orange, use a pH meter for this adjustment.

6.6 Add 3 drops KMnO_4 solution to each fleaker and heat to boiling on a hotplate, adding KMnO_4 as required to maintain a purple tint. If a precipitate of MnO_2 forms at this point, it will have no adverse effect.

6.7 After the volume has been reduced to approx 50 mL, add 2 mL 0.1M NaOH; evaporate

to dryness, and allow the fleakers to cool. Avoid prolonged heating of the residue.

6.8 Add 5 mL concentrated HCl and 10 mL NH_4Cl solution. Heat in a boiling-water or steam bath for 20 + 0.5 min (NOTE 3).

NOTE 3. Samples can be heated on a hotplate at low temperature if boiling can be prevented.

6.9 Dilute each sample, blank, and standard to approx 100 mL with 6M HCl.

6.10 Attach one fleaker at a time to the rubber stopper containing the gas dispersion tube.

6.11 Fill the medicine dropper with 1 mL SnCl_2 solution and insert into hole in rubber stopper.

6.12 Add the SnCl_2 solution to the sample solution. After the absorbance has reached a maximum and has returned to the baseline, remove the fleaker. Rinse the gas dispersion tube in demineralized water before proceeding to the next sample. Treat each succeeding sample, blank, and standard in a like manner.

7. Calculations

7.1 Determine the micrograms of selenium in each sample from a plot of absorbances of standards. Exact reproducibility is not obtained, and an analytical curve must be prepared with each set of samples.

7.2 Determine the concentration of dissolved or total selenium in each sample as follows:

$$\text{Se } (\mu\text{g/L}) = \frac{1,000}{\text{mL sample}} \times \mu\text{g Se in sample}$$

7.3 To determine the concentration of total suspended selenium, subtract dissolved-selenium concentration from total-selenium concentration.

7.4 Determine the concentration of selenium in air-dried bottom-material samples as follows:

$$\text{Se } (\mu\text{g/g}) = \frac{\mu\text{g Se in sample}}{\text{wt of sample (g)}}$$

8. Report

8.1 Report selenium, dissolved (01145), total (01147), and suspended-total (01146), concentrations as follows: less than 100 $\mu\text{g/L}$, nearest

microgram per liter; 100 $\mu\text{g/L}$ and above, two significant figures.

8.2 Report selenium, total-in-bottom-material (01148), concentrations as follows: less than 100 $\mu\text{g/g}$, to the nearest microgram per gram; 100 $\mu\text{g/g}$ and above, two significant figures.

9. Precision

9.1 Precision for dissolved selenium for 14 samples within the range of 2 to 42 $\mu\text{g/L}$ may be expressed as follows:

$$S_T = 0.484 X - 1.447$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of selenium, micrograms per liter.

The correlation coefficient is 0.9412.

9.2 Precision for dissolved selenium for five of the 14 samples expressed in terms of percent relative standard deviation is as follows:

Number of laboratories	Mean ($\mu\text{g/L}$)	Relative standard deviation (percent)
5	2.0	0
7	3.6	27
3	9.0	29
5	19	47
5	42	50

9.3 It is estimated that the percent relative standard deviation for total and suspended selenium and for total selenium in bottom material will be greater than that reported for dissolved selenium.

9.4 Precision for total selenium expressed in terms of the percent relative standard deviation for one water-suspended sediment mixture is as follows:

Number of laboratories	Mean ($\mu\text{g/L}$)	Relative standard deviation (percent)
8	6.5	34

References

- Freeman, H. C., and Uthe, J. F., 1974, An improved hydride generation apparatus for determining arsenic and selenium by atomic absorption spectrometry: Atomic Absorption Newsletter, v. 13, p. 75-6.
- Lansford, Myra, McPherson, E. M., and Fishman, M. J., 1974, Determination of selenium in water: Atomic Absorption Newsletter, v. 13, p. 103-5.