Selenium, atomic absorption spectrometric, hydride, automated

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 1 *µglL* of selenium. Samples containing more than 15 *µg*/L need to be diluted.

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

1.3 Water-suspended sediment may be analyzed by this procedure after each sample has been thoroughly mixed by vigorous shaking and a suitable portion has been rapidly withdrawn from the mixture. Suspended-sediment concentrations must be less than 2.6 *g/L.* Greater concentrations can cause less than 100-percent recovery of selenium from some organic selenium compounds such as diphenyl selenide.

1.4 This method may be used to analyze bottom material containing at least 1 *µg*/g of selenium. For samples containing more than 5.6 *µg*/g, use less sediment. The amount of sediment that can be used is limited to 40-mg dry weight because, if greater amounts are used, selenium will not be recovered completely from some organic selenium compounds such as diphenyl selenide.

1.5 Bottom material may be analyzed by this procedure after it has been prepared as directed in method I-0520.

2. Summary of method

2.1 Organic selenium-containing compounds are decomposed by hydrochloric acid-potassium persulfate digestion. The selenium so liberated, with inorganic selenium originally present, is then reduced to the tetravalent state using a stannous chloride-potassium iodide mixture and is further converted to selenium hydride with sodium borohydride. The selenium hydride gas is stripped from the solution by a stream of nitrogen gas and conveyed to a tube furnace placed in the optical path of an atomic absorption spectrometer, where it is decomposed to atomic selenium. The optical absorbance is measured and related to the selenium concentration in the original sample.

2.2 For additional information on the determination of selenium in water, see Goulden and Brooksbank (1974), and Pierce and others (1976).

3. Interferences

3.1 No interferences have been observed with the decomposition of selenium hydride in the tube furnace and its subsequent measurement.

3.2 Goulden and Brooksbank (1974) reported no significant interferences in the digestion, reduction, and selenium hydride-generation processes.

3.3 Pierce and Brown (1976) reported interferences from trace elements commonly found in water at concentrations greater than 300 ~tg/L when sodium borohydride was introduced in the sample stream before hydrochloric acid.

3.4 Nitric acid in excess of that usually added as a preservative in water and water-suspended sediment samples, is reported to cause erratic results.

4. Apparatus

4.1 *Atomic absorption spectrometer* and recorder.

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

Grating---------------------- Ultraviolet
Wavelength counter . 196.0 nm
Source (electrodeless
    discharge lamp) ... Selenium

4.2 *Autotransformer, variable:* Superior Power stat type 3 PN 1010 or equivalent. Two are needed, one for the stripping column and one for the tube furnace.

4.3 *Dri-bath,* 0-110°C. Thermolyne Model DB16525 or equivalent.

4.4 *Pyrometer,* portable, 0-1200°C. Thermolyne Model PM-20700 or equivalent.

4.5 *Stripping-condensing column,* Pyrex, packed with 3- to 5-mm Pyrex beads (fig. 41). Wrap the stripping column with heating tape and cool the condensing column with water. The nitrogen gas flow rate is adjusted for maximum sensitivity by analyzing a series of identical standards. A flow rate of approximately 200 mL/min has been found satisfactory~

4.6 *Tube furnace,* quartz, 10-mm IDX100-mm length with a quartz eyelet at each end of tube to anchor nickel-chrome wire and tube fused at the center with a 2-mm ID quartz tuba Wrap the tube furnace with a 5.5 m (18 ft) of 26-gauge, nickel-chrome wire and cover with asbestos doth. Mount lengthwise in the optical path of the atomic absorption spectrometer.

4.7 *Technicon AutoAnalyzer II,* consisting of sampler, manifold, proportioning pump, and heating bath.

Heating bath temperature .   95°C
Cam   30 (112)

4.8 *Test tubes,* graduated, 25-mL capacity, Pyrex 9802 or equivalent.

5. Reagents

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

5.2 *Nitrogen gas,* N$_2$.

5.3 *Potassium iodide solution,* 20 g/L: Dissolve 20 g KI in demineralized water and dilute to 1 L

5.4 *Potassium persulfate solution,* 20 gIL: Dissolve 20 g K$_2$S$_2$O$_8$ in demineralized water and dilute to 1 L.

5.5 *Selenium standard solution I,* 1.00 mL = 1.00   mg Se: Dissolve 2.3928 g Na$_2$SeO$_4$ in demineralized water. Add 1 mL concentrated HNO$_3$ (sp gr 1.41) and dilute to 1,000 mL with demineralized water.
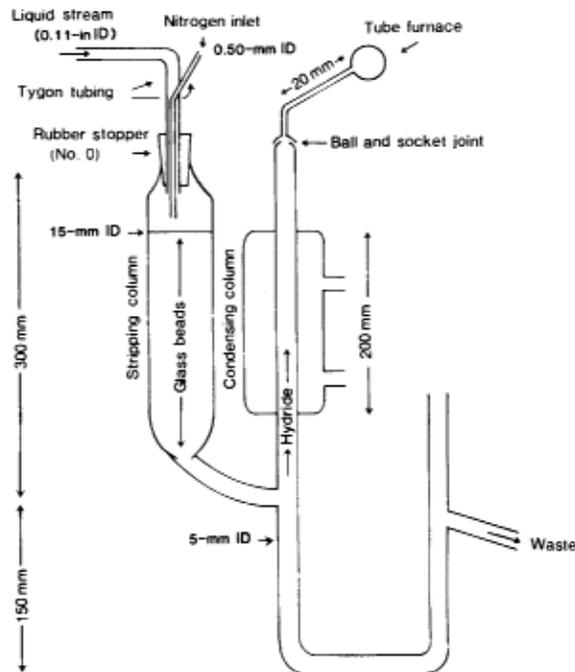
Figure 41.—Stripping-condensIng column and quartz-tube furnace

5.6 *Selenium standard solution II,* 1.00 mL = 10.0 μg Se: Dilute 5.00 mL selenium standard solution I and 1 mL concentrated HNO$_3$ (sp gr 1.41) to 500 mL with demineralized water. Discard after 3 months.

5.7 *Selenium standard solution III,* 1.00 mL = 0.10 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.

5.8 *Selenium working standards:* Prepare daily a blank and 100 mL each of a series of selenium working standards containing 0.15 mL concentrated HNO$_3$ by appropriate quantitative dilution of selenium standard solution III.

Selenium standard solution lt (mL)	Selenium concentration (μg/L)
1.0	1
2.0	2
5.0	5
10.0	10
15.0	15

5.9 *Sodium borohydride solution* 0.5 g/L: Dissolve 0.5 g NaBH$_4$ and 4 g NaOH in demineralized water and dilute to 1 L.

5.10 *Stannous chloride solution,* 1.3 gIL: Dissolve 1.6 g $SnCl_2 \cdot 2H_2O$ in 1 L concentrated HC1 (sp gr 1.19). This solution is unstable. Prepare fresh daily.

6. Procedure

6.1   Follow instructions in paragraph 6.1.1 for waters or 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 0.225 μg Se (15 mL max) into a 25-mL graduated test tube.

6.1.2 Weigh 40 mg or less of bottom-material sample (0.225 μg Se max), transfer into a 25 mL graduated test tube, and add 15 mL demineralized water.

6.2   Pipet 15 mL blank and a complete set of standard solutions (sufficient to satisfy the requirements of 6.8) containing from 1.0 to 15.0 $\mu g/L$ into 25-mL graduated test tubes.

6.3   To each tube, add 1.5 mL $K_2S_2O_8$ solution and 0.3 mL concentrated HC1, and mix.

6.4   Add a boiling stone and place the test tubes in a dri-bath at a temperature of 100°C, and boil each tube for a minimum of 15 min. but no longer than 20 min. (NOTE 1). Cool the solution to room temperature, dilute to 17.0 mL with demineralized water, and mix (NOTE 2).

NOTE 1. Alternatively, the solutions may be digested in an autoclave. After addition of HC1 and $K_2S_2O_8$, autoclave solutions for 20 min. at 15 psi pressure. Cool the solutions and add 3.0 mL oxalic acid solution (dissolve 35 g oxalic acid dihydrate in demineralized water and dilute to 1 L). Autoclave solutions for an additional 20 min. at 15 psi pressure. Cool solutions and dilute to 17.0 mL with demineralized water. Proceed to paragraph 6.5.

NOTE 2. A different volume may be used as long as the same volumes of standards and samples are used in each run.

6.5   Set up manifold (fig. 42) (NOTE 3).

NOTE 3. Change the acid flex tubing weekly.

6.6   Set stripping-column and tube-furnace temperatures by applying necessary voltage as follows:
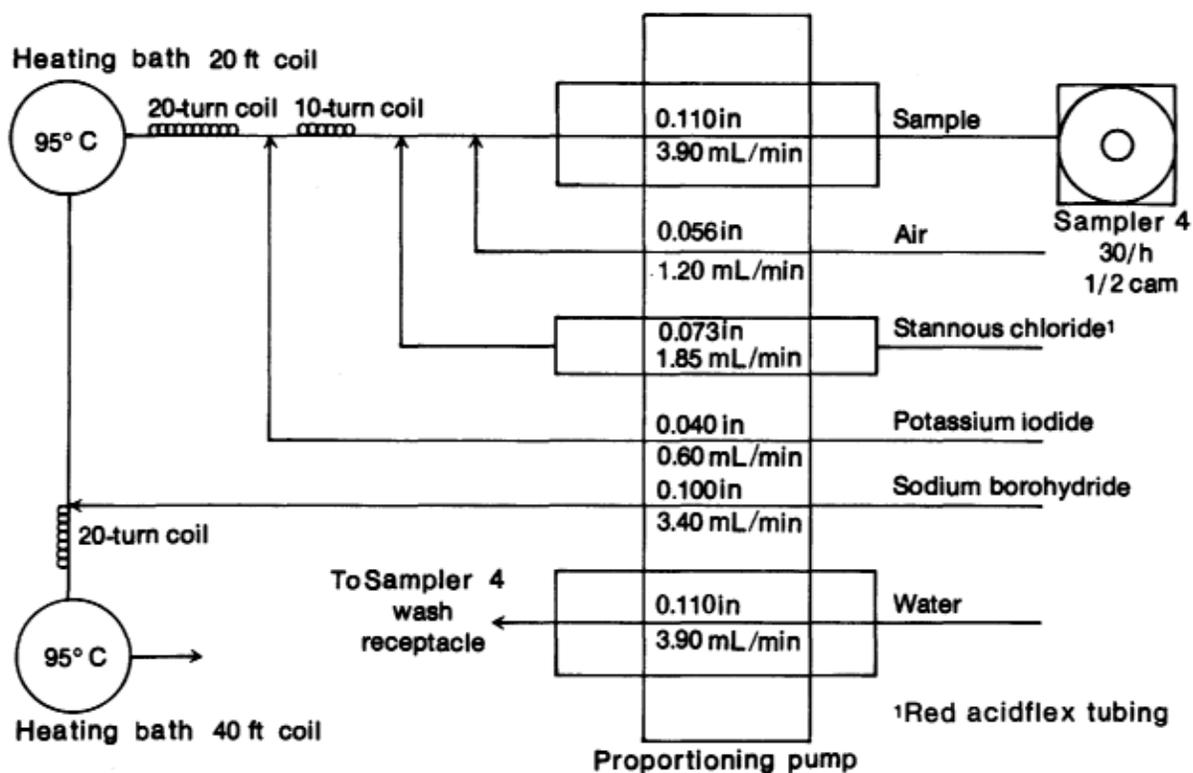
Figure 42.—Selenium, hydride manifold

Stripping-column tem-
perature--------- 75°C (about 36 V)
Tube-furnace tempera-
ture-------------- 800°C (about 47 V)

Stripping column temperatures higher than 75°C cause the peak to split. Monitor the tube-furnace temperature using a portable pyrometer with the thermocouple placed in the middle of the tube, and monitor the waste-stream temperature using a laboratory thermometer. Adjust voltages on the autotransformers as necessary to control these temperatures.

6.7 Initially, feed all reagents through the system using demineralized water in the sample line and allow the baseline to stabilize.

6.8 Prepare the sample tray as follows: (1) !n the first tray, place three tubes of the most concentrated standard followed by one tube each of the remaining standards and blank, in decreasing concentrations; (2) place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent trays; (3) fill the remainder of each sample tray with unknown samples.

6.9 When the baseline stabilizes, remove the sample line from the demineralized wash solution and begin analysis.

6.10 With a 5-mV recorder, 10 μg/L of selenium produces a peak approx 60 percent of full scale. If the sensitivity drops by 30 percent or more, replace or treat the tube furnace ~ce11~ by one of the following methods:

6.10.1 Soak the tube furnace for 30 minutes in 1:1 water-hydrofluoric acid solution and rinse with demineralized water.

6.10.2 Grind the cell with silicon carbide as follows: Mount cell with suitable cushioning in a 3/4-inch chuck on a slowly-revolving shaft. Wet inside of cell and apply grinding compound such as commercial auto-valve-grinding compound. Using a standard speed drill and an aluminum oxide grinding wheel suitably reduced in diameter to give adequate clearance, and plenty of water, begin grinding cell with a steady movement from inside to outside of cell. Grind one-half of cell at a time and regrind if necessary to achieve an even frosting.

7.   Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective selenium concentration; use the value from the third tube for the reading on the most concentrated standard (the first two tubes usually give low readings).

7.2 Determine the concentration of dissolved or total selenium in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

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

7.4 To determine micrograms per gram of selenium in bottom-material samples, first determine the micrograms per liter of selenium in each sample as in paragraph 7.2; then:

$$\text{Se in } \mu\text{g/g} = \frac{\mu\text{g/L Se} \times 0.015 \text{ L}}{\text{wt of sample (g)}}$$

8.   Report

8.1 Report selenium, dissolved (01145), total (01147), and suspended-total (01146), concentrations as follows: less than 10 μg/L, nearest μg/L; 10 μg/L and above, two significant figures.

8.2 Report selenium, total-in-bottom-material (01148), concentrations as follows: less than 10 μg/g, nearest μg/g; 10 μg/g and above, two significant figures.

9.   Precision

9.1 Analysis of four samples for dissolved selenium five times each by one operator resulted in mean values of 3.3, 4.2, 6.4, and 8.5 μg/L and standard deviations of 0.1, 0.4, 0.2, and 0.1 μg/L, respectively.

9.2 Precision for dissolved selenium also may be expressed in terms of percent relative standard deviation as follows:

Number of replicates	Mean (μg/L)	Relative standard deviation (percent)
5	3.3	3
5	4.2	10
5	6.4	3
5	8.5	1

9.3 Analysis of four samples for total selenium five times each by one operator resulted in mean values of 2.0, 8.6, 10.4, and 20.0 μg/L and standard deviations of 0.5, 0.2, 0.3, and 0.9 μg/L, respectively.

9.4 Precision for total selenium also may be expressed in terms of percent relative standard deviation as follows:

Number of replicates	Mean (μg/L)	Relative standard deviation (percent)
5	2.0	25
5	8.6	2
5	10.4	3
5	20.0	4

9.5 Analysis of four bottom-material samples for selenium five times each by one operator resulted in mean values of 1.4, 1.7, 2.4, and 3.4 μg/g and standard deviations of 0.3, 0.1, 0.2, and 0.1 μg/g, respectively.

9.6 Precision for selenium in bottom-material samples also may be expressed in terms of percent relative standard deviation as follows:

Number of replicates	Mean (μg/L)	Relative standard deviation (percent)
5	1.4	21
5	1.7	6
5	2.4	8
5	3.4	3

References

Goulden, P. D., and Brooksbank, Peter, 1974, Automated atomic absorption determination of arsenic, antimony, and selenium in natural waters: Analytical Chemistry, v. 46, p. 1431—6.

Pierce, F. D., and Brown, H. R., 1976, Inorganic interference study of automated arsenic and selenium determination with atomic absorption spectrometry: Analytical Chemistry, v. 48, p. 693-5.

Pierce, F. D., Lamoreaux, T. C., Brown, H. R., and Fraser, R. S., 1976, An automated technique for the sub-microgram determination of selenium and arsenic in surface waters by atomic absorption spectroscopy. Applied Spectroscopy, v. 30, p. 38-42.