



**Techniques of Water-Resources Investigations  
of the United States Geological Survey**

**Chapter A1**

**METHODS FOR DETERMINATION  
OF INORGANIC SUBSTANCES  
IN WATER  
AND FLUVIAL SEDIMENTS**

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Book 5  
LABORATORY ANALYSIS

# Potassium, atomic absorption spectrometric, direct

## Parameters and Codes:

Potassium, dissolved, I-1630-85 (mg/L as K): 00935  
Potassium, total recoverable, I-3630-85 (mg/L as K): none assigned  
Potassium, recoverable-from-bottom-material, dry wt, I-5630-85 (mg/kg as K): 00938

## 1. Application

1.1 This method may be used to analyze atmospheric precipitation, water, brines, and water-suspended sediment.

1.2 Two analytical ranges for potassium are included: from 0.01 to 1.0 mg/L and from 0.10 to 10.0 mg/L. Sample solutions containing potassium concentrations greater than 10 mg/L need to be diluted.

1.3 This method may be used to analyze bottom material containing at least 10 mg/kg of potassium.

1.4 Total recoverable potassium in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485 and recoverable potassium in bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

## 2. Summary of method

2.1 Potassium is determined by atomic absorption spectrometry by direct aspiration of the sample solution into an air-acetylene flame (Fishman and Downs, 1966).

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer.

## 3. Interferences

3.1 Of the substances commonly occurring in water, only sodium has been found to interfere, and its interference is greatly minimized if a reducing flame is used and the burner is raised to approximately 0.05 cm below the optical light path. The following data are indicative of the magnitude of sodium interference under these conditions:

| Potassium added (mg/L) | Sodium added (mg/L) | Potassium found (mg/L) |
|------------------------|---------------------|------------------------|
| 1.00                   | 0.0                 | 1.00                   |
| 1.00                   | 100                 | 1.03                   |
| 1.00                   | 500                 | 1.05                   |
| 1.00                   | 1,000               | 1.07                   |

3.2 Alternatively, an excess of sodium or cesium may be added to all samples and standards. Such additions essentially eliminate the effects of the then comparatively minor contributions of sodium present in the samples.

## 4. Apparatus

4.1 Atomic absorption spectrometer equipped with electronic digital readout and automatic zero and concentration controls.

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

|                                    |                   |
|------------------------------------|-------------------|
| Grating -----                      | Visible           |
| Wavelength -----                   | 766.5 nm          |
| Source (hollow-cathode lamp) ----- | Potassium         |
| Oxidant -----                      | Air               |
| Fuel -----                         | Acetylene         |
| Type of flame -----                | Slightly reducing |

4.3 The 50-mm (2-in.), flathead, single-slot burner allows working ranges of 0.01 to 1.0 mg/L and 0.1 to 10 mg/L. The burner, rotated 90°, extends the range to 100 mg/L. Different burners may be used according to manufacturers' instructions.

## 5. Reagents

5.1 Potassium standard solution I, 1.00 mL = 0.100 mg K: Dissolve 0.1907 g KCl, dried at 180°C for 1 h, in demineralized water and dilute to 1,000 mL.

5.2 *Potassium working standards*: Prepare a series of at least six working standards containing either from 0.01 to 1.0 mg/L or from 0.1 to 10.0 mg/L of potassium by appropriate dilution of potassium standard solution I.

## 6. Procedure

While aspirating the blank use the automatic zero control to set the digital display to read zero concentration. While aspirating standards use the automatic concentration control to set the digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

## 7. Calculations

7.1 Determine the milligrams per liter of dissolved or total recoverable potassium in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing potassium concentrations that exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine milligrams per kilogram of potassium in bottom-material samples, first determine the milligrams per liter of potassium as in paragraph 7.1; then:

$$K \text{ (mg/kg)} = \frac{\text{mg/L K} \times \frac{\text{mL original digest}}{1000}}{\text{wt of sample (kg)}}$$

## 8. Report

8.1 Report potassium, dissolved (00935), and total recoverable (none assigned), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 to 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

8.2 Report potassium, recoverable-from-bottom-material (00938), concentrations as follows: less than 1,000 mg/kg, nearest 10 mg/kg; 1,000 mg/kg and above, two significant figures.

## 9. Precision

9.1 Precision for dissolved potassium for 36 samples within the range of 0.09 to 26.1 mg/L may be expressed as follows:

$$S_T = 0.113X - 0.050$$

where

$S_T$  = overall precision, milligrams per liter, and

$X$  = concentration of potassium, milligrams per liter.

The correlation coefficient is 0.9350.

9.2 Precision for dissolved potassium for five of the 36 samples expressed in terms of the percent relative standard deviation is as follows:

| Number of laboratories | Mean (mg/L) | Relative standard deviation (percent) |
|------------------------|-------------|---------------------------------------|
| 24                     | 0.09        | 55                                    |
| 17                     | 2.48        | 10                                    |
| 32                     | 5.20        | 11                                    |
| 23                     | 11.7        | 8                                     |
| 19                     | 26.1        | 13                                    |

9.3 Precision for dissolved potassium within the range of 0.01 to 1.0 mg/L in terms of the percent relative standard deviation by a single operator is as follows:

| Number of replicates | Mean (mg/L) | Relative standard deviation (percent) |
|----------------------|-------------|---------------------------------------|
| 18                   | 0.023       | 38.9                                  |
| 12                   | .078        | 9.7                                   |
| 11                   | .358        | 2.7                                   |
| 10                   | .585        | 1.8                                   |
| 11                   | 1.02        | 4.6                                   |

9.4 It is estimated that percent relative standard deviation for total recoverable potassium and for recoverable potassium from bottom material will be greater than that reported for dissolved potassium.

## Reference

Fishman, M. J., and Downs, S. C., 1966, Method for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540-C, p. 36-8.

# Potassium, atomic absorption spectrometric, direct-EPA

Parameter and Code:

Potassium, total recoverable, 1-3631-85 (mg/L as K): 00937

## 1. Application

1.1 This method may be used to analyze water-suspended sediment. Sample solutions containing from 0.1 to 100 mg/L of potassium may be analyzed without dilution, but those containing more than 100 mg/L need to be diluted.

1.2 For ambient water, analysis may be made on a portion of the acidified water-suspended sediment sample.

1.3 For all other water, including domestic and industrial effluent, the atomic absorption procedure must be preceded by a digestion-solubilization as specified below. In cases where the analyst is uncertain about the type of sample, the digestion-solubilization procedure must be used.

## 2. Summary of method

2.1 Potassium is determined by atomic absorption spectrometry by direct aspiration of the filtered or digested and filtered sample into an air-acetylene flame (Fishman and Downs, 1966).

2.2 Effluent samples must undergo a preliminary nitric acid digestion followed by a hydrochloric acid solubilization.

## 3. Interferences

3.1 Of the substances commonly occurring in water, only sodium has been found to interfere, and its interference is greatly minimized if a reducing flame is used and the burner is raised to approximately 0.05 cm below the optical light path. The following data are indicative of the magnitude of sodium interference under these conditions:

| Potassium added (mg/L) | Sodium added (mg/L) | Potassium found (mg/L) |
|------------------------|---------------------|------------------------|
| 1.00                   | 0.0                 | 1.00                   |
| 1.00                   | 100                 | 1.03                   |
| 1.00                   | 500                 | 1.05                   |
| 1.00                   | 1,000               | 1.07                   |

3.2 Alternatively, an excess of sodium or cesium may be added to all samples and standards. Such additions essentially eliminate the effects of the then comparatively minor contributions of sodium present in the samples.

## 4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout and automatic zero and concentration controls.

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

Grating ----- Visible  
Wavelength ----- 766.5 nm  
Source (hollow-cathode lamp) ----- Potassium  
Oxidant ----- Air  
Fuel ----- Acetylene  
Type of flame ----- Slightly reducing

4.3 The 50-mm (2-in.), flathead, single-slot burner allows a working range of 0.1 to 10 mg/L. The burner, rotated 90°, extends the range to 100 mg/L. Different burners may be used according to manufacturers' instructions.

## 5. Reagents

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

5.2 *Hydrochloric acid, 0.3M*: Dilute 25 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.3 *Nitric acid, concentrated*, (sp gr 1.41).

5.4 *Potassium standard solution I*, 1.00 mL = 0.100 mg K: Dissolve 0.1907 g KCl, dried at 180°C for 1 h, in demineralized water and dilute to 1,000 mL.

5.5 *Potassium working standards*: Prepare a series of at least six working standards

containing from 0.1 to 100 mg/L of potassium by appropriate dilution of potassium standard solution.

## 6. Procedure

6.1 Transfer the entire sample to a beaker.

6.2 Rinse the sample bottle with 3 mL concentrated  $\text{HNO}_3$  for each 100 mL of sample and add to the beaker. Prepare a blank using 3 mL concentrated  $\text{HNO}_3$  per 100 mL demineralized water.

6.3 Evaporate samples and blank to dryness on a hotplate, making sure the samples do not boil.

6.4 Cool and add an additional 3 mL concentrated  $\text{HNO}_3$  to each beaker. Cover with a watchglass, return to the hotplate, and gently reflux the samples.

6.5 Continue heating, adding additional acid as necessary, until the digestion is complete (indicated by a light-colored residue). Evaporate just to dryness.

6.6 Add 6 mL 6M HCl solution per 100 mL original sample and warm the beaker to dissolve the residue.

6.7 Wash the watchglass and beaker with demineralized water and filter the sample (Whatman No. 41 or equivalent), rinsing the filter with hot 0.3M HCl. Dilute to the original volume with demineralized water.

6.8 While aspirating the blank use the automatic zero control to set the digital display to read zero concentration. While aspirating standards use the automatic concentration

control to set the digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

## 7. Calculations

Determine the milligrams per liter of total recoverable potassium in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing potassium concentrations that exceed the working range of the method and multiply by the proper dilution factors.

## 8. Report

Report potassium, total-recoverable (00937), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

## 9. Precision

It is estimated that the percent relative standard deviation for total recoverable potassium over the range of the method will be greater than 13 percent.

## References

- Fishman, M. J., and Downs, S. C., 1966, Method for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540-C, p. 36-8.
- U.S. Environmental Protection Agency, 1979, Methods for chemical analysis of water and wastes: Cincinnati, p. 258.1-1.

## Potassium, total-in-sediment, atomic absorption spectrometric, direct

### Parameters and Codes:

Potassium, total, I-5473-85 (mg/kg as K): none assigned

Potassium, total, I-5474-85 (mg/kg as K): none assigned

### 2. Summary of method

2.1 A sediment sample is dried, ground, and homogenized. The sample is then treated and analyzed by one of the following techniques.

2.1.1 The sample is fused with a mixture of lithium metaborate and lithium tetraborate in a graphite crucible in a muffle furnace at 1000°C. The resulting bead is dissolved in acidified, boiling, demineralized water, and potassium is determined by atomic absorption spectrometry. See

method I-5473, metals, major, total-in-sediment, atomic absorption spectrometric, direct.

2.1.2 The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hot plate at 200°C. Potassium is determined on the resulting solution by atomic absorption spectrometry. See method I-5474, metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct.

# 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  $196.0 \text{ nm}$  (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  $42 \text{ mg}$  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 -----                             | $196.0 \text{ nm}$ |
| Source (electrodeless<br>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.

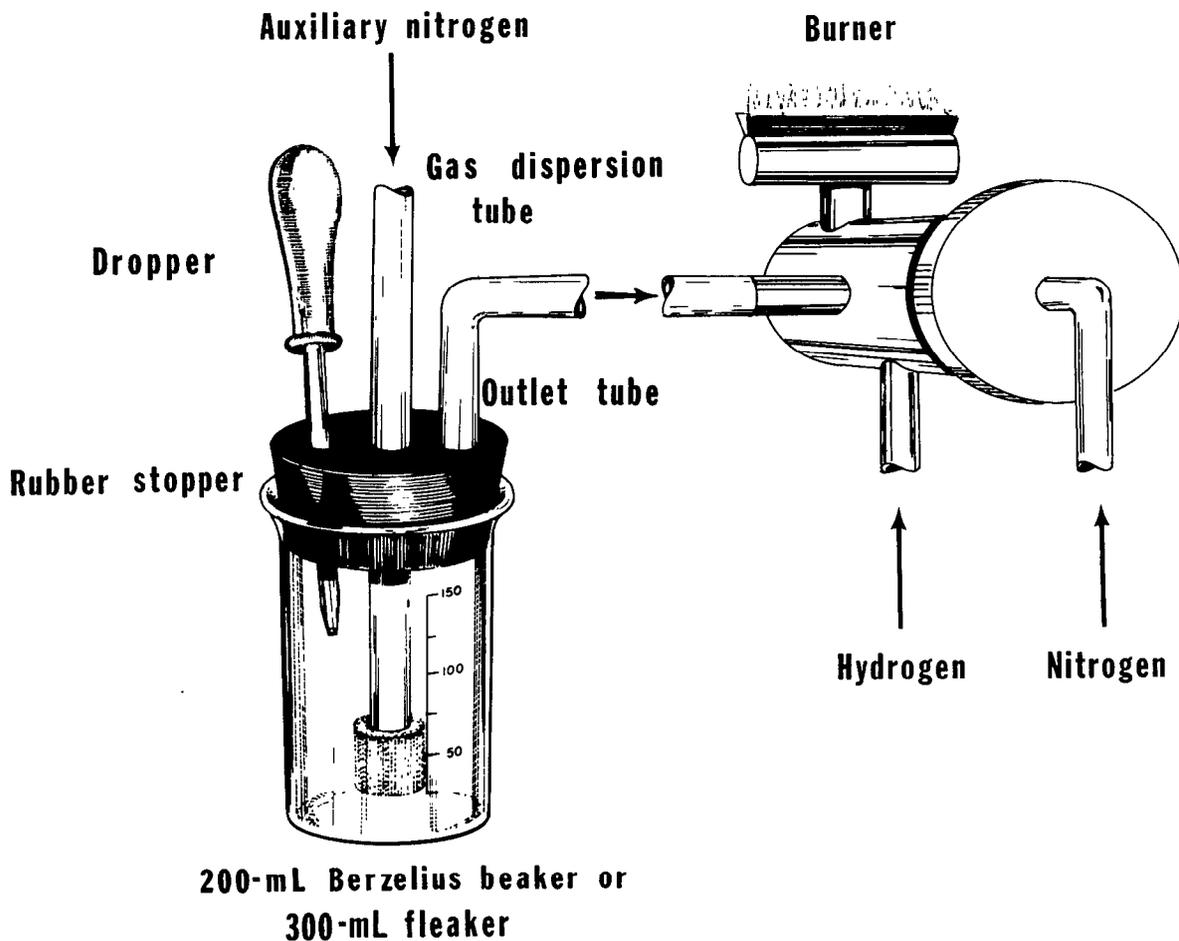


Figure 40.—Selenium hydride vapor analyzer

## 5. Reagents

5.1 *Ammonium chloride solution, 250 g/L:* Dissolve 250 g  $\text{NH}_4\text{Cl}$  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  $\text{KMnO}_4$  in 1 L demineralized water.

5.8 *Selenium standard solution I, 1.00 mL = 1.00 mg Se:* Dissolve 2.3928 g  $\text{Na}_2\text{SeO}_4$  in demineralized water. Add 1 mL concentrated  $\text{HNO}_3$  (sp gr 1.41) and dilute to 1000 mL with demineralized water.

5.9 *Selenium standard solution II, 1.00 mL = 10.0  $\mu\text{g}$  Se:* Dilute 10.0 mL selenium standard solution I and 1 mL concentrated  $\text{HNO}_3$  (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  $\mu\text{g}$  Se:* Dilute 5.00 mL selenium standard solution II and 1 mL concentrated  $\text{HNO}_3$  (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  $\mu\text{g}$  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  $\mu\text{g}$  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  $\mu\text{g}$  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  $\text{CaCl}_2$  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  $\text{KMnO}_4$  solution to each fleaker and heat to boiling on a hotplate, adding  $\text{KMnO}_4$  as required to maintain a purple tint. If a precipitate of  $\text{MnO}_2$  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  $\text{NH}_4\text{Cl}$  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  $\text{SnCl}_2$  solution and insert into hole in rubber stopper.

6.12 Add the  $\text{SnCl}_2$  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.

# Selenium, atomic absorption spectrometric, hydride, automated

## Parameters and Codes:

Selenium, dissolved, I-2667-85 ( $\mu\text{g/L}$  as Se): 01145  
Selenium, total, I-4667-85 ( $\mu\text{g/L}$  as Se): 01147  
Selenium, suspended total, I-7667-85 ( $\mu\text{g/L}$  as Se): 01146  
Selenium, total-in-bottom-material, dry wt, I-6667-85 ( $\mu\text{g/g}$  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  $15 \mu\text{g/L}$  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  $2.6 \text{ g/L}$ . 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  $1 \mu\text{g/g}$  of selenium. For samples containing more than  $5.6 \mu\text{g/g}$ , 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  $300 \mu\text{g/L}$  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 Powerstat 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 tube. Wrap the tube furnace with a 5.5 m (18 ft) of 26-gauge, nickel-chrome wire and cover with asbestos cloth. 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 (1/2)

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<sub>2</sub>.

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 g/L: Dissolve 20 g K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> 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<sub>2</sub>SeO<sub>4</sub> in demineralized water. Add 1 mL concentrated HNO<sub>3</sub> (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

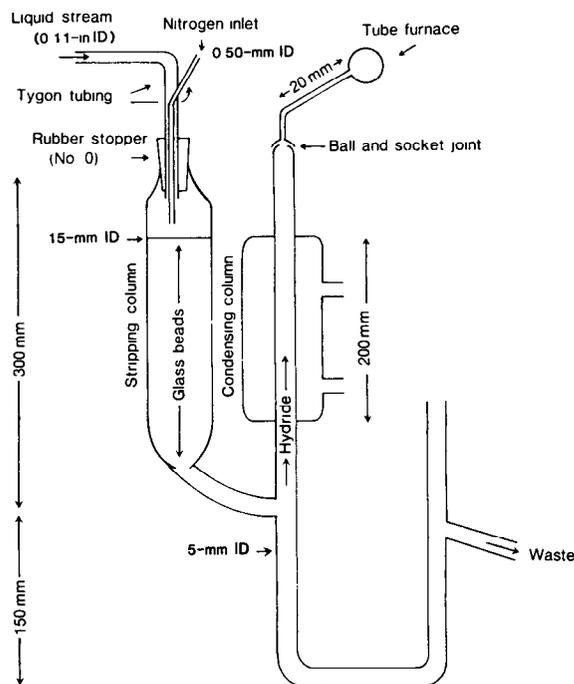


Figure 41.—Stripping-condensing column and quartz-tube furnace

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<sub>3</sub> (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<sub>3</sub> (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<sub>3</sub> by appropriate quantitative dilution of selenium standard solution III.

| Selenium standard solution II (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<sub>4</sub> and 4 g NaOH in demineralized water and dilute to 1 L.

5.10 *Stannous chloride solution, 1.3 g/L:* Dissolve 1.6 g  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 1 L 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 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  $0.225 \mu\text{g}$  Se (15 mL max) into a 25-mL graduated test tube.

6.1.2 Weigh 40 mg or less of bottom-material sample ( $0.225 \mu\text{g}$  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  $\mu\text{g/L}$  into 25-mL graduated test tubes.

6.3 To each tube, add 1.5 mL  $\text{K}_2\text{S}_2\text{O}_8$  solution and 0.3 mL concentrated HCl, and mix.

6.4 Add a boiling stone and place the test tubes in a dri-bath at a temperature of  $100^\circ\text{C}$ , 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 HCl and  $\text{K}_2\text{S}_2\text{O}_8$ , 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:

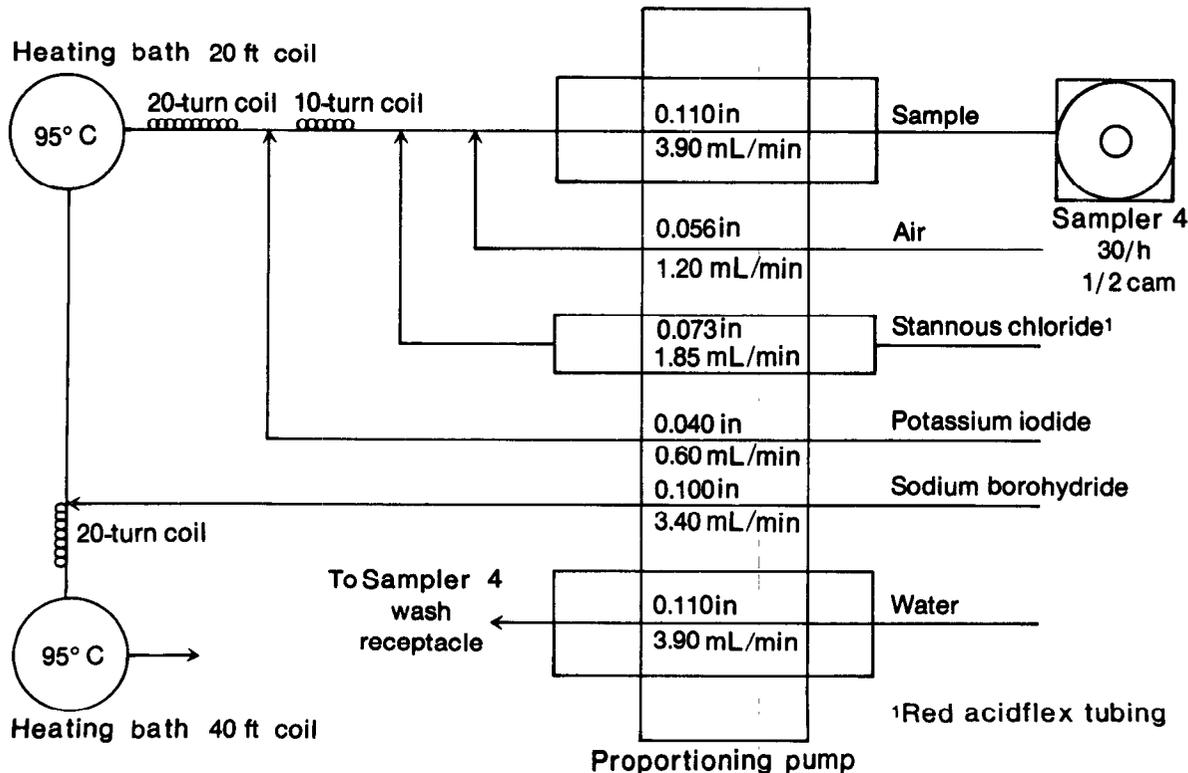


Figure 42.—Selenium, hydride manifold

Stripping-column temperature ----- 75°C (about 36 V)  
 Tube-furnace temperature ----- 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) In 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 (cell) 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 ( $\mu\text{g/L}$ ) | 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  $\mu\text{g/g}$  and standard deviations of 0.3, 0.1, 0.2, and 0.1  $\mu\text{g/g}$ , 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 ( $\mu\text{g/L}$ ) | 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.

## **Selenium, total-in-sediment, atomic absorption spectrometric, hydride**

### **Parameter and Code:**

Selenium, total, I-5475-85 (mg/kg as Se): none assigned

### **2. Summary of method**

A sediment sample is dried, ground, and homogenized. The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a

hotplate at 200 °C. Selenium is determined on the resulting solution by atomic absorption spectrometry. See method I-5475, metals, minor, total-in-sediment, atomic absorption spectrometric, hydride.

# Silica, atomic absorption spectrometric, direct

## Parameter and Code:

Silica, dissolved, I-1702-85 (mg/L as SiO<sub>2</sub>): 00955

### 1. Application

This method may be used to analyze water containing at least 0.5 mg/L of silica. Samples containing more than 35 mg/L need either to be diluted or to be read on a less expanded scale. The sensitivity of the determination is dependent on the amount of acetylene remaining in the cylinder. When a full cylinder is used (290 psi), a sensitivity of about 0.40 mg SiO<sub>2</sub> per scale division may be expected. However, when a near-empty cylinder is used (for example, 50 psi), a sensitivity of only about 0.55 mg SiO<sub>2</sub> per scale division is observed. The significant amount of acetone vapor present in the last acetylene to be withdrawn from a cylinder decreases the sensitivity for silica in the nitrous oxide-acetylene flame.

### 2. Summary of method

Silica is determined by atomic absorption spectrometry by direct aspiration of the sample into a nitrous oxide-acetylene flame without preconcentration or pretreatment of the sample.

### 3. Interferences

None of the substances commonly occurring in natural water interfere with this method.

### 4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout and automatic zero and concentration controls.

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

|                                    |               |
|------------------------------------|---------------|
| Grating -----                      | Ultraviolet   |
| Wavelength -----                   | 251.6 nm      |
| Source (hollow-cathode lamp) ----- | Silica        |
| Burner -----                       | Nitrous oxide |

|                     |               |
|---------------------|---------------|
| Oxidant -----       | Nitrous oxide |
| Fuel -----          | Acetylene     |
| Type of flame ----- | Fuel-rich     |

### 5. Reagents

5.1 *Silica standard solution*, 1.00 mL = 0.500 mg SiO<sub>2</sub>: Dissolve 1.7655 g sodium metasilicate (Na<sub>2</sub>SiO<sub>3</sub>·5H<sub>2</sub>O) in demineralized water and dilute to 1,000 mL. Store in a plastic bottle.

5.2 *Silica working standards*: Prepare a series of at least six working standards containing from 0.5 to 35 mg/L of silica by appropriate dilution of silica standard solution. Store in plastic bottles.

### 6. Procedure

While aspirating the blank use the automatic zero control to set the digital display to read zero concentration. While aspirating standards use the automatic concentration control to set the digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

### 7. Calculations

Determine the milligrams per liter of dissolved silica (as SiO<sub>2</sub>) in each sample from the digital display or printer output while aspirating each sample. Dilute those samples containing concentrations of silica that exceed the working range of the method and multiply by the proper dilution factors.

### 8. Report

Report silica, dissolved (00955), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

**9. Precision**

9.1 The standard deviation for dissolved silica within the range of 1.10 to 16.5 mg/L for 20 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 1.49 mg/L ranged from 1.30 to 1.75 mg/L.

9.2 Precision for dissolved silica for four of

the 20 samples expressed in terms of the percent relative standard deviations is as follows:

| <u>Number of<br/>laboratories</u> | <u>Mean<br/>(mg/L)</u> | <u>Relative standard deviation<br/>(percent)</u> |
|-----------------------------------|------------------------|--|
| 3                                 | 3.83                   | 21   |
| 8                                 | 10.4                   | 12   |
| 7                                 | 16.4                   | 8  |
| 4                                 | 16.5                   | 4  |

## Silica, atomic emission spectrometric, ICP

### Parameter and Code:

Silica, dissolved, I-1472-85 (mg/L as SiO<sub>2</sub>): 00955

### 2. Summary of method

Silica is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric

method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

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# Silica, colorimetric, molybdate blue

## Parameter and Code:

Silica, dissolved, I-1700-85 (mg/L as SiO<sub>2</sub>): 00955

### 1. Application

This method may be used to analyze water containing from 0.1 to 100 mg/L of silica. Samples containing more than 100 mg/L need to be analyzed by standard gravimetric procedures (American Society for Testing and Materials, 1984; Kolthoff and others, 1969).

### 2. Summary of method

2.1 Silica in solution as silicic acid or silicate has the property of reacting with ammonium molybdate in an acid medium to form the yellow silicomolybdate complex. The silicomolybdate complex is then reduced by sodium sulfite to form the molybdate blue color. The silicomolybdate complex may form in water as alpha and beta polymorphs (Strickland, 1952), which have absorbance maxima at different wavelengths. In order to favor the development of the beta form, the pH of the reaction mixture is reduced below 2.5 (Govett, 1961).

2.2 The possibility of having unreactive silica is greater in water containing high concentrations of silica than in water containing low concentrations of silica. When significant amounts of unreactive silica are known or suspected to be present, a 1-h digestion of 50-mL sample with 5.0 mL of 1.0M NaOH is suggested to make all the silica available for reaction with the molybdate reagent.

### 3. Interferences

Phosphate produces a similar molybdate complex under certain pH conditions. In the following determination, tartaric acid is added to suppress phosphate interference. Hydrogen sulfide and ferric and ferrous iron apparently interfere with the determination. Hydrogen sulfide may be removed by boiling an acidified

sample. The addition of disodium dihydrogen ethylenediamine tetraacetate (Na<sub>2</sub>EDTA) eliminates the effect of high concentrations of iron, and also complexes calcium and prevents precipitation of calcium sulfite.

### 4. Apparatus

4.1 *Spectrometer* for use at 700 nm.

4.2 Refer to the manufacturer's manual to optimize instrument.

### 5. Reagents

5.1 *Ammonium molybdate solution*: 49 g/L: Dissolve 52 g (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O in water, adjust the pH to between 7 and 8 with 10M NaOH, and dilute to 1 L with demineralized water. Filter through 0.45- $\mu$ m membrane filter if necessary.

5.2 *Hydrochloric acid, 1.0M*: Mix 88 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L.

5.3 *Silica standard solution I*, 1.00 mL = 0.500 mg SiO<sub>2</sub>: Dissolve 1.7655 g sodium metasilicate (Na<sub>2</sub>SiO<sub>3</sub>·5H<sub>2</sub>O) in demineralized water. Store in a plastic bottle.

5.4 *Silica standard solution II*, 1.00 mL = 0.005 mg SiO<sub>2</sub>: Dilute 10.0 mL silica standard solution I to 1,000 mL with demineralized water. Store in a plastic bottle.

5.5 *Na<sub>2</sub>EDTA solution*, 10 g/L: Dissolve 10 g Na<sub>2</sub>EDTA in demineralized water and dilute to 1 L.

5.6 *Sodium hydroxide solution*, 10M: Dissolve 400 g NaOH in demineralized water and dilute to 1 L.

5.7 *Sodium sulfite solution*, 170 g/L: Dissolve 170 g Na<sub>2</sub>SO<sub>3</sub> in demineralized water and dilute to 1 L.

5.8 *Tartaric acid solution*, 100 g/L: Dissolve 100 g  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$  in demineralized water and dilute to 1 L.

## 6. Procedure

6.1 Pipet a volume of sample containing less than 0.5 mg  $\text{SiO}_2$  (10.0 mL max) into a 50-mL beaker, and adjust the volume to 10.0 mL.

6.2 Pipet a demineralized water blank and sufficient standards into 50-mL beakers, and adjust the volume of each to 10.0 mL.

6.3 Add to each solution, with stirring, 5.0 mL 1.0M HCl, 5.0 mL  $\text{Na}_2\text{EDTA}$  solution, and 5.0 mL ammonium molybdate solution.

6.4 After 5 min add 5.0 mL tartaric acid solution and mix.

6.5 Add 10.0 mL  $\text{Na}_2\text{SO}_3$  solution and mix.

6.6 Allow to stand approx 30 min. The color is stable for several hours.

6.7 Determine the absorbance of each test sample and standards against the blank.

## 7. Calculations

7.1 Determine milligrams of silica in each sample from a plot of absorbances of standards.

7.2 Determine the concentration of dissolved silica in milligrams per liter as follows:

$$\text{SiO}_2 \text{ (mg/L)} = \frac{1,000}{\text{mL sample}} \times \text{mg SiO}_2 \text{ in sample.}$$

## 8. Report

Report silica, dissolved (00955), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

## 9. Precision

9.1 Precision for dissolved silica for 35 samples within the range of 2.15 to 24.4 mg/L may be expressed as follows:

$$S_T = 0.065X + 0.10$$

where

$S_T$  = overall precision, milligrams per liter, and

$X$  = concentration of silica, milligrams per liter.

The correlation coefficient is 0.8053.

9.2 Precision for dissolved silica for four of the 35 samples expressed in terms of the percent relative standard deviation is as follows:

| Number of laboratories | Mean (mg/L) | Relative standard deviation (percent) |
|------------------------|-------------|---------------------------------------|
| 19                     | 2.15        | 16                                    |
| 11                     | 9.08        | 5                                     |
| 6                      | 10.2        | 15                                    |
| 24                     | 24.4        | 7                                     |

## References

- American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, v. 11.01, p. 613-8.
- Govett, G. J. S., 1961, Critical factors in the colorimetric determination of silica: *Analytica Chimica Acta*, v. 25, p. 69-80.
- Kolthoff, I. M., Sandell, E. B., Meehan, E. J., and Bruckenstein, S., 1969, *Quantitative chemical analysis*, (4th ed.): New York, Macmillan, 1199 p.
- Strickland, J. D. H., 1952, The preparation and properties of silicomolybdic acid; I. The properties of alpha silicomolybdic acid: *American Chemical Society Journal*, v. 74, p. 862-7.

# Silica, colorimetric, molybdate blue, automated-segmented flow

## Parameter and Code:

Silica, dissolved, I-2700-85 (mg/L as SiO<sub>2</sub>): 00955

### 1. Application

This method may be used to determine concentrations of silica in surface, domestic, and industrial water in the range from 0.1 to 60 mg/L. Two analytical ranges are used: from 0.1 to 6.0 mg/L and from 1.0 to 60 mg/L.

### 2. Summary of method

2.1 Silica reacts with molybdate reagent in acid media to form a yellow silicomolybdate complex. This complex is reduced by ascorbic acid to form the molybdate blue color. The silicomolybdate complex may form either as an alpha or beta polymorph or as a mixture of both. Because the two polymorphic forms have absorbance maxima at different wavelengths, the pH of the mixture is kept below 2.5, a condition that favors formation of the beta polymorph (Govett, 1961; Mullen and Riley, 1955; Strickland, 1952).

2.2 The possibility of having "unreactive" silica is greater in water containing high concentrations of silica than in water containing low concentrations of silica. When significant amounts of unreactive silica are known or suspected to be present, a 1-h digestion of a 50-mL sample with 5.0 mL of 1.0M NaOH is suggested as a means of making all the silica available for reaction with the molybdate reagent.

### 3. Interferences

Interference from phosphate, which forms a phosphomolybdate complex, is suppressed by the addition of oxalic acid. Hydrogen sulfide must be removed by boiling the acidified sample prior to analysis. Large amounts of iron interfere.

### 4. Apparatus

4.1 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold, proportioning pump, colorimeter, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 0.1 to 60 mg/L:

|                 |       |            |
|-----------------|-------|------------|
| Absorption cell | ----- | 15 mm      |
| Wavelength      | ----- | 660 nm     |
| Cam             | ----- | 60/h (6/1) |

### 5. Reagents

5.1 *Ammonium molybdate solution*, 9.4 g/L: Dissolve 5 g (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O in 0.05M H<sub>2</sub>SO<sub>4</sub> and dilute to 500 mL with 0.05M H<sub>2</sub>SO<sub>4</sub>. Filter and store in an amber plastic container.

5.2 *Ascorbic acid solution*, 17.6 g/L: Dissolve 17.6 g ascorbic acid in 500 mL demineralized water containing 50 mL acetone. Dilute to 1 L with demineralized water. Add 0.5 mL Levor IV solution. The solution is stable for 1 week if stored at 4°C.

5.3 *Levor IV solution*: Technicon No. 21-0332 or equivalent.

5.4 *Oxalic acid solution*, 50 g/L: Dissolve 50 g oxalic acid in demineralized water and dilute to 1 L.

5.5 *Silica standard solution*, 1.00 mL = 0.500 mg SiO<sub>2</sub>: Dissolve 1.7655 g sodium metasilicate (Na<sub>2</sub>SiO<sub>3</sub>·5H<sub>2</sub>O) in demineralized water and dilute to 1,000 mL. Store in a plastic bottle.

5.6 *Silica working standards*: Prepare a blank and 1,000 mL each of a series of silica working standards by appropriate quantitative dilution of silica standard solution as follows:

| Silica standard solution (mL) | Silica concentration (mg/L) |
|-------------------------------|-----------------------------|
| 0.0                           | 0.0                         |
| .5                            | 0.25                        |
| 1.0                           | .5                          |
| 2.0                           | 1.0                         |
| 12.0                          | 6.0                         |
| 20.0                          | 10                          |
| 40.0                          | 20                          |
| 80.0                          | 40                          |
| 120.0                         | 60                          |

5.7 *Sulfuric acid, 0.05M: Cautiously add 2.8 mL concentrated H<sub>2</sub>SO<sub>4</sub> (sp gr 1.84) to demineralized water and dilute to 1 L.*

## 6. Procedure

6.1 Set up manifold (fig. 43).

6.2 Allow colorimeter and recorder to warm up for at least 30 min.

6.3 Adjust baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

6.4 Place a complete set of standards and a blank in the first positions of the first sample

tray, beginning with the most concentrated standard. Place individual standards of differing concentrations in approximately every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each tray with unknown samples.

6.5 Begin analysis. When the peak from the most concentrated working standard (6.0 or 60 mg/L) appears on the recorder, adjust the STD CAL control until the flat portion of the curve reads full scale.

## 7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective silica concentration.

7.2 Compute the concentration of dissolved silica 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.

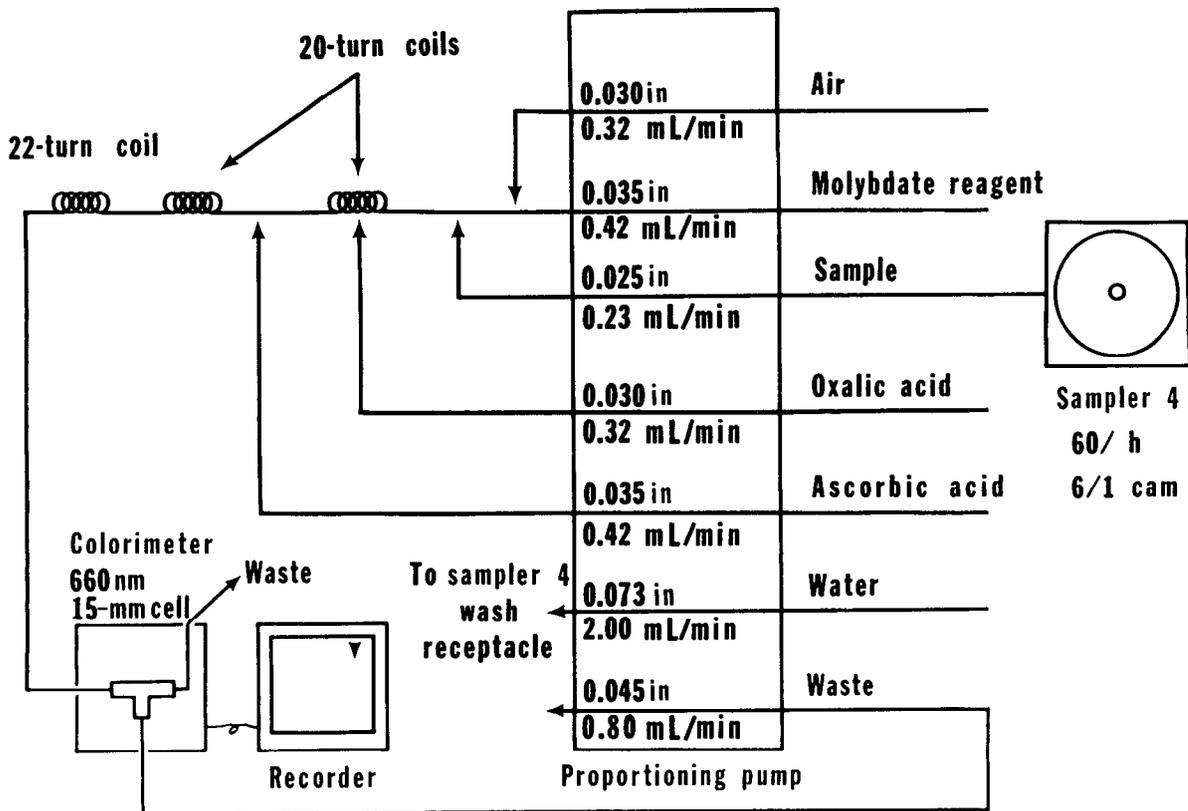


Figure 43.—Silica, molybdate manifold

### 8. Report

Report silica, dissolved (00955), concentrations as follows: less than 10 mg/L, nearest 0.1 mg/L; 10 mg/L and above, two significant figures.

### 9. Precision

9.1 The standard deviation for dissolved silica within the range of 4.70 to 17.4 mg/L for 20 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 1.10 mg/L ranged from 0.97 to 1.26 mg/L.

9.2 Precision for dissolved silica for four of the 20 samples expressed in terms of the percent relative standard deviation is as follows:

| Number of laboratories | Mean (mg/L) | Relative standard deviation (percent) |
|------------------------|-------------|---------------------------------------|
| 5                      | 4.70        | 7                                     |
| 8                      | 8.95        | 23                                    |
| 6                      | 10.6        | 6                                     |
| 5                      | 17.4        | 7                                     |

### References

- Govett, G. J. S., 1961, Critical factors in the colorimetric determination of silica: *Analytica Chimica Acta*, v. 25, p. 69-80.
- Mullen, J. B., and Riley, J. P., 1955, The colorimetric determination of silicate with special reference to sea and natural waters: *Analytica Chimica Acta*, v. 12, p. 162-76.
- Strickland, J. D. H., 1952, The preparation and properties of silicomolybdic acid: I. The properties of alpha silicomolybdic acid: *American Chemical Society Journal*, v. 74, p. 862-7.

## Silica, total-in-sediment, atomic absorption spectrometric, direct

### Parameter and Code:

Silica, total, I-5473-85 (mg/kg as SiO<sub>2</sub>): none assigned

### 2. Summary of method

A sediment sample is dried, ground, and homogenized. The sample is fused with a mixture of lithium metaborate and lithium tetraborate in a graphite crucible in a muffle furnace at 1,000°C.

The resulting bead is dissolved in acidified, boiling, demineralized water, and silica is determined by atomic absorption spectrometry. See method I-5473, metals, major, total-in-sediment, atomic absorption spectrometric, direct.

# Silver, atomic absorption spectrometric, chelation-extraction

## Parameters and Codes:

Silver, dissolved, I-1720-85 ( $\mu\text{g/L}$  as Ag): 01075  
Silver, total recoverable, I-3720-85 ( $\mu\text{g/L}$  as Ag): 01077  
Silver, suspended recoverable, I-7720-85 ( $\mu\text{g/L}$  as Ag): 01076

### 1. Application

1.1 This method may be used to analyze water, brines, and water-suspended sediment containing from 1 to 10  $\mu\text{g/L}$  of silver. Samples containing more than 10  $\mu\text{g/L}$  need to be diluted or to be read on a less expanded scale.

1.2 Suspended recoverable silver is calculated by subtracting dissolved silver from total recoverable silver.

1.3 Total recoverable silver in water-suspended sediment needs to undergo a preliminary digestion-solubilization by method I-3485 before being determined.

### 2. Summary of method

Silver is determined by atomic absorption spectrometry following chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into an air-acetylene flame of the spectrometer.

### 3. Interferences

Concentrations of iron greater than 25,000  $\mu\text{g/L}$  interfere by suppressing the silver absorption.

### 4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout and automatic zero and concentration controls.

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

|                                    |             |
|------------------------------------|-------------|
| Grating -----                      | Ultraviolet |
| Wavelength -----                   | 328.1 nm    |
| Source (hollow-cathode lamp) ----- | Silver      |

|                     |           |
|---------------------|-----------|
| Oxidant -----       | Air       |
| Fuel -----          | Acetylene |
| Type of flame ----- | Oxidizing |

4.3 Different burners may be used according to manufacturers' instructions.

### 5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate (APDC) solution*, 1 g/100 mL: Dissolve 1 g APDC in 100 mL demineralized water. Prepare fresh daily.

5.2 *Citric acid-sodium citrate buffer solution*: Dissolve 126 g citric acid monohydrate and 44 g sodium citrate dihydrate in demineralized water and dilute to 1 L with demineralized water. See NOTE 3 before preparation.

5.3 *Methyl isobutyl ketone (MIBK)*.

5.4 *Silver standard solution I*, 1.00 mL = 100  $\mu\text{g}$  Ag: Crush approx 2 g of  $\text{AgNO}_3$  crystals and dry to constant mass at 40°C. Dissolve 0.1575 g  $\text{AgNO}_3$  in demineralized water and dilute to 1,000 mL. Store in amber bottle.

5.5 *Silver standard solution II*, 1.00 mL = 1.00  $\mu\text{g}$  Ag: Dilute 10.0 mL silver standard solution I and 1.0 mL concentrated  $\text{HNO}_3$  (sp gr 1.41) to 1,000 mL with demineralized water. This solution is used to prepare working standards at the time of analysis. Store in amber bottle.

5.6 *Potassium hydroxide, 10M*: Dissolve 56 g KOH in demineralized water, cool, and dilute to 100 mL.

5.7 *Potassium hydroxide, 2.5M*: Dissolve 14 g KOH in demineralized water and dilute to 100 mL (NOTE 1).

NOTE 1. Alternatively, a 2.5M  $\text{NH}_4\text{OH}$  solution may be used. Add 167 mL concentrated

$\text{NH}_4\text{OH}$  (sp gr 0.90) to 600 mL demineralized water. Cool and dilute to 1 L.

5.8 *Water, acidified:* Add 1.5 mL concentrated  $\text{HNO}_3$  (sp gr 1.41) to 1 L of demineralized water.

## 6. Procedure

6.1 Clean all glassware used in this determination with warm, dilute nitric acid (1 + 9) and rinse with demineralized water immediately before use.

6.2 Pipet a volume of sample solution containing less than  $1.0 \mu\text{g Ag}$  (100 mL max) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.3 Prepare a blank of acidified water and sufficient standards, and adjust the volume of each to approx 100 mL with acidified water.

6.4 With a pH meter, adjust the pH of each solution to 2.4 with 2.5M KOH (NOTES 2 and 3).

NOTE 2. For water-suspended sediment samples that have been digested, add 1 to 2 mL 10M KOH or concentrated  $\text{NH}_4\text{OH}$  (sp gr 0.90) before pH adjustment.

NOTE 3. If an automated titration system is used to adjust the pH, add 2.5 mL citric acid-sodium citrate buffer solution prior to pH adjustment. This will prevent over-shooting the end point in poorly buffered samples.

6.5 Add 2.5 mL APDC solution and shake for 3 min.

6.6 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.7 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

6.8 Aspirate the ketone layer of the blank to set the automatic zero control. Use the automatic concentration control to set the concentrations of the standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

## 7. Calculations

7.1 Determine the micrograms per liter of dissolved or total recoverable silver in each sample from the digital display or printer. Dilute those samples containing concentrations of

silver that exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factors.

7.2 To determine micrograms per liter of suspended recoverable silver, subtract dissolved-silver concentration from total-recoverable-silver concentration.

## 8. Report

Report silver, dissolved (01075), total-recoverable (01077), and suspended-recoverable (01076), concentrations as follows: less than  $10 \mu\text{g/L}$ , nearest microgram per liter;  $10 \mu\text{g/L}$  and above, two significant figures.

## 9. Precision

9.1 Precision for dissolved silver for 16 samples within the range of 1.5 to  $13.6 \mu\text{g/L}$  may be expressed as follows:

$$S_T = 0.478X - 1.29$$

where

$S_T$  = overall precision, micrograms per liter, and

$X$  = concentration of silver, micrograms per liter.

The correlation coefficient is 0.7681.

9.2 Precision for dissolved silver for five of the 16 samples expressed in terms of the percent relative standard deviation is as follows:

| Number of laboratories | Mean ( $\mu\text{g/L}$ ) | Relative standard deviation (percent) |
|------------------------|--------------------------|---------------------------------------|
| 4                      | 1.5                      | 40                                    |
| 5                      | 2.0                      | 0                                     |
| 5                      | 5.4                      | 20                                    |
| 6                      | 10.4                     | 14                                    |
| 5                      | 13.4                     | 26                                    |

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable silver will be greater than that reported for dissolved silver.

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

| Number of laboratories | Mean ( $\mu\text{g/L}$ ) | Relative standard deviation (percent) |
|------------------------|--------------------------|---------------------------------------|
| 8                      | 8.1                      | 30                                    |