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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

# Anions, ion-exchange chromatographic, automated

Parameters and Codes:

Anions, dissolved, I-2057-85 (see below)

| Parameter | Code | Parameter | Code |
|---|---|---|---|
| Bromide (mg/L as Br) | 71870 | Nitrite (mg/L as N) | 00613 |
| Chloride (mg/L as Cl) | 00940 | Orthophosphate (mg/L as P) | 00671 |
| Fluoride (mg/L as F) | 00950 | Sulfate (mg/L as $SO_4$) | 00945 |
| Nitrate (mg/L as N) | 00618 | | |

## 1. Application

1.1 This method may be used only for the determination of dissolved bromide, chloride, fluoride, nitrate, nitrite, orthophosphate, and sulfate in natural water. Table 11 shows approximate lower and upper concentration limits. Actual limits depend on many factors including the column age, which affects column resolution, the relative concentrations of closely eluting species, and the volume of the sample injected. Samples containing anion concentrations high enough to overload the column resins or interfere with closely eluting species need to be diluted or a sample loop smaller than the 200-$\mu$L sample loop specified in this method needs to be used. Sample dilution or use of smaller volumes will change the detection limits for all anions.

1.2 Analyses must be performed on filtered and unacidified samples.

1.3 The ion chromatographic (IC) technology is so new that instruments and associated data-processing equipment and software available on the commercial market are not standardized and operating conditions vary enormously. Until operating conditions of various manufacturers' instruments become more comparable and the equivalency of methods using those instruments is established by extensive testing, the IC method approved for U.S. Geological Survey use will specify instrument and associated software brands. This does not imply endorsement of one product over another, but rather, acknowledges that IC technology is rapidly changing and developing.

Table 11.—Working ranges of anions by ion chromatography

| Constituent | Minimum concentration[1] (mg/L) | Maximum concentration (mg/L) |
|---|---|---|
| Fluoride | 0.01 | 50 |
| Chloride | .20 | 50 |
| Nitrite-nitrogen | .02 | 70 |
| Orthophosphate-phosphorus | .06 | 40 |
| Bromide | .10 | 150 |
| Nitrate-Nitrogen | .05 | 150 |
| Sulfate | .20 | 100 |

[1]With a larger sample loop (for example, 600 $\mu$L), minimum concentration levels can be lowered.

## 2. Summary of method

2.1 A sample is injected into an ion chromatograph and is pumped through three different ion-exchange columns into a specific-conductivity detector. The first two columns, a precolumn and separator column, are packed with low-capacity anion exchanger. Ions are separated based on their affinity for the exchange sites of the resin. The last column is a suppressor column that contains cation-exchange resin in the hydrogen form. The suppressor column reduces the background conductivity of the eluent to a low or negligible level and converts the anions in the sample into their corresponding acids. The separated anions in their acid form are measured using an electrical-conductivity cell. Anions are identified based

on their retention times compared with known standards. Quantitation is accomplished by measuring the peak height or area and by comparing it with an analytical curve generated from known standards.

2.2 During analysis, the suppressor column will slowly be exhausted and, therefore, will need to be regenerated. Other suppressors, such as the hollow-fiber suppressor, which is continuously regenerated, may be used.

2.3 For additional information on ion chromatography, see Small and others (1975) and Fishman and Pyen (1979).

## 3. Interferences

3.1 Because bromide and nitrate elute very closely together, they potentially interfere with each other. Bromide-to-nitrate ratios should not exceed 1:10 or 10:1 if both ions are to be quantitated.

3.2 High levels of organic acids may be present in industrial and domestic wastes which may interfere with inorganic-anion analysis. Two common species, formate and acetate, elute between fluoride and chloride.

3.3 Water from the sample injection will cause a negative peak or dip in the chromatogram when it elutes, because its conductivity is less than that of the suppressed eluent. This dip usually occurs between $F^{-1}$ and $Cl^{-1}$. Any peak of interest eluting near the water dip must be sufficiently resolved from the dip to be accurately quantitated. A method of eliminating the conductivity drop due to bicarbonate and carbonate is to introduce into the sample concentrations of bicarbonate and carbonate that closely approximate those of the eluent used for analysis. Adjustment of the sample background may be accomplished in two ways.

3.3.1 Dilute the sample with eluent if sample dilution is required prior to analysis.

3.3.2 A volume of 1.0 mL of a prepared eluent concentrate (a solution that is 100 times more concentrated than the eluent with respect to bicarbonate and carbonate ions) can be added per 100.0 mL of sample. CAUTION: Samples prepared in this manner have a pH of about 10 and will readily absorb carbon dioxide if left exposed to the atmosphere. The result will cause a positive-peak interference.

3.3.3 Standard solutions need to be prepared in the same manner as the samples. It is important to prepare a blank using demineralized water at eluent strength in bicarbonate and carbonate to indicate any interferences that may have been introduced by the sample-preparation technique.

3.4 Samples containing high concentrations of chloride or other anions may prevent resolution of closely eluting peaks. For example, the peak for 0.1 mg of bromide per liter in the presence of greater than 1,000 mg of chloride per liter is swamped by the chloride peak. Bromide begins to elute before the chloride peak completely returns to the baseline.

3.5 Unexpected, late-eluting peaks are a potential source of interference. A peak eluting about two minutes after sulfate, believed to be oxalate, has been observed in some precipitation samples.

## 4. Apparatus

4.1 *Ion Chromatograph, Dionex Model 12; auto-sampler, Gilson; integrator (NOTE 1), Spectra Physics* using the following operating conditions:

| | |
|---|---|
| Sample loop -------- | 200 μL |
| Eluent flow rate ----- | 138 mL/h (30 percent of full capacity) |
| Sample pump flow rate | 50 percent of full capacity |
| Specific conductance meter settings ---- | 10, 30, or 100 μS |

NOTE 1. A dual pen recorder (1 V and 100 mV) may replace an integrator. The recorder should be capable of full-scale response in two seconds or less. A typical chart speed is 0.5 cm/min.

4.1.1 *Precolumn*, 4 × 50-mm, fast-run, anion-resin column (Dionex P/N 030831 or equivalent) placed before the separator column to protect the separator column from contamination by particulates or species strongly retained by the ion-exchange resin.

4.1.2 *Separator column*, 4 × 250-mm, fast-run, anion-separator column packed with low-capacity, pellicular, anion-exchange resin (Dionex P/N 030830 or equivalent) that is styrene divinylbenzene-based. This is suitable for resolving fluoride, chloride, nitrite, orthophosphate, bromide, nitrate, and sulfate.

4.1.3 *Suppressor column*, 6 × 250-mm, column-packed, with a high-capacity, column-exchange resin (Dowex 50W-X 16-H form resin or equivalent) that is capable of converting the

eluent and separated anions to their respective acid forms.

4.2 For additional information, refer to the different manufacturers' instruction manuals.

## 5. Reagents

5.1 *Eluent*, 0.003 *M* sodium bicarbonate-0.0024 *M* sodium carbonate: Dissolve 0.2520 g $NaHCO_3$ and 0.2544 g $Na_2CO_3$ in demineralized water and dilute to 1 L (NOTE 2).

NOTE 2: Eluent concentration may be varied slightly to obtain the same retention times for each anion when a new separator column is used. The $NaHCO_3$ is subject to thermal decomposition and must be weighed without prior drying.

5.2 *Suppressor regeneration solution*, 1*N* $H_2SO_4$: *Cautiously* add 111 mL concentrated $H_2SO_4$ (sp gr 1.84) to approx 600 mL demineralized water. Cool and dilute to 4 L with demineralized water.

5.3 *Standard anion solutions*: Dry all salts for 1 h at 105°C unless otherwise specified. Store each standard solution in TFE-fluorocarbon bottles.

5.3.1 *Bromide standard solution*, 1.00 mL = 1.00 mg Br: Dissolve 1.2877 g NaBr in demineralized water and dilute to 1,000 mL.

5.3.2 *Chloride standard solution*, 1.00 mL = 1.00 mg Cl: Dissolve 1.6484 g NaCl in demineralized water and dilute to 1,000 mL.

5.3.3 *Fluoride standard solution*, 1.00 mL = 1.00 mg F: Dissolve 2.2101 g NaF in demineralized water and dilute to 1,000 mL.

5.3.4 *Nitrate-nitrogen standard solution*, 1.00 mL = 1.00 mg $NO_3$-N: Dissolve 6.0681 g $NaNO_3$ in demineralized water and dilute to 1,000 mL.

5.3.5 *Nitrite-nitrogen standard solution*, 1.00 mL = 1.00 mg $NO_2$-N: Dissolve 4.9259 g $NaNO_2$ in demineralized water and dilute to 1,000 mL.

5.3.6 *Phosphorus standard solution*, 1.00 mL = 1.00 mg P: Dissolve 4.3936 g anhydrous $KH_2PO_4$ in demineralized water and dilute to 1,000 mL.

5.3.7 *Sulfate standard solution*, 1.00 mL = 1.00 mg $SO_4$: Dissolve 1.8140 g $K_2SO_4$ in demineralized water and dilute to 1,000 mL.

5.4 *Mixed stock solution*: Prepare 1,000 mL mixed stock solution by appropriate quantitative dilution of each standard solution (NOTES 3 and 4).

| Anion | Concentration (mg/L) | Volume (mL) |
|---|---|---|
| F | 5.00 | 5 |
| Cl | 50.0 | 50 |
| $NO_2$-N | 5.0 | 5 |
| $PO_4$-P | 5.0 | 55 |
| Br | 5.0 | 5 |
| $NO_3$-N | 50.0 | 50 |
| $SO_4$ | 50.0 | 50 |

NOTE 3. If nitrite is omitted from the mixed stock solution, the solution is stable for at least 1 month when stored and refrigerated in a clean TFE-fluorocarbon bottle. If nitrite is included in the mixed-stock solution, the solution needs to be prepared fresh daily.

NOTE 4. The above is only an example of a mixed-stock solution. Other appropriate concentrations can be prepared.

5.5 *Mixed standard solutions*: Prepare at least three mixed standard solutions by appropriate dilution of the mixed stock solution. The solutions should bracket the concentration range of interest.

## 6. Procedure

6.1 Set up the ion chromatograph according to the operating parameters described in 4.1. Equilibrate the columns with eluent until a stable baseline is obtained. Allow approximately 30 min for equilibration.

6.2 Set the full-scale conductivity to 10, 30, or 100 μS as is appropriate for the expected sample-anion concentrations. The higher settings are required for higher sample-anion concentrations.

6.3 Level the integrator at 10 mV (a display of 1000 with no signal). Adjust the ion chromatograph's offset to approximately 11 mV (a display of 1100). This ensures that the ion chromatograph's signal will not fall below 10 mV during the course of the analyses. The baseline signal tends to drift in a negative direction over a long period of time. Each chromatogram can be started at a signal level of 10 mV using the integrator's automatic-zero control.

6.4 Enter an appropriate program into the main program controller of the ion chromatograph according to the manufacturer's instruction manual. The system is configured so that the ion chromatograph controls the autosampler and starts the integrator at the beginning of each sample injection (NOTE 5).

NOTE 5. For additional information on computerized data reduction, see Hedley and Fishman (1982).

6.5 Place the mixed standard solutions in the first positions of the sample tray followed by a standard reference material and then the samples. Place a standard reference material in every twentieth position of the remainder of the sample tray.

6.6 Create an information file in the integrator by pressing the DIALOG key. Through this information file, various integrator functions can be enabled or disabled during the recording of a chromatogram. The only necessary function is ER (end run). It terminates the chromatogram at the appropriate time as determined by the operator's setting of the ion chromatograph's controller, which actuates the sampler and causes the injection of a new sample.

6.7 Press the integrator's PT EVAL key before starting a series of analyses. The integrator will take about 50 s to store the baseline signal so that a peak can be distinguished from baseline noise. The baseline noise can be evaluated before each chromatogram, using the integrator's ET function.

6.8 Set the ion chromatograph's PGM/AUTO/MANUAL switch from MANUAL to AUTO and press Start/Step to begin the analyses.

## 7. Calculation

7.1 The integrator automatically computes the concentration of each anion in each sample by comparing its peak height or area to the analytical curve. Retention times for the seven anions are given in table 12.

## 8. Report

8.1 Report bromide (71870), chloride (00940), fluoride (00950), nitrate-nitrogen (00618), nitrite-nitrogen (00613), orthophosphate-phosphorus (00660), and sulfate (00945), dissolved, concentrations as follows: less than 1 mg/L, nearest 0.01 mg/L; 1 mg/L and above, two significant figures.

## 9. Precision

9.1 Analysis of a number of test samples 10 times each by one operator resulted in mean values, standard deviations, and percent relative standard deviations as shown in table 13.

Table 12.—Approximate retention times of anions by ion chromatography

| Constituent | Time (min) |
|---|---|
| Fluoride | 2.2 |
| Chloride | 3.3 |
| Nitrate-nitrogen | 4.0 |
| Orthophosphate-phosphorus | 4.9 |
| Bromide | 6.5 |
| Nitrate-nitrogen | 7.5 |
| Sulfate | 8.6 |

Table 13.—Precision for ion chromatographic determination of anions

| Constituent | Mean (mg/L) | Standard deviation (mg/L) | Relative standard deviation (percent) |
|---|---|---|---|
| Bromide | 0.295 | 0.020 | 6.8 |
| Chloride | .72 | .04 | 5.6 |
| Do. | 1.71 | .06 | 3.5 |
| Do. | 2.72 | .24 | 8.8 |
| Do. | 5.84 | .19 | 3.2 |
| Do. | 9.90 | .39 | 3.9 |
| Do. | 58.6 | .7 | 1.2 |
| Do. | 119 | 1.2 | 1.0 |
| Fluoride | .018 | .004 | 22.2 |
| Do | .080 | .010 | 12.5 |
| Do | .79 | .02 | 2.5 |
| Do | .92 | .01 | 1.1 |
| Do. | 2.02 | .15 | 7.4 |
| Nitrate-nitrogen | .12 | .01 | 8.3 |
| Do | .42 | .051 | 1.9 |
| Do | .70 | .081 | 1.4 |
| Do. | 1.27 | .05 | 3.9 |
| Do. | 5.26 | .14 | 2.7 |
| Nitrite-nitrogen | .03 | .01 | 33.3 |
| Orthophosphate-phosphorus | .273 | .010 | 3.7 |
| Sulfate | 1.68 | .05 | 3.0 |
| Do. | 3.88 | .10 | 2.6 |
| Do. | 15.1 | .80 | 5.3 |
| Do. | 62.1 | .9 | 1.4 |
| Do. | 100 | 1.4 | 1.4 |
| Do. | 146 | 3 | 2.0 |

## References

Fishman, M. J., and Pyen, G. S., 1979, Determination of selected anions in water by ion chromatography: U.S. Geological Survey Water-Resources Investigations, 79-101, 30 p.

Hedley, A. G., and Fishman, M. J., 1982, Automation of an ion chromatograph for precipitation analysis with computerized data reduction: U.S. Geological Survey Water-Resources Investigations, 81-78, 33 p.

Small, H., Stevens, T. S., Bauman, W. C., 1975, Novel ion exchange chromatographic method using conductimetric detection: Analytical Chemistry, v. 47, p. 1801-9.

# Anions, ion-exchange chromatographic, low ionic-strength water, automated

Parameters and Codes:

Anions, dissolved, I-2058-85 (see below)

| Parameter | Code | Parameter | Code |
|---|---|---|---|
| Bromide (mg/L as Br) | 71870 | Nitrate (mg/L as N) | 00618 |
| Chloride (mg/L as Cl) | 00940 | Orthophosphate (mg/L as P) | 00671 |
| Fluoride (mg/L as F) | 00950 | Sulfate (mg/L as $SO_4$) | 00945 |

## 1. Application

1.1 This method may be used only for the determination of dissolved bromide, chloride, fluoride, nitrate, orthophosphate, and sulfate in water with a specific conductance of approx 100 $\mu$S/cm or less. Table 14 specifies the lower and upper concentration limits using a 200-$\mu$L sample loop. Samples containing anion concentrations greater than the upper concentration limits must be diluted or the conductivity meter must be changed to a less sensitive setting before analysis.

1.2 Analyses must be performed on a filtered (rinsed 0.45-$\mu$m membrane filter) or particulate-free, unacidified sample.

Table 14.—Analytical ranges used in the determination of the six anions

| Constituent | Minimum concenration (mg/L) | Maximum concentration (mg/L) |
|---|---|---|
| Fluoride | 0.01 | 0.5 |
| Chloride | .01 | 3.0 |
| Orthophosphate-phosphorus | .01 | .6 |
| Bromide | .01 | .6 |
| Nitrate-nitrogen | .01 | .6 |
| Sulfate | .01 | 10.0 |

## 2. Summary of method

2.1 All six anions are determined on a single filtered or particulate-free, unacidified sample with an ion chromatograph.

2.2 In anion analysis, the ions of interest elute through an anion-ion exchange separator column at different rates, depending upon the affinity of each anion for the ion- exchange resin. Then the ions elute through a fiber suppressor, which consists of a semi-permeable membrane in the interior of the suppressor's outer shell. The membrane is wrapped around the interior of the fiber, which is packed with inert beads. A suppressor regenerant solution flows countercurrent to the eluent intrained samples and surrounds the outside of the semi-permeable fiber. The regenerant is continuously fed by gravity through the suppressor's interior. This latter process operates continuously.

2.3 For additional information on ion chromatography, see Small and others (1975).

## 3. Interferences

3.1 A negative peak or dip, which is caused by a combination of water and carbonate, is seen in the chromatogram using a fiber suppressor. This interference is eliminated by adding concentrated eluent to the sample.

3.2 Because low ionic-strength samples contain low concentrations of these six anions, there will be no unresolved peaks and, therefore, no interferences.

3.3 Oxalate, acetate, or formate may interfere if present.

## 4. Apparatus

4.1 *Ion Chromatograph, Dionex Model 2120i* (NOTE 1) or equivalent, using the following operating conditions:

| | |
|---|---|
| Eluent-pump flow rate | 2.0 mL/min |
| Sample loop -------- | 200 μL |
| Specific-conductance meter settings ---- | 1,3,10,30 μS |

NOTE 1. Concentration limits and operating conditions may vary according to model of instrument.

4.2 *Pump, LDC/Milton Roy miniMetric I* (NOTE 2) or equivalent that gives pulse-free flow of liquid. These pumps are used to eliminate "water and carbonate dip" by adding a volume of concentrated eluent (10x) to each sample.

| | |
|---|---|
| Sample pump flow rate | 2.4 mL/min |
| Concentrated eluent pump flow rate --- | 0.23 mL/min (NOTE 3) |

NOTE 2. Deactivate the Reset switch to bypass the low-pressure-limit adjustment.

NOTE 3. These flow rates will vary slightly depending on the eluent concentration. Adjust flow rates of pumps by injecting a blank until "water and carbonate dip" disappears.

4.2.1 Sample and concentrated eluent pumps are connected to the ion chromatographic Relays 3 and 4, respectively, and are controlled by Auto Ion 100 Controller program.

4.3 *Integrator, Spectra Physics; auto sampler, Gilson* or their equivalents, connected to the ion chromatograph's Relays 1 and 2, respectively.

4.4 *Proportioning pump, Technicon*, or equivalent, provides demineralized water into the wash receptacle of the sampler.

4.5 *Precolumn*, HPIC AS-4 Dionex pellicular anion-resin or equivalent.

4.6 *Separator column*, HPIC AS-4 Dionex pellicular anion-resin or equivalent.

4.7 *Suppressor*, Dionex anion fiber suppressor, No. 35350.

4.8 For additional information, refer to the manufacturers' instruction manuals.

## 5. Reagents

5.1 *Anion stock solutions I*, 1.00 mL = 1.00 mg: Prepare six individual anion stock solutions I by dissolving indicated amount of reagent-grade chemicals, dried to a constant weight at 105°C, in demineralized water and dilute to 1,000 mL and store in Teflon bottles.

| Anion | Salt | g/L |
|---|---|---|
| Br | NaBr | 1.2877 |
| Cl | NaCl | 1.6484 |
| F | NaF | 2.2101 |
| $NO_3$-N | $NaNO_3$ | 6.0681 |
| $PO_4$-P | $KH_2PO_4$ | 4.3936 |
| $SO_4$ | $K_2SO_4$ | 1.8140 |

5.2 *Anion Stock Solutions II*, 1.00 mL = 0.10 mg: Prepare chloride and sulfate stock solutions by diluting 100 mL each of chloride and sulfate stock solutions I to 1,000 mL with demineralized water and store in Teflon bottles.

5.3 *Concentrated eluent*, 0.0280*M* sodium bicarbonate-0.0225*M* sodium carbonate: Dissolve 9.408 g $NaHCO_3$ and 9.540 g $Na_2CO_3$ in demineralized water and dilute to 4 L.

5.4 *Demineralized water*: Pass water through a post column (millipore or equivalent) with 0.2-μm pore size filter which is placed after laboratory demineralized water system.

5.5 *Eluent*, 0.00280*M* sodium bicarbonate-0.00225*M* sodium carbonate (NOTE 4): Dissolve 5.410 g $NaHCO_3$ and 5.486 g $Na_2CO_3$ in demineralized water and diulute to 23 L.

NOTE 4. Eluent concentration may be varied slightly to obtain the same retention times for each anion when a new separator column is used.

5.6 *Mixed-anion standard solution I*: Prepare 1,000 mL by appropriate quantitative dilution of anion stock solutions I with demineralized water.

| Anion | Concentration (mg/L) | Volume (mL) |
|---|---|---|
| Br | 10 | 10.0 |
| Cl | 250 | 250 |
| F | 10 | 10.0 |
| $NO_3$-N | 30 | 30.0 |
| $PO_4$-P | 10 | 10.0 |
| $SO_4$ | 300 | 300 |

5.7 *Mixed-anion standard solution II*: Dilute 10.0 mL mixed anion standard solution I to 1,000 mL with demineralized water.

| Anion | Concentration (mg/L) |
|---|---|
| Br | 0.1 |
| Cl | 2.5 |
| F | .1 |
| $NO_3$-N | .3 |
| $PO_4$-P | .1 |
| $SO_4$ | 3.0 |

5.8 *Mixed-anion standard solution III*: Prepare 1,000 mL by appropriate dilution of anion stock solutions II.

| Anion | Concentration (mg/L) | Volume (mL) |
|---|---|---|
| Cl | 0.2 | 2.0 |
| $SO_4$ | 0.2 | 2.0 |

5.9 *Suppressor-regeneration solution*, 0.025*N* $H_2SO_4$: *Cautiously* add 2.8 mL concentrated $H_2SO_4$ (sp gr 1.84) to demineralized water, cool, and dilute to 4L with demineralized water.

## 6. Procedure

6.1 Operate instrument according to parameters described in paragraph 4.1. Supply continuously by gravity-feeding suppressor-regeneration solution for fiber supressor (0.025*N* $H_2SO_4$) at a flow rate of 2.4 mL/min. Equilibrate the columns with 0.00280*M* $NaHCO_3$-0.00225*M* $Na_2CO_3$ eluent until baseline stabilizes. Allow approximately 30 min for equilibration.

6.2 Enter appropriate program into the Auto Ion 100 Controller of ion chromatograph according to manufacturer's instructions. This controls autosampler, integrator, sample pump, and concentrated-eluent pump. This program is best suited for most of the precipitation samples. Set the OutPut Range of the conductivity meter similar to the expected concentration of samples.

6.3 Press the PT EVAL (peak threshold evaluation) key for integrator to evaluate the detector signal for noise and drift.

6.4 Create the information file through a "dialog" with the integrator.

Select calculation of the best straight-line fit using method 5 (external standard method) (NOTE 5).

NOTE 5. For additional information on computerized data reduction, see Hedley and Fishman (1982).

6.5 Run a demineralized water blank through the system to ensure that flow rates of sample and concentrated-eluent pumps are in correct proportion to eliminate the "water and carbonate dip."

6.6 Place mixed-anion standard solutions III and II at the beginning of the sample holder followed by standard reference materials and samples. Place a standard reference material in every tenth position of the remainder of this sample holder.

6.7 Turn on the proportioning pump to deliver demineralized water into the wash receptacle of the sampler.

6.8 Press START on the OPERATION-SELECT of AutoIon 100 Controller to begin the analysis.

## 7. Calculations

7.1 The integrator automatically computes the concentrations of six anions in each sample by comparing their peak heights to the analytical curve. Approximate retention times for the six anions are given in table 15.

## 8. Report

8.1 Report bromide (71870), chloride (00940), fluoride (00950), nitrate-nitrogen (00618), orthophosphate-phosphorus (00660), and sulfate (00945), dissolved, concentrations as follows: less than 1 mg/L, nearest 0.01 mg/L; 1.0 mg/L and above, nearest 0.1 mg/L.

## 9. Precision and Bias

9.1 Analysis of a number of test samples 10 times each by one operator resulted in mean values, standard deviations, and percent relative standard deviations as shown in table 16.

Table 15.—Approximate retention times of anions

| Constituent | Time (min) |
|---|---|
| Fluoride | 1.4 |
| Chloride | 2.2 |
| Orthophosphate-phosphorus | 3.4 |
| Bromide | 4.8 |
| Nitrate-nitrogen | 5.6 |
| Sulfate | 7.6 |

Table 16.—Precision and bias for ion chromatography on simulated precipitation samples

| Standard reference water sample number | Constituent | Ion chromatography data[1] | | | Interlaboratory standard reference water sample data | |
|---|---|---|---|---|---|---|
| | | Mean (mg/L) | Standard deviation (mg/L) | Relative standard deviation (percent) | Mean (mg/L) | Standard deviation[2] (mg/L) |
| 70 (1:10) | F | 0.09 | 0.01 | 8.1 | 0.089 | 0.06 |
| | Cl | .23 | .01 | 4.3 | .271 | .84 |
| | $NO_3$-N | .06 | .005 | 7.7 | .069 | .065 |
| | $SO_4$ | 2.60 | .07 | 2.6 | 2.62 | 1.4 |
| 72 (1:10) | F | .10 | .01 | 9.3 | .09 | 0.06 |
| | Cl | 4.89 | .14 | 2.8 | 4.50 | 1.4 |
| | $PO_4$-P | .05 | .004 | 8.8 | .059 | .048 |
| | $NO_3$-N | .30 | .01 | 4.4 | .302 | .29 |
| | $SO_4$ | 10.6 | .34 | 3.2 | 11.1 | 10 |
| P-1 | Cl | .40 | .01 | 2.3 | .44 | .045 |
| | $NO_3$-N | .13 | .003 | 2.3 | .12 | .016 |
| | $SO_4$ | 1.14 | .03 | 2.5 | 1.18 | .09 |
| P-2 | F | .10 | .01 | 7.8 | .10 | .00 |
| | Cl | .47 | .01 | 1.8 | .60 | .33 |
| | $NO_3$-N | .04 | .002 | 6.0 | .074 | .068 |
| | $SO_4$ | 2.96 | .06 | 1.9 | 3.24 | 1.43 |
| 80 (1:10) | F | .11 | .01 | 9.4 | .114 | .07 |
| | Cl | 3.20 | .09 | 3.0 | 3.15 | 1.5 |
| | $PO_4$-P | .06 | .005 | 9.6 | .073 | .063 |
| | $NO_3$-N | .06 | .004 | 7.3 | .055 | .070 |
| | $SO_4$ | 7.08 | .16 | 2.3 | 7.24 | 5.15 |

[1]Values based on 10 replicate determinations of SRWS.
[2]Standard deviations for undiluted SRWS.

## References


Fishman, M. J., and Pyen, G. S., 1979, Determination of selected anions in water by ion chromatography: U.S. Geological Survey Water-Resources Investigations, 79-101, 30 p.

Hedley, A. G., and Fishman, M. J., 1982, Automation of an ion chromatograph for precipitation analysis with computerized data reduction: U.S. Geological Survey Water-Resources Investigations, 81-78, 33 p.

Small, H., Stevens, T. S., Bauman, W. C., 1975, Novel ion exchange chromatographic method using conductimetric detection: Analytical Chemistry, v. 47, p. 1801-9.

Stevens, T. S., Davis J. C., and Small, H., 1981, Hollow fiber ion-exchange suppressor for ion chromatography: Analytical Chemistry, v. 53, p. 1488-92.

# Metals, major, total-in-sediment, atomic absorption spectrometric, direct

Parameters and Codes:
Metals, total, (I-5473-85): none assigned
Aluminum (mg/kg as Al)
Calcium (mg/kg as Ca)
Iron (mg/kg as Fe)
Magnesium (mg/kg as Mg)
Manganese (mg/kg as Mn)
Potassium (mg/kg as K)
Silica (mg/kg as Si)
Sodium (mg/kg as Na)

## 1. Application

1.1 This method may be used to analyze suspended and bottom sediment for the determination of total concentrations of the constituents. The upper- and lower-concentration-reporting limits are specified below. Samples containing analyte concentrations greater than the upper limit may be analyzed after appropriate dilution.

| Constituent | Lower limit (mg/kg) | Upper limit (mg/kg) |
|---|---|---|
| Aluminum | 20,000 | 150,000 |
| Calcium | 1,000 | 50,000 |
| Iron | 5,000 | 100,000 |
| Magnesium | 1,000 | 20,000 |
| Manganese | 100 | 4,000 |
| Potassium | 1,000 | 35,000 |
| Silica | 40,000 | 150,000 |
| Sodium | 1,000 | 25,000 |

1.2 Analyses must be performed on dried and ground samples that have been fused with a lithium metaborate-lithium tetraborate flux, with the resulting bead dissolved in acidified, deionized water. These solutions are then analyzed by atomic absorption spectrometry.

## 2. Summary of method

2.1 A sediment sample is dried, ground, and homogenized. The dried, ground, and homogenized 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. The resulting solutions are analyzed by atomic absorption spectrometry after the addition of appropriate matrix modifiers. Additional interferences are removed or compensated for by the use of mixed-salt standards.

2.2 Additional information on the principles of the method may be found in Shapiro (1975), Johnson and Maxwell (1981), and Pinta (1982).

## 3. Interferences

3.1 Both positive and negative, interelement interferences occur and have been documented (Johnson and Maxwell, 1981; Pinta, 1982).

3.2 Interferences are eliminated and (or) compensated for by use of cesium chloride (CsCl), orthoboric acid ($H_3BO_3$), lithium metaborate ($LiBO_2$), lithium tetraborate ($Li_2B_4O_7$), and by the use of mixed-salt standards.

## 4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero and concentration controls, and an autosampler (optional).

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

| Constituent | Grating: ultraviolet (uv) or visible (vis) | Wavelength (nm) | Burner: nitrous oxide ($N_2O$) or air | Oxidant: nitrous oxide ($N_2O$) or air | Flame type |
|---|---|---|---|---|---|
| Al | uv | 309.3 | $N_2O$ | $N_2O$ | fuel-rich |
| Ca | vis | 422.7 | $N_2O$ | $N_2O$ | oxidizing |
| Fe | uv | 372.0 | $N_2O$ | $N_2O$ | oxidizing |
| Mg | uv | 202.6 | $N_2O$ | $N_2O$ | oxidizing |
| Mn | uv | 279.5 | $N_2O$ | $N_2O$ | oxidizing |
| K | vis | 766.5 | air | air | oxidizing |
| Si | uv | 251.6 | $N_2O$ | $N_2O$ | reducing |
| Na | vis | 589.0 | air | air | oxidizing |

4.3 *Fuel*, acetylene.

4.4 *Graphite crucibles*, drill-point, 7.5-mL capacity, 1-in. OD, ¾-in. ID, and 1 $^3/_8$-in. total depth.

4.5 *Hollow-cathode lamps*, single-element lamps.

4.6 *Magnetic stirrer.*

4.7 *Muffle furnace*, capable of reaching a temperature of at least 1000 °C.

## 5. Reagents

5.1 *Cesium chloride solution*, 4 g/L: Dissolve 4 g CsCl of at least 5/9ths (<10 ppm impurities) purity in demineralized water and dilute to 1L.

5.2 *Flux mixture*: Thoroughly mix 1 part reagent-grade powdered anhydrous lithium metaborate, $LiBO_2$, and 2 parts anhydrous lithium tetraborate, $Li_2B_4O_7$. Store in a tightly closed bottle (NOTE 1).

5.3 *Lithium metaborate*, $LiBO_2$, at least 5/9ths purity (<10 ppm impurities) (NOTE 1).

5.4 *Lithium tetraborate*, $Li_2B_4O_7$ at least 5/9ths purity (<10 ppm impurities) (NOTE 1). NOTE 1. Pre-mixed fusion fluxes are available from several suppliers and, if sufficiently pure, are satisfactory.

5.5 *Mixed-salt standard solution*: Dissolve, by appropriate means, the following compounds or elements: Al powder (1.500 g), $CaCO_3$ (1.249 g), Fe wire (1.000 g), Mg rod (0.200 g), Mn flakes (0.040 g), KCl (0.668 g), $(NH_4)_2SiF_6$ (18.987 g), NaCl (0.636 g), and $(NH_4)_2TiO(C_2O_4)_2 \cdot H_2O$ (1.227 g), and dilute to 1000 mL with standard diluent solution. This solution will contain the following concentrations: Al (1500 mg/L), Ca (500 mg/L), Fe (1000 mg/L), Mg (200 mg/L), Mn (40 mg/L), K (350 mg/L), Si (3000 mg/L), Na (250 mg/L), and Ti (200 mg/L). Store in a plastic or Teflon bottle.

5.6 *Working standard solutions 1, 2, and 3*: Pipet 10 mL (standard 1), 6 mL (standard 2), and 2 mL (standard 3) mixed-salt standard solutions (5.5) into 100 mL volumetric flasks, and dilute each to 100 mL with standard diluent solution (5.10). Concentrations are as follows:

| Constituent | Standard 1 (mg/L) | Standard 2 (mg/L) | Standard 3 (mg/L) |
|---|---|---|---|
| Fe | 100 | 60 | 20 |
| Mg | 20 | 12 | 4 |
| Si | 300 | 180 | 60 |
| Al | 150 | 90 | 30 |
| Ti | 20 | 12 | 4 |
| Ca | 50 | 30 | 10 |
| Na | 25 | 15 | 5 |
| K | 35 | 21 | 7 |
| Mn | 4 | 2 | 1 |

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

5.8 *Nitric acid*, dilute (1+1): Add 250 mL concentrated $HNO_3$ (sp. gr. 1.41) to 250 mL demineralized water. Store in a plastic bottle.

5.9 *Orthoboric acid solution*, 50 g/L: Dissolve 50 g $H_3BO_3$ of at least 5/9ths ( 10 ppm impurities) purity in demineralized water and dilute to 1 L. Heat may be required to complete dissolution. Prepare fresh daily, because orthoboric acid will precipitate within 12 to 18 hours.

5.10 *Standard diluent solution*: Dissolve 6 g of flux mixture in 500 mL demineralized water. Add 12.5 mL concentrated $HNO_3$ (sp. gr. 1.41), and dilute to 1 L with demineralized water.

## 6. Procedure

Immediately before each use, clean all glassware by rinsing, first with dilute nitric acid (1 + 1) and then with demineralized water.

6.1 Dry the sediment sample by an appropriate procedure such as freeze-drying or oven-drying at 105 °C.

6.2 If the sediment sample is greater than 100 g, split to less than 100 g by the use of a non-metallic sample splitter (riffle sampler) or by coning and quartering.

6.3 Grind the sample with a mixer mill or with an agate mortar and pestle until all material is finer than 100 mesh.

6.4 Transfer approximately 1.2 g of flux mixture to a waxed or plastic-coated weighing paper (6 in. × 6 in). Weigh and transfer 0.2000 g of finely ground sample to the flux mixture and mix by rolling successive corners of the paper about 30 times. Carefully transfer the combined sample-flux to a graphite crucible, and tamp.

6.5 Weigh appropriate standard reference materials and treat as in paragraph 6.4.

6.6 Carry several blanks through the procedure by using only flux and treat as in paragraph 6.4.

6.7 Fuse the mixtures in a muffle furnace, pre-heated to 1,000 °C, for 30 min (NOTE 2).

NOTE 2. When the crucibles, samples, and crucible racks are placed in the muffle furnace, the temperature may drop as much as 200 °C. Time is measured from the time of insertion in the furnace.

6.8 Remove the crucibles from the furnace and allow to cool; dislodge the beads by gentle tapping or with a spatula (NOTE 3).

NOTE 3. The beads can be dissolved immediately after cooling or can be stored in plastic vials for dissolution at a later time.

6.9 Place the beads in an acid-washed, 250-mL, plastic bottle and add a ¾- to 1-in. stirring bar. Add approx 50 mL boiling demineralized water using a plastic graduate, place the bottle on a magnetic stirrer, and mix. Add 5 mL dilute nitric acid (1 + 1) to each bottle and stir rapidly for about 60 min. Cap the bottle lightly to prevent contamination and possible spattering.

6.10 Immediately after 60 min, remove the bottles from the magnetic stirrers, and add about 100 mL demineralized water to prevent the polymerization of silica (NOTE 4).

NOTE 4. The solutions may contain small amounts of graphite from the crucibles, which can be ignored. However, if the solution is cloudy, this indicates that the original sample contained a very high concentration of silica that has polymerized. Discard the solution and perform a new fusion using a smaller quantity of sample.

6.11 Pour each solution into a 200-mL volumetric flask, using a funnel, in order to retain the stirring bar. Rinse the bottle and cap, and dilute to volume with demineralized water. Pour the solution back into the plastic bottle for storage.

6.12 Add 10 mL CsCl solution and 20 mL $H_3BO_3$ solution to each bottle (NOTE 5).

6.13 Prepare the mixed-salt working standards (see paragraph 5.6), and to each 100 mL, add 5 mL CsCl solution and 10 mL $H_3BO_3$ solution (NOTE 5).

NOTE 5. The CsCl acts as an ionization suppressant and the $H_3BO_3$ stabilizes the silica.

6.14 Set up the atomic absorption spectrometer as outlined in paragraph 4.2, and analyze the solutions for Fe, Mn, Mg, Si, and Al. Dilute samples if required (NOTE 6).

NOTE 6. Although the mixed-salt standard contains as much as 300 mg/L Si, samples containing more than 150 mg/L Si should be diluted prior to quantitation. There is a significant suppression of Si above 150 mg/L. The high Si level in the mixed salt is necessary for matrix-matching requirements.

6.15 Transfer 10.0-mL aliquots of each sample and working standard solution to 100-mL volumetric flasks and dilute to 100 mL. Transfer solutions to plastic bottles and add 5 mL CsCl and 10 mL $H_3BO_3$ solutions.

6.16 Set up the atomic absorption spectrometer as outlined in paragraph 4.2, and analyze the solutions for Ca, K, and Na. Dilute samples if required.

## 7. Calculations

7.1 Determine the concentration of each constituent (Fe, Mn, Mg, Si, and Al) in each sample solution from the digital display or printer output while aspirating each sample, and record the results. The concentration of each constituent (in mg/kg) is obtained by multiplying the concentration in each sample solution by 1000, if no dilutions are made.

7.2 Determine the concentration of each constituent (Ca, K, and Na) in each sample solution from the digital display or printer output while aspirating each sample and record the results.

The concentration of each constituent (in mg/kg) is obtained by multiplying the concentration in each sample solution by 10,000, if no dilutions are made.

## 8. Report

Report aluminum, calcium, iron, magnesium, potassium, silica, and sodium, total, concentrations to the nearest 1000 mg/kg (0.1 percent). Report manganese, total, concentration to the nearest 100 mg/kg (0.01 percent).

## 9. Precision

The precision on the two samples expressed in terms of the relative standard deviation is as follows:

| | Sample 1 | | | Sample 2 | | |
|---|---|---|---|---|---|---|
| Constituent | Number of replicates | Mean (percent) | Relative standard deviation (percent) | Number of replicates | Mean (percent) | Relative standard deviation (percent) |
| Aluminum | 5 | 3.5 | 3 | 10 | 8.5 | 1 |
| Calcium | 5 | .7 | 11 | 10 | 7.8 | 3 |
| Iron | 5 | 1.2 | 3 | 10 | 9.3 | 1 |
| Magnesium | 10 | .5 | 2 | 5 | 4.3 | 3 |
| Manganese | 10 | .02 | 20 | 5 | .16 | 12 |
| Potassium | 10 | .5 | 10 | 10 | 3.7 | 3 |
| Silica | 5 | 13.2 | 2 | 10 | 32.4 | 1 |
| Sodium | 5 | .7 | 9 | 10 | 3.1 | 3 |

## References

Johnson, W. M., and Maxwell, J. A., 1981, Rock and mineral analysis, 2d ed. : New York, John Wiley & Sons, 489 p.

Pinta, M., 1982, Modern methods for trace element analysis, translated by STS Inc., Ann Arbor, Ann Arbor Science Publishers, 492 p.

Shapiro, L., 1975, Rapid analysis of silicate, carbonate, and phosphate rocks: U.S. Geological Survey Bulletin 1401, 76 p.

# Metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct

Parameters and Codes:

Metals, total, (I-5474-85): none assigned
Aluminum (mg/kg as Al)
Cadmium (mg/kg as Cd)
Calcium (mg/kg as Ca)
Chromium (mg/kg as Cr)
Cobalt (mg/kg as Co)
Copper (mg/kg as Cu)
Iron (mg/kg as Fe)
Lead (mg/kg as Pb)
Lithium (mg/kg as Li)
Magnesium (mg/kg as Mg)
Manganese (mg/kg as Mn)
Nickel (mg/kg as Ni)
Potassium (mg/kg as K)
Sodium (mg/kg as Na)
Strontium (mg/kg as Sr)
Titanium (mg/kg as Ti)
Zinc (mg/kg as Zn)

## 1. Application

1.1 This method may be used to analyze suspended and bottom sediment for the determination of total concentration of the constituents. The upper- and lower-concentration reporting limits are specified below. Samples containing analyte concentrations greater than the upper limit may be analyzed after appropriate dilution.

| Constituent | Lower limit (mg/kg) | Upper limit (mg/kg) |
|---|---|---|
| Aluminum | 20,000 | 150,000 |
| Cadmium | .5 | 100 |
| Calcium | 1,000 | 50,000 |
| Chromium | 3 | 400 |
| Cobalt | 3 | 600 |
| Copper | 1 | 400 |
| Iron | 5,000 | 100,000 |
| Lead | 3 | 1,000 |
| Lithium | 2 | 200 |
| Magnesium | 1,000 | 20,000 |
| Manganese | 100 | 4,000 |
| Nickel | 3 | 600 |
| Potassium | 1,000 | 35,000 |
| Sodium | 1,000 | 25,000 |
| Strontium | 2.5 | 500 |
| Titanium | 1,000 | 20,000 |
| Zinc | 1 | 160 |

1.2 Analyses must be performed on dried and ground samples that have been solubilized with a combination of nitric, hydrofluoric, and perchloric acids heated in open Teflon beakers. These solutions are then analyzed by atomic absorption spectrometry.

## 2. Summary of method

2.1 A sediment sample is dried, ground, and homogenized. The dried, ground, and homogenized sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200 °C. The resulting salts are dissolved in hydrochloric acid and demineralized water. The resulting solutions are analyzed by atomic absorption spectrometry after the addition, in certain cases, of appropriate matrix modifiers. Additional interferences are removed or compensated for through the use of mixed-salt standards and background correction.

2.2 Additional information on the principles of the method may be found in Walsh (1977), Johnson and Maxwell (1981), and Pinta (1982).

## 3. Interferences

3.1 Both positive and negative interelement interferences occur and have been documented (Walsh, 1977; Johnson and Maxwell, 1981; Pinta, 1982).

3.2 Interferences are eliminated or compensated for by the use of cesium chloride (CsCl), the use of mixed-salt standards, and the use of a deuterium-source background corrector.

## 4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero and concentration controls, a deuterium-source background corrector, and an autosampler (optional).

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

| Constituent | Grating: ultraviolet (uv) or visible (vis) | Wavelength (nm) | Burner: nitrous oxide($N_2O$) or air | Oxidant: nitrous oxide ($N_2O$) or air | Flame type | Background corrector |
|---|---|---|---|---|---|---|
| Al | uv | 309.3 | $N_2O$ | $N_2O$ | fuel-rich | no |
| Cd | uv | 228.8 | air | air | oxidizing | yes |
| Ca | vis | 422.7 | $N_2O$ | $N_2O$ | oxidizing | no |
| Cr | uv | 357.9 | $N_2O$ | $N_2O$ | oxidizing | no |
| Co | uv | 240.7 | air | air | oxidizing | yes |
| Cu | uv | 324.7 | air | air | oxidizing | yes |
| Fe | uv | 372.0 | air | air | oxidizing | no |
| Pb | uv | 217.0 | air | air | oxidizing | yes |
| Li | vis | 670.8 | air | air | oxidizing | no |
| Mg | uv | 202.6 | $N_2O$ | $N_2O$ | oxidizing | no |
| Mn | uv | 279.5 | air | air | oxidizing | no |
| Ni | uv | 232.0 | air | air | oxidizing | yes |
| K | vis | 766.5 | air | air | oxidizing | no |
| Na | vis | 589.0 | air | air | oxidizing | no |
| Sr | vis | 460.7 | $N_2O$ | $N_2O$ | oxidizing | no |
| Ti | uv | 364.3 | $N_2O$ | $N_2O$ | fuel-rich | no |
| Zn | uv | 213.9 | air | air | oxidizing | yes |

4.3 *Beakers*, Teflon, 100-mL capacity, thick-wall, capable of withstanding temperatures up to 260 °C.

4.4 *Fuel*, acetylene.

4.5 *Hollow-cathode lamps*, single-element lamps.

4.6 *Hot plate*, electric or gas, capable of reaching at least 250 °C.

4.7 *Perchloric acid hood*, with appropriate washdown facility and gas or electric outlets.

## 5. Reagents

5.1 *Aluminum standard solution*, 1.00 mL = 1.00 mg Al: Dissolve 1.000 g Al powder in a minimum of HCl (1 + 1). Heat to increase rate of dissolution. Add 10.0 mL HCl (1 + 1) and dilute to 1000 mL with demineralized water.

5.2 *Cesium chloride solution*, 4 g/L: Dissolve 4 g CsCl of at least 5/9ths purity (<10 ppm impurities) in demineralized water and dilute to 1 L.

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

5.4 *Hydrochloric acid*, dilute (1 + 1): Add 250 mL concentrated HCl (sp gr 1.19) to 250 mL demineralized water. Store in a plastic bottle.

5.5 *Hydrochloric acid*, dilute (1 + 49): Add 10 mL concentrated HCl (sp gr 1.19) to 490 mL demineralized water. Store in a plastic bottle.

5.6 *Hydrofluoric acid*, concentrated, 48- to 51-percent, (sp gr 1.17).

5.7 *Iron standard solution*, 1.00 mL = 1.00 mg Fe: Dissolve 1.000 g Fe wire in 20 mL HCl (1 + 1) and dilute to 1000 mL with demineralized water.

5.8 *Mixed-salt standard stock solution I*: Dissolve, by appropriate means, the following compounds or elements: Cd splatters (0.200 g), Cr metal (0.800 g), Co metal (1.200 g), Cu shot (0.800 g), Pb shot (2.000 g), $Li_2CO_3$ (2.130 g), Mn flakes (2.000 g), Ni powder (1.200 g), $SrCO_3$ (1.685 g), and Zn powder (0.320 g). Add 20 mL

concentrated HCl (sp gr 1.19), and dilute to 1,000 mL with demineralized water. This solution will contain the following concentrations: Cd (200 mg/L), Cr (800 mg/L), Co (1200 mg/L), Cu (800 mg/L), Pb (2000 mg/L), Li (400 mg/L), Mn (2000 mg/L), Ni (1200 mg/L), Sr (1000 mg/L), and Zn (320 mg/L). Store in a plastic or Teflon bottle.

5.9 *Mixed-salt standard stock solution II*: Dilute 100 mL of mixed salt standard stock solution I (5.8) and 20 mL concentrated HCl (sp gr 1.19) to 1,000 mL with demineralized water. This solution will contain the following concentrations: Cd (20 mg/L), Cr (80 mg/L), Co (120 mg/L), Cu (80 mg/L), Pb (200 mg/L), Li (40 mg/L), Mn (200 mg/L), Ni (120 mg/L), Sr (100 mg/L), and Zn (32 mg/L). Alternatively, certified standard solutions for each constituent may be purchased and the mixed standard solution prepared. Store in a plastic or Teflon bottle. This solution is stable for 3 months.

5.10 *Mixed-salt standard stock solution III*: Dissolve, by appropriate means, the following compounds or elements: Al powder (1.500 g), $CaCO_3$ (1.249 g), Fe wire (1.000 g), Mg rod (0.200 g), Mn flakes (0.040 g), KCl (0.668 g), NaCl (0.636 g), and $(NH_4)_2TiO(C_2O_4)_2 \cdot H_2O$ (1.227 g). Add 20 mL concentrated HCl (sp gr 1.19), and dilute to 1,000 mL with demineralized water. This solution will contain the following concentrations: Al (1,500 mg/L), Ca (500 mg/L), Fe (1,000 mg/L), Mg (200 mg/L), Mn (40 mg/L), K (350 mg/L), Na (250 mg/L), and Ti (200 mg/L). Store in a plastic or Teflon bottle.

5.11 *Working standard solutions 1, 2, and 3*: Pipet 10 mL (standard 1), 5 mL (standard 2), and 1 mL (standard 3) mixed-salt standard stock solution II into 200-mL volumetric flasks. Add 4 mL concentrated HCl (sp gr 1.19) and 20 mL mixed-salt standard stock solution III (5.10) to each flask, and dilute to 200 mL with demineralized water. Store in plastic or Teflon bottles and prepare fresh daily. Concentrations are as follows:

| Constituent | Standard 1 (mg/L) | Standard 2 (mg/L) | Standard 3 (mg/L) |
|---|---|---|---|
| Cd | 1 | 0.5 | 0.10 |
| Cr | 4 | 2 | .40 |
| Co | 6 | 3 | .60 |
| Cu | 4 | 2 | .40 |
| Pb | 10 | 5 | 1.00 |
| Li | 2 | 1 | .20 |
| Ni | 6 | 3 | .60 |
| Sr | 5 | 2.5 | .5 |
| Zn | 1.6 | 0.8 | .16 |

5.12 *Working standard solutions 4, 5, and 6*: Pipet 10 mL (standard 4), 6 mL (standard 5), and 2 mL (standard 6) mixed-salt standard stock solution III into 100-mL volumetric flasks. Add 2 mL concentrated HCl (sp gr 1.19) and 10 mL CsCl solution (5.2) to each flask, and dilute to 100 mL with demineralized water. Store in plastic or Teflon bottles and prepare fresh daily. Concentrations are as follows:

| Constituent | Standard 4 (mg/L) | Standard 5 (mg/L) | Standard 6 (mg/L) |
|---|---|---|---|
| Al | 150 | 90 | 30 |
| Fe | 100 | 60 | 20 |
| Mg | 20 | 12 | 4 |
| Mn | 4 | 2 | 1 |

5.13 *Working standard solutions 7, 8, and 9*: Pipet 10 mL of standards 4, 5, and 6 (5.12) into 100-mL volumetric flasks. Add 2 mL concentrated HCl (sp gr 1.19) and 10 mL CsCl solution (5.2) to each flask, and dilute to 100 mL with demineralized water. Store in plastic or Teflon bottles and prepare fresh daily. Concentrations are as follows:

| Constituent | Standard 7 (mg/L) | Standard 8 (mg/L) | Standard 9 (mg/L) |
|---|---|---|---|
| Ca | 5.0 | 3 | 1 |
| K | 3.5 | 2.1 | .7 |
| Na | 2.5 | 1.5 | .5 |

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

5.15 *Perchloric acid*, concentrated, 70- to 72-percent (sp gr 1.67).

5.16 *Sodium standard solution*, 1.00 mL = 1.00 mg Na: Dissolve 2.542 g NaCl in demineralized water, add 20 mL HCl (sp gr 1.19), and dilute to 1,000 mL with demineralized water.

5.17 *Titanium standard solution*, 1.00 mL = 1.00 mg Ti: Dissolve 6.135 g $(NH_4)_2TiO(C_2O_4)_2 \cdot H_2O$ in demineralized water, and dilute to 1,000 mL with demineralized water.

5.18 *Titanium working standard solutions*: Pipet 2 mL, 1 mL, and 0.5 mL of titanium standard solution (5.17) into 100-mL volumetric flasks. Add 10 mL aluminum standard solution (5.1), 5 mL iron standard solution (5.7), 3.5 mL sodium standard solution (5.16), 10 mL CsCl solution (5.2), and 2 mL concentrated HCl (sp gr 1.19) to each flask, and dilute to 100 mL with demineralized water. The standards contain 20, 10, and 5 mg/L titanium, respectively.

**6. Procedure**

Immediately before each use, clean all glassware by rinsing, first with dilute HCl (1 + 1), and then with demineralized water.

6.1 Dry the sediment sample by an appropriate procedure such as freeze-drying or oven drying at 105 °C.

6.2 If the sediment sample is greater than 100 g, split to less than 100 g by the use of a non-metallic sample splitter (riffle sampler) or by coning and quartering.

6.3 Grind the sample with a mixer mill or with an agate mortar and pestle until all material is finer than 100 mesh.

6.4 Weigh and transfer 0.5000 g of finely ground sample to a 100 mL Teflon beaker; weigh appropriate reference standard materials as well (NOTE 1).

NOTE 1. The procedure can be used with sample weights between 0.2500 and 1.000 g, with appropriate adjustments to the final-solution volumes and acid strengths (paragraphs 6.4 through 6.12). Weights greater than 1.000 g may be used, but may require an extra digestion with HF and $HClO_4$ (see steps 6.8 and 6.9).

6.5 Carry several blanks through the procedure.

6.6 Place hotplate in a perchloric acid hood, and adjust the hotplate to produce a surface temperature of 200 °C.

6.7 Add 6 mL concentrated $HNO_3$ (sp gr 1.41) to each beaker and place the beakers on the hotplate for approx 30 min (NOTE 2).

NOTE 2. CAUTION: This step is designed to oxidize organic matter in the sample. This step must be carried out prior to the addition of perchloric acid; otherwise, a violent explosion could occur.

6.8 Remove the beakers from the hotplate and wait 5 min. Add 6 mL HF (sp gr 1.17 and 2 mL $HClO_4$ (sp gr 1.67), and return the beakers to the hotplate. Continue heating the beakers until white perchloric fumes are produced and the solution has reached incipient dryness; however, do not bake the residues.

6.9 Remove the beakers from the hotplate and wait 5 min. Repeat paragraph 6.8.

6.10 Remove the beakers from the hotplate and wait 5 min. Add 2 mL $HClO_4$ (sp gr 1.67) and return the beakers to the hotplate. Continue heating until the solution has reached incipient dryness; however, do not bake the residues.

6.11 Remove the beakers from the hotplate, and lower the temperature of the hotplate to 100 °C. Add 2 mL dilute HCl (1 + 1) to each beaker and swirl; add 10 mL demineralized water to each beaker, mix, and return to the hotplate to dissolve the residue.

6.12 Cool the solutions, and pour each into a 50-mL volumetric flask. Rinse the beaker several times with demineralized water and bring to volume with demineralized water (NOTE 3). Pour the solutions into acid-rinsed plastic bottles for storage. These solutions represent a dilution factor of 100 ×.

NOTE 3. If a sample contained a large amount of organic matter, the final solution will commonly contain black "flecks." These can be ignored if they are allowed to settle before aspiration of the solutions into an atomic absorption spectrometer.

6.13 Pipet 5 mL from the 100 × solutions (paragraph 6.12) into 50-mL volumetric flasks. Add 1 mL concentrated HCl (sp gr 1.19) and 5 mL CsCl solution (paragraph 5.2) (NOTE 4) to each flask, and bring to volume with demineralized water. Pour the solutions into acid-rinsed plastic bottles for storage. These solutions represent a dilution factor of 1000 ×.

NOTE 4. The cesium chloride acts as an ionization suppressant.

6.14 Pipet 5 mL from the 1000 × solutions (paragraph 6.13) into 50-mL volumetric flasks. Add 1 mL concentrated HCl (sp gr 1.19) and 5 mL CsCl solution (paragraph 5.2) to each, and bring to volume with demineralized water. Pour the solutions into acid-rinsed plastic bottles for storage. These solutions represent a dilution factor of 10,000 ×.

6.15 Set up the atomic absorption spectrometer as outlined in paragraph 4.2, and analyze the 100 × solutions (paragraph 6.12) for Cd, Cr, Co, Cu, Pb, Ni, and Zn using standards 1, 2, and 3 (paragraph 5.11). Dilute samples if required.

6.16 Pipet 5.0 mL of each sample (paragraph 6.12) and working standard solution (paragraph 5.11) to an appropriate container. Add 5.0 mL dilute HCl (1+49) (paragraph 5.5) and 1.0 mL CsCl solution (paragraph 5.2). Analyze the solutions for Li and Sr using the atomic-absorption spectrometer conditions outlined in paragraph 4.1 (NOTE 5).

NOTE 5. The added dilution is required to eliminate interferences due to density differences (Abbey, 1967).

6.17 Set up the atomic-absorption spectrometer as outlined in paragraph 4.2, and analyze the 1000 × solutions (paragraph 6.13) for Fe, Mn, Mg, and Al using standards 4, 5, and 6 (paragraph 5.12). Dilute samples if required.

6.18 Set up the atomic-absorption spectrometer as outlined in paragraph 4.2, and analyze 1000 × solutions (paragraph 6.13) for Ti, using the titanium working standards (paragraph 5.18) (NOTE 6).

NOTE 6. Titanium determinations by atomic absorption are subject to severe interferences and sensitivity is heavily dependent on flame stoichiometry (Walsh, 1977). Adjust the nitrous oxide flame until it is nearly luminous (increase the fuel flow until the reducing red cone turns orange-yellow, then reduce the fuel flow until the flame just becomes red again).

6.19 Set up the atomic absorption spectrometer as outlined in paragraph 4.2, and analyze the 10,000 × solutions (paragraph 6.14) for Ca, K, and Na using standards 7, 8, and 9 (paragraph 5.13). Dilute samples if required.

## 7. Calculations

7.1 Determine the concentration of each constituent (Cd, Cr, Co, Cu, Pb, Ni, and Zn) from the digital display or printer output while aspirating each sample, and record the results. The concentration of each constituent (in mg/kg) is obtained by multiplying the concentration in each sample solution by 100, if no dilutions are made.

7.2 Determine the concentration of each constituent (Li and Sr) from the digital display or printer output while aspirating each sample, and record the results. The concentration of each constituent (in mg/kg) is obtained by multiplying the concentration in each sample solution by 200, if no dilutions are made.

7.3 Determine the concentration of each constituent (Fe, Mn, Al, Mg, and Ti) from the digital display or printer output while aspirating each sample, and record the results. The concentration of each constituent (in mg/kg) is obtained by multiplying the concentration in each sample solution by 1000, if no dilutions are made.

7.4 Determine the concentration of each constituent (Ca, K, and Na) from the digital display or printer output while aspirating each sample, and record the results. The concentration of each constituent (in mg/kg) is obtained by multiplying the concentration in each sample solution by 10,000, if no dilutions are made.

## 8. Report

Report aluminum, calcium, iron, magnesium, potassium, sodium, and titanium, total, concentrations to the nearest 1000 mg/kg (0.1 percent). Report manganese, total, concentration to the nearest 100 mg/kg (0.01 percent). Report cadmium, total, concentrations to the nearest 0.1 mg/kg. Report chromium, cobalt, copper, lead, lithium, nickel, strontium, zinc, total, concentrations to the nearest 1 mg/kg.

## 9. Precision

9.1 The precision for five replicates expressed in terms of relative standard deviation is as follows:

| Constituent | Sample mean (percent) | Relative standard deviation (percent) | Sample mean (percent) | Relative standard deviation (percent) |
|---|---|---|---|---|
| Aluminum | 2.4 | 2 | 8.7 | 3 |
| Calcium | .7 | 7 | 7.7 | 3 |
| Iron | 1.8 | 0 | 10.8 | 2 |
| Magnesium | .44 | 2 | 3.8 | 4 |
| Manganese | .02 | 25 | .14 | 0 |
| Potassium | .6 | 8 | 3.7 | 2 |
| Sodium | .6 | 15 | 2.9 | 3 |
| Titanium | .2 | 5 | 1.4 | 4 |

9.2 The precision for six replicates expressed in terms of relative standard deviation is as follows:

| Constituent | Sample mean (mg/kg) | Relative standard deviation (percent) | Sample mean (mg/kg) | Relative standard deviation (percent) |
|---|---|---|---|---|
| Cadmium | 0.4 | 20 | 10.0 | 4 |
| Chromium | 8 | 13 | 102 | 3 |
| Cobalt | 6 | 17 | 44 | 5 |
| Copper | 10 | 20 | 106 | 2 |
| Lead | 13 | 7 | 708 | 1 |
| Lithium | 8 | 13 | 132 | 4 |
| Nickel | 3 | 33 | 51 | 2 |
| Strontium | 163 | 4 | 475 | 3 |
| Zinc | 80 | 4 | 134 | 2 |

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# Metals, minor, total-in-sediment, atomic absorption spectrometric, hydride

Parameters and Codes:
Metals, total (I-5475-85): none assigned
Arsenic (mg/kg as As)
Antimony (mg/kg as Sb)
Selenium (mg/kg as Se)

## 1. Application

1.1 This method may be used to analyze suspended and bottom sediment for the determination of total concentrations of arsenic, antimony, and selenium. The upper and lower concentration reporting limits are specified below. Samples containing analyte concentrations greater than the upper limit may be analyzed after appropriate dilution.

| Constituent | Lower limit (mg/kg) | Upper limit (mg/kg) |
|---|---|---|
| Arsenic | 0.05 | 5.0 |
| Antimony | 0.05 | 5.0 |
| Selenium | 0.05 | 5.0 |

1.2 Analyses must be performed on dried and ground samples that have been solubilized with a combination of nitric, hydrofluoric, and perchloric acids heated in open Teflon beakers. These solutions are then analyzed by atomic absorption spectrometry, coupled with hydride generation.

## 2. Summary of method

2.1 A sediment sample is dried, ground, and homogenized, and then is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200 °C. The resulting salts are dissolved in concentrated hydrochloric acid and demineralized water. This serves to reduce the selenium to the +4 valence state for subsequent quantitation. Separate aliquots are then heated with a reductant; a stabilizer is added, and arsenic and antimony are determined. All determinations are made by hydride generation, coupled with atomic absorption spectrometry.

2.2 Additional information on the principles of the method can be found in Thompson and Thomerson (1974), Aslin (1976), Chapman and Dale (1979), Johnson and Maxwell (1981), Crock and Lichte (1982), and Narasaki and Ikeda (1984).

## 3. Interferences

3.1 Total digestion, dilution, and hydride generation frees the arsenic, antimony and selenium from the original matrix, and minimizes interferences. Mixed-salt standards for antimony and selenium, and background correction for selenium, further compensate for any interferences.

3.2 Interferences, primarily negative, do occur and are documented by Johnson and Maxwell (1981), and Narasaki and Ikeda (1984).

## 4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero and concentration controls, and a deuterium-source background corrector; an autosampler and printer or chart recorder permits automation of the analytical process.

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

| Constituent | Grating: ultra-violet(uv) | Wavelength (nm) | Burner | Fuel | Oxidant | Background Flame type | correction |
|---|---|---|---|---|---|---|---|
| As | uv | 193.7 | $N_2O$ | $C_2H_2$ | air | lean | off |
| Sb | uv | 217.6 | $N_2O$ | $C_2H_2$ | air | lean | off |
| Se | uv | 196.0 | $N_2O$ | $C_2H_2$ | air | lean | on |

The $N_2O$ burner head is used because of its shorter flame width. This burner produces very good analytical results while considerably extending the life of the quartz cell. The effect of the $N_2O$ burner may vary with different instrumentation.

4.3 *Hydride generator*, Varian VGA 76 or equivalent. This system consists of a peristaltic pump, reaction coil, gas-liquid separator, and a flame-heated quartz cell.

4.4 *Beakers*, Teflon, 100-mL capacity, thick-walled, capable of withstanding temperatures as high as 260 °C.

4.5 *Hotplate*, gas or electric, capable of reaching at least 250 °C.

4.6 Perchloric acid hood, with appropriate washdown facility and gas or electrical outlets.

## 5. Reagents

5.1 *Antimony standard solution*, 1.00 mL = 1000 μg Sb: Dissolve 1.0000 g Sb metal in 10 mL concentrated $HNO_3$ (sp gr 1.41) plus 5 mL concentrated HCl (sp gr 1.19). Dilute to 1000 mL with dilute HCl (1+1).

5.2 *Arsenic standard solution*, 1.00 mL = 1000 μg As: Dissolve 1.3203 g $As_2O_3$ in a minimum of concentrated HCl (sp gr 1.19). Dilute to 1000 mL with dilute HCl (1+1).

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

5.4 *Hydrochloric acid*, dilute (1 + 1): Add 500 mL concentrated HCl (sp gr 1.19) to 500 mL demineralized water. Store in glass or plastic bottle.

5.5 *Hydroxylamine hydrochloride solution*, in a saturated solution of oxalic acid: Dissolve 200 g $NH_2OH{\cdot}HCl$ in 800 g of saturated solution of oxalic acid.

5.6 Hydrofluoric acid, concentrated, 48- to 51-percent (sp gr 1.17).

5.7 *Mixed-element standard solution*, 1.00 mL = 50.0 μg Sb, As, and Se: Pipet 10.0 mL of each element standard solution (As, Sb, Se) into a 200-mL volumetric flask. Add 100 mL concentrated HCl (sp gr 1.19), and dilute to volume with demineralized water. Store in plastic bottle. Solution should be remade weekly.

5.8 *Mixed-salt standard solution I*: Dissolve, by appropriate means, the following compounds or elements: Cd splatters (0.200 g), Cr metal (0.800 g), Co metal (1.200 g), Cu shot (0.800 g), Pb shot (2.000 g), $Li_2CO_3$ (2.130 g), Mn flakes (2.000 g), Ni powder (1.200 g), $SrCO_3$ (1.685 g), and Zn powder (0.320 g). Add 20 mL concentrated HCl (sp gr 1.19), and dilute to 1000 mL with demineralized water. This solution will contain the following concentrations: Cd (200 mg/L), Cr (800 mg/L), Co (1200 mg/L), Cu (800 mg/L), Pb (2000 mg/L), Li (400 mg/L), Mn (2000 mg/L), Ni (1200 mg/L), Sr (1000 mg/L), and Zn (320 mg/L). Store in plastic or Teflon bottle.

5.9 *Mixed-salt standard solution II*: Dissolve, by appropriate means, the following compounds or elements: Al powder (1.500 g), $CaCO_3$ (1.249 g), Fe wire (1.000 g), Mg rod (0.200 g), Mn flakes (0.040 g), KCl (0.688 g), NaCl (0.636 g), and $(NH_4)_2TiO(C_2O_4)_2{\cdot}H_2O$ (1.227 g). Add 20 mL concentrated HCl (sp gr 1.19), and dilute to 1000 mL with demineralized water. This solution will contain the following concentrations: Al (1500 mg/L), Ca (500 mg/L), Fe (1000 mg/L), Mg (200 mg/L), Mn (40 mg/L), K (350 mg/L), Na (250 mg/L), and Ti (200 mg/L). Store in plastic or Teflon bottle.

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

5.11 *Oxalic acid solution*, saturated: Dissolve approximately 150 g oxalic acid in demineralized water using mild heating. Cool until crystallization stops.

5.12 *Perchloric acid*, concentrated, 70- to 72-percent (sp gr 1.67).

5.13 *Potassium iodide solution*, 100 g/L: Dissolve 100 g KI in demineralized water and dilute to 1 L. Store in plastic bottle.

5.14 *Selenium standard solution*, 1.00 mL = 1000 μg Se: Dissolve 1.0000 g Se metal in 5 mL concentrated $HNO_3$ (sp gr 1.41). Dilute to 1000 mL with dilute HCl (1 + 1).

5.15 *Sodium borohydrate solution*, 0.6 g/100 mL: Dissolve 3.0 g $NaBH_4$ and 2.5 g NaOH in demineralized water and dilute to 500 mL.

5.16 *Working standard solutions 1, 2, 3*: Pipet 200 μL (standard 1), 100 μL (standard 2), and 8 μL (standard 3) of the mixed-element standard solution into 200-mL volumetric flasks. Add 100 mL concentrated HCl (sp gr 1.19), 1 mL mixed-salt standard stock solution I, and 20 mL mixed-salt standard stock solution II to each flask and dilute to 200 mL with demineralized water. Store in plastic or Teflon bottles and prepare fresh daily. Concentrations are as follows:

| Constituent | Standard 1 (μg/L) | Standard 2 (μg/L) | Standard 3 (μg/L) |
|---|---|---|---|
| Sb | 50 | 25 | 2 |
| Se | 50 | 25 | 2 |

5.17 *Working standard solutions 4, 5, 6*: Pipet 200 μL (standard 4), 100 μL (standard 5), and 8 μL (standard 6) mixed-element standard solution into 200-mL volumetric flasks. Add 100 mL concentrated HCl (sp gr 1.19) to each flask, and dilute to 200 mL with demineralized water. Store in plastic or Teflon bottles. Concentrations are as follows:

| Constituent | Standard 4 (μg/L) | Standard 5 (μg/L) | Standard 6 (μg/L) |
|---|---|---|---|
| As | 50 | 25 | 2 |

## 6. Procedure

Immediately before each use, clean all glassware by rinsing first with dilute HCl (1 + 1) and then with demineralized water.

6.1 Dry the sediment by freeze-drying or air-drying at room temperature.

6.2 If the sediment sample is greater than 100 g, split to less than 100 g by the use of a nonmetalic sample splitter (riffle sampler) or by coning and quartering.

6.3 Grind the sample with a mixer mill or an agate mortar and pestle until all material is finer than 100 mesh.

6.4 Weigh and transfer 0.5000 g of finely ground sample to a 100-mL Teflon beaker; weigh appropriate reference standard materials (NOTE 1).

NOTE 1. The procedure can be used with sample weights between 0.2500 and 1.000 g, with appropriate adjustment to the final solution volumes and acid strengths (paragraphs 6.4 through 6.12). Weights greater than 1.000 g may be used, but will require an extra digestion with HF and $HClO_4$ (see paragraphs 6.8 and 6.9).

6.5 Carry several blanks (reagents only) through the procedure.

6.6 Place hotplate in a perchloric acid hood and adjust to produce a surface temperature of 200 °C.

6.7 Add 6 mL concentrated $HNO_3$ (sp gr 1.41)—CAUTION: Explosive with perchloric acid—to each beaker and place the beakers on the hotplate. Continue heating until the residue is nearly dry, approx 30 min. If sample is still evolving brown fumes of $NO_X$ at this point, repeat this step (NOTE 2).

NOTE 2. **CAUTION: This step is designed to oxidize organic matter in the sample. This step must be carried out prior to the addition of perchloric acid; otherwise, a violent explosion could occur.**

6.8 Remove the beakers from the hotplate and cool for 5 min. Add 6 mL HF (sp gr 1.17) and 2 mL $HClO_4$ (sp gr 1.67), and return the beakers to the hotplate. Continue heating the beakers until dense, white perchloric fumes have been produced and the solution has reached incipient dryness; however, do not bake the residues.

6.9 Remove beakers from the hotplate and cool for 5 min; repeat paragraph 6.8.

6.10 Remove beakers from the hotplate and cool for 5 min. Add 2 mL $HClO_4$ (sp gr 1.67) and return the beakers to the hotplate. Continue heating until the solution has reached incipient dryness; however, do not bake the residues.

6.11 Remove the beakers from the hotplate, and lower the temperature of the hotplate to 100 °C. Add 25 mL concentrated HCl (sp gr 1.19) to each beaker and swirl; return to hotplate to dissolve the residue.

6.12 Cool the solutions, and pour each into a 50-mL volumetric flask. Rinse the beaker several times with demineralized water and dilute to the mark with demineralized water

(NOTE 3). Pour the solutions into acid-rinsed plastic bottles for storage.

NOTE 3. If a sample contained a large amount of organic matter, the final solution will commonly contain black "flecks." Allow the flecks to settle before pumping the solutions into the hydride generator.

6.13 Determination of selenium:

6.13.1 Feed the concentrated HCl (sp gr 1.19) and $NaBH_4$ solution into the hydride generator using demineralized water in the sample line.

6.13.2 Set up the atomic absorption spectrometer as outlined in paragraph 4.2. Allow the quartz cell to come to thermal equilibrium (approx 5 min). Analyze the 50 μg/L of Se and blank alternately until stable readings are attained for each. Analyze the solutions (paragraph 6.12) for selenium, using working standards 1, 2, and 3. Dilute the samples if required.

6.14 Determination of antimony and arsenic:

6.14.1 Pipet 20 mL of each sample (paragraph 6.12), working standard solutions 1, 2, and 3 (Sb), and working standard solutions 4, 5, and 6 (As) into 18 × 150-mm (or larger) test tubes. Add 2 mL KI solution and heat in a dry bath at 90 °C for 1 h. Allow to cool, add 2 mL $NH_2OH \cdot HCl$/oxalic acid solution, and mix thoroughly with a vortex mixer (NOTE 4).

NOTE 4. The addition of KI reduces the As and Sb to valence states most favorable to hydride generation (+3). The addition of the $NH_2OH \cdot HCl$-oxalic acid solution was found to stabilize the solutions and to give more consistent results. The oxalic acid also appears to minimize interference from Fe (Crock and Lichte, 1982).

6.14.2 Set up the atomic absorption spectrometer as outlined paragraph section 4.2. Allow the quartz cell to come to thermal equilibrium (approx 5 min). Analyze the 50 μg/L As and Sb standards and blanks alternately until stable readings are attained for each. Analyze the solutions for As and Sb using working standards 1, 2, and 3 for Sb, and working standards 4, 5, and 6 for As. Dilute the samples if required. (NOTE 5)

NOTE 5. With use, the quartz cell may become coated with a white layer of oxides. If left on the cell, these oxides can cause the cell to crack when heated. To remove the oxides, soak the cell for a short time (10 to 15 min is usually sufficient) in concentrated HF (sp gr 1.17); then rinse the cell thoroughly to remove any traces of HF. A strong (45-percent) solution of NaOH or KOH may be used in place of HF.

## 7. Calculations

7.1 Determine the concentration of As, Sb, and Se (in μg/L) from the digital display, printer, or chart recorder, and record the results.

7.2 To convert the results from μg/L to mg/kg, use the following equation:

$$\text{As, Sb, or Se (mg/kg)} = \frac{\mu\text{g/L (As, Sb, or Se)} \times \frac{\text{mL digest}}{1000}}{\text{wt of sample (g)}}$$

## 8. Report

Report the concentration of each determined constituent to the nearest 0.1 mg/kg.

## 9. Precision

The precision for ten replicates on U.S. Geological Survey and National Bureau of Standards reference materials expressed in terms of relative standard deviation is as follows:

| Constituent | Mean sample 1 mean (mg/kg) | Relative standard deviation (percent) | Mean sample 2 mean (mg/kg) | Relative standard deviation (percent) |
|---|---|---|---|---|
| Arsenic | 0.4 | 25 | 12.4 | 9 |
| Antimony | .4 | 13 | 3.3 | 6 |
| Selenium | .5 | 13 | 3.4 | 4 |

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