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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

# Arsenic, atomic absorption spectrometric, hydride

## Parameters and Codes:3

Arsenic, dissolved, I-1062-85 ($\mu$g/L as As): 01000
Arsenic, total, I-3062-85 ($\mu$g/L as As): 01002
Arsenic, suspended total, I-7062-85 ($\mu$g/L as As): 01001
Arsenic, total-in-bottom-material, dry wt, I-5062-85 ($\mu$g/g as As): 01003

## 1. Application

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

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

1.3 This method may be used to analyze bottom material containing at least 1 $\mu$g/g of arsenic. Ordinarily, a 100-mg sample of prepared bottom material (method P-0520) is taken for analysis. However, if the sample contains more than 10 $\mu$g/g of arsenic, a smaller sample needs to be used.

1.4 Total arsenic 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after each sample has been thoroughly mixed by vigorous shaking and a suitable sample portion has been rapidly withdrawn from the mixture.

1.5 Both inorganic and organic forms of arsenic are determined. To determine only inorganic arsenic, omit the strong-acid digestion, paragraphs 6.4 and 6.5 of the procedure.

## 2. Summary of method

Organic arsenic-containing compounds are decomposed by adding sulfuric and nitric acids and repeatedly evaporating the sample to fumes of sulfur trioxide. The arsenic (V) so liberated, together with inorganic arsenic originally present, is subsequently reduced to arsenic (III) by potassium iodide and stannous chloride, and finally to gaseous arsine by sodium borohydride in hydrochloric acid solution. The arsine is 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 193.7 nm.

## 3. Interferences

Since the arsine is freed from the original sample matrix, interferences in the flame are minimized.

## 4. Apparatus

4.1 *Atomic absorption spectrometer* and recorder.

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

Grating ------------ Ultraviolet
Wavelength -------- 193.7 nm
Source (electrodeless discharge
lamp) -------------- Arsenic
Burner ------------ Three-slot
Fuel --------------- Hydrogen
Diluent ------------ Nitrogen
Carrier ------------ Nitrogen

4.3 *Arsine vapor analyzer* (fig. 11) consisting of ____

4.3.1 *Beaker, Berzelius*, 200-mL capacity, or fleaker, 300-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, minimum, or automatic pipettor, 5-mL capacity.

## 5. Reagents

5.1 *Arsenic standard solution I*, 1.00 mL= 1.00 mg As: Dissolve 1.320 g As$_2$O$_3$, dried for 1 h at 110°C, in 10 mL 10$M$ NaOH and dilute to 1,000 mL with demineralized water. This solution is stable. However, it should be prepared fresh every 6 months.

5.2  *Arsenic standard solution II*, 1.00 mL= 10.0 $\mu$g As: Dilute 5.00 mL arsenic standard solution I and 1 mL concentrated $HNO_3$ (sp gr 1.41) to 500.0 mL with demineralized water. Discard after 3 months.

5.3  *Arsenic standard solution III*, 1.00 mL= 0.10 $\mu$g As: Dilute 5.00 mL arsenic standard solution II and 1 mL concentrated $HNO_3$ (sp gr 1.41) to 500.0 mL with demineralized water. Prepare fresh weekly.

5.4  *Hydrochloric acid*, concentrated (sp gr 1.19): Use analytical-grade acid with arsenic content not greater than $1 \times 10^{-6}$ percent.

5.5  *Nitric acid*, concentrated (sp gr 1.41): Use analytical-grade acid with arsenic content not greater than $5 \times 10^{-7}$ percent.

5.6  *Potassium iodide solution*, 15 g/100 mL: Dissolve 15 g KI in 100 mL demineralized water. This solution is stable when stored in an amber bottle.

5.7  *Sodium borohydride solution*, 4 g/100 mL: Dissolve 4 g $NaBH_4$ and 2 g NaOH in 100 mL demineralized water. Prepare fresh before each use.

5.8  *Stannous chloride solution*, 33.6 g/100mL concentrated HCl: Dissolve 40g $SnCl_2 \cdot 2H_2O$ in 100 mL concentrated HCl. This solution is unstable. Prepare fresh daily.

5.9  *Sulfuric acid, 9M: Cautiously*, and with constant stirring and cooling, add 250 mL concentrated $H_2SO_4$ (sp gr 1.84) to 250 mL demineralized water.

## 6. Procedure

6.1  Clean all glassware used in this determination with dilute HCl (1+4) and rinse with demineralized water immediately before each use.

6.2  Follow instructions in paragraph 6.2.1 for water or water-suspended sediment and paragraph 6.2.2 for bottom material.
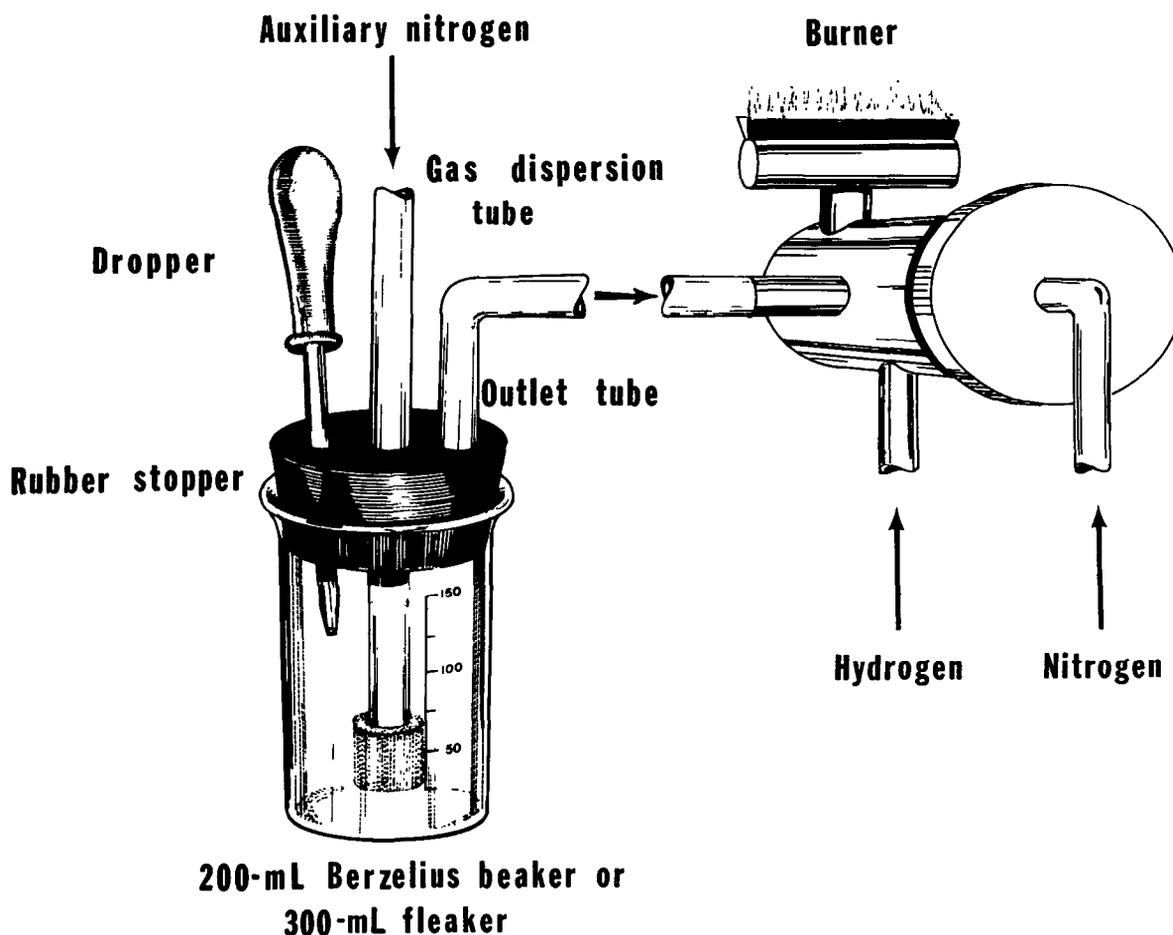


Figure 11.—Arsine vapor analyzer

6.2.1 Pipet a volume of well-mixed sample containing less than 1.0 $\mu$g As (50 mL max) into a 200-mL Berzelius beaker or 300-mL fleaker and dilute to 50 mL (NOTE 1).

NOTE 1. If fleakers are used, maximum volume can be 100 mL. Reagent volumes should be doubled.

6.2.2 Weigh a portion of prepared bottom-material sample containing less than 1 $\mu$g of As (100 mg max) (NOTE 2); transfer to a 200-mL Berzelius beaker or 300-mL fleaker and add 50 mL demineralized water (NOTE 1).

NOTE 2. Do not use more than 100 mg of bottom material to avoid severe bumping and loss of arsenic.

6.3 Prepare, in 200-mL Berzelius beakers or 300-mL fleakers, a blank, and sufficient standards containing from 0.1 to 1.0 $\mu$g As by diluting 1.0 to 10.0-mL portions of arsenic standard solution III. Dilute each to approx 50 mL.

6.4 To each beaker, add 7 mL 9$M$ $H_2SO_4$ and 5 mL concentrated $HNO_3$. Add a small boiling chip or glass beads and carefully evaporate to fumes of $SO_3$. Maintain an excess of $HNO_3$ until all organic matter is destroyed. This prevents darkening of the solution and possible reduction and loss of arsenic. Cool, add 25 mL demineralized water, and again evaporate to fumes of $SO_3$ to expel oxides of nitrogen (NOTE 3).

NOTE 3. If only inorganic arsenic is to be determined, omit steps 6.4 and 6.5.

6.5 Cool, and adjust each beaker to approx 50 mL with demineralized water.

6.6 To each beaker, add successively, with thorough mixing after each addition, 8 mL concentrated HCl, 4 mL KI solution, and 1 mL $SnCl_2$ solution. Allow about 15 min for reduction of the arsenic to the tervalent state.

6.7 Attach one beaker at a time to the rubber stopper containing the gas dispersion tube.

6.8 Fill the medicine dropper with 2 mL $NaBH_4$ solution and insert into the hole in the rubber stopper. Alternatively, the $NaBH_4$ solution may be delivered from an automatic pipettor.

6.9 Add the $NaBH_4$ solution to the sample solution. After the absorbance has reached a maximum and has returned to the baseline, remove the beaker. Rinse the gas dispersion tube in demineralized water before proceeding to next sample. Test each succeeding sample, blank, and standard in a like manner.

## 7. Calculations

7.1 Determine the micrograms of arsenic in the 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 arsenic in each sample as follows:

$$\text{As } (\mu g/L) = \mu g \text{ As in sample} \times \frac{1000}{\text{mL sample}}$$

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

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

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

## 8. Report

8.1 Report arsenic, dissolved (01000), total (01002), and suspended-total (01001), concentrations as follows: less than 10 $\mu$g/L, nearest microgram per liter; 10 $\mu$g/L and above, two significant figures.

8.2 Report arsenic, total-in-bottom-material (01003), concentrations as follows: less than 10 $\mu$g/g, nearest microgram per gram; 10 $\mu$g/g and above, two significant figures.

## 9. Precision

9.1 Precision for dissolved arsenic for 14 samples within the range of 1.8 to 43.7 $\mu$g/L may be expressed as follows:

$$S_T = 0.262X + 0.346$$

where

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

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

The correlation coefficient is 0.8801.

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

| Number of laboratories | Mean (µg/L) | Relative standard deviation (percent) |
|---|---|---|
| 5 | 1.8 | 61 |
| 7 | 10.9 | 30 |
| 8 | 19.5 | 32 |
| 6 | 41.7 | 18 |
| 6 | 43.7 | 35 |

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

9.4   Precision for total arsenic for two water-suspended sediments expressed in terms of the percent relative standard deviation is as follows:

| Number of laboratories | Mean (µg/L) | Relative standard deviation (percent) |
|---|---|---|
| 6 | 16 | 22 |
| 9 | 6.1 | 38 |

# Arsenic, atomic absorption spectrometric, hydride, automated

Parameters and Codes:
Arsenic, dissolved, I-2062-85 (µg/L as As): 01000
Arsenic, total, I-4062-85 (µg/L as As): 01002
Arsenic, suspended total, I-7062-85 (µg/L as As): 01001
Arsenic, total-in-bottom-material, dry wt, I-6062-85 (µg/g as As): 01003

## 1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 1 µg/L of arsenic. Samples containing more than 20 µg/L need to be diluted.

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

1.3 This method may be used to analyze bottom material containing at least 1 µg/g of arsenic (NOTE 1). For samples containing more than 20 µg/g, use less sediment.

NOTE 1. Do not use more than 100 mg sediment, because erratic results and large blanks will occur.

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

1.5 Total arsenic in water-suspended sediment may be determined after each sample has been thoroughly mixed by vigorous shaking and a suitable portion has been rapidly withdrawn from the mixture (NOTE 2).

NOTE 2. Do not use a sample containing more than 1 g/L sediment. Concentrations greater than 1 g/L cause erratic results.

1.6 Both inorganic and organic forms of arsenic are determined. To determine only inorganic arsenic, omit the acid-persulfate digestion or the ultraviolet radiation.

## 2. Summary of method

2.1 Organic arsenic-containing compounds are decomposed either by sulfuric acid-potassium persulfate digestion or by ultraviolet radiation. The arsenic so liberated, together with inorganic arsenic originally present, is subsequently reduced to arsine with sodium borohydride. The arsine is stripped from the solution with the aid of nitrogen and is then decomposed in a tube furnace placed in the optical path of an atomic absorption spectrometer.

2.2 For additional information on the determination of arsenic in water, see Pierce and others (1976), and Fishman and Spencer (1977).

## 3. Interferences

3.1 Since the arsine is freed from the original sample matrix, interferences are minimized.

3.2 A detailed inorganic-interferences study showed that most trace elements at concentration levels of less than 300 µg/L do not interfere (Pierce and Brown, 1976).

## 4. Apparatus

4.1 *Atomic absorption spectrometer* and recorder.

4.2 Refer to manufacturer's manual to optimize instrument for the following:
    Grating ------------ Ultraviolet
    Wavelength -------- 193.7 nm
    Source (electrodeless-
      discharge lamp) --- Arsenic

4.3 *Autotransformer, variable*: Superior Powerstat type 3 PN 1010 or equivalent.

4.4 *Pyrometer*, portable, 0 °C to 1,200 °C. Thermolyne Model PM-20700 or equivalent.

4.5 *Stripping-condensing column*, Pyrex, packed with 3- to 5-mm Pyrex beads (fig. 12). Cooling of the condensing column is not required. 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.
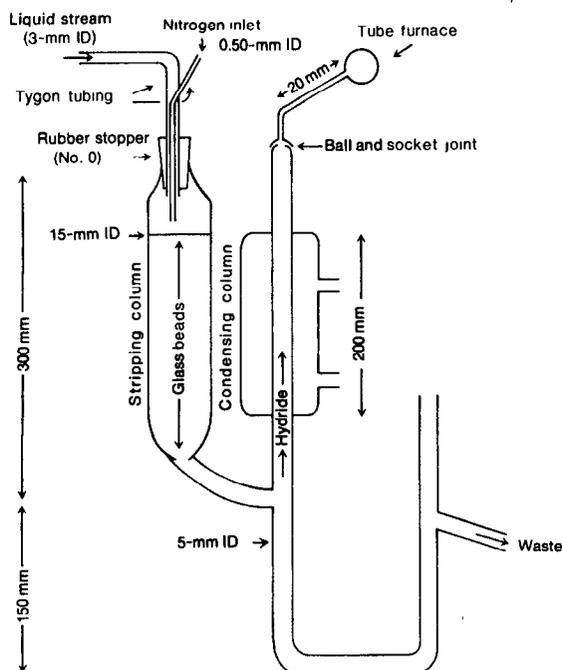
Figure 12.—Stripping-condensing column and quartz-tube furnace

4.6 *Tube furnace*, quartz, 10-mm ID×100-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 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 with stirrer, manifold, ultraviolet digestor (optional, NOTE 3), proportioning pump, and heating bath (optional, NOTE 4).

Heating-bath temperature --- 95°C.

NOTE 3.   The ultraviolet digestor can be used only when determining dissolved arsenic; it cannot be used when analyzing water-suspended sediment or bottom material.

NOTE 4.   The heating bath is used only in the acid-persulfate digestion procedure.

## 5. Reagents

5.1 *Arsenic standard solution I*, 1.00 mL= 1.00 mg As: Dissolve 1.320 g As$_2$O$_3$, dried for 1 h at 110°C, in 10 mL 10$M$ NaOH and dilute to 1,000 mL with demineralized water. This solution is stable. However, it should be prepared fresh every 6 months.

5.2 *Arsenic standard solution II*, 1.00 mL= 10.0 $\mu$g As: Dilute 5.00 mL arsenic standard solution I and 1 mL concentrated HNO$_3$ (sp gr 1.41) to 500.0 mL with demineralized water. Discard after 3 months.

5.3 *Arsenic standard solution III*, 1.00 mL= 0.10 $\mu$g As: Dilute 5.00 mL arsenic standard solution II and 1 mL concentrated HNO$_3$ to 500.0 mL with demineralized water. Prepare fresh weekly.

5.4 *Arsenic working standards*: Prepare daily a blank and 100 mL each of a series of arsenic working standards containing 0.15 mL concentrated HNO$_3$ by appropriate dilution of arsenic standard solution III.

| Arsenic standard solution III (mL) | Arsenic concentration ($\mu$g/L) |
|---|---|
| 1.0 | 1 |
| 2.0 | 2 |
| 5.0 | 5 |
| 10.0 | 10 |
| 15.0 | 15 |
| 20.0 | 20 |

5.5 *Hydrochloric acid, 6M*: Add 500 mL concentrated HCl (sp gr 1.19) to demineralized water and dilute to 1 L.

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

5.7 *Potassium persulfate solution*, 50 g/L: Dissolve 50 g K$_2$S$_2$O$_8$ in demineralized water with warming and dilute to 1 L after the solution has cooled.

5.8 *Sodium borohydride solution*, 5 g/L: Dissolve 5 g NaBH$_4$ and 40 g NaOH in demineralized water and dilute to 1 L.

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

5.10 *Sulfuric acid solution, 3M*: Cautiously, add, with constant stirring and cooling, 167 mL concentrated H$_2$SO$_4$ (sp gr 1.84) to demineralized water and dilute to 1 L.

## 6. Procedure

6.1   Set up manifold-acid persulfate (fig. 13) or ultraviolet radiation (fig. 14). See NOTE 2.

6.2   Apply a voltage of 47 volts or more (variable autotransformer) as necessary to the tube furnace to maintain a constant temperature of 800°C. Monitor the tube-furnace temperature

Heating bath 40-foot coil

95°C

22-turn coil

10-turn coil

0.056 in
1.20 mL/min    Air

0.110 in
3.90 mL/min    Sample

Cooling coil
114-0209-01

0.035 in
0.42 mL/min    Sulfuric acid

0.073 in
2.00 mL/min    Potassium persulfate

0.035 in
0.42 mL/min    Sodium hydroxide

0.035 in
0.42 mL/min    Potassium iodide

10-turn coil
0.110 in
3.90 mL/min    Sodium borohydride

20-turn coil
0.110 in
3.90 mL/min    Hydrochloric acid

20-turn coil

40-foot time delay coil

To separator

To sampler 4
wash receptacle

0.110 in
3.90 mL/min    Water

Sampler 4
30 / h
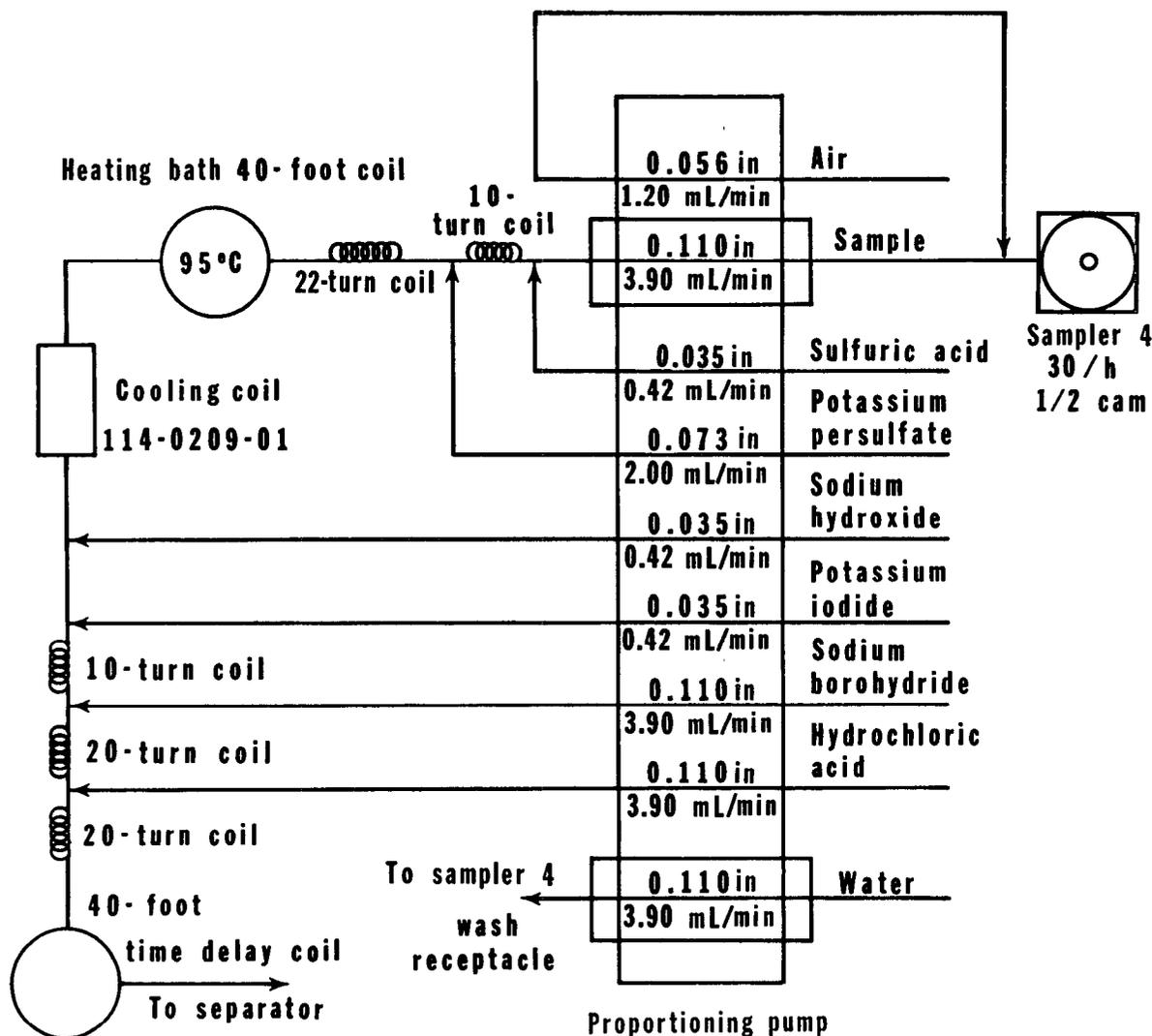1/2 cam

Proportioning pump

Figure 13.—Arsenic, acid-persulfate manifold

using portable pyrometer with the thermocouple placed in the middle of the tube.

6.3  If bottom-material samples are being analyzed, weigh 100 mg or less of bottom-material sample (2.0 μg As max), transfer to a 100-mL volumetric flask, and dilute to volume with demineralized water. Sample as directed for water and water-suspended sediment samples in paragraph 6.5 (NOTE 5).

NOTE 5.  Bottom material may be manually digested using method I-5062 (arsenic, atomic absorption spectrometric) if standards and blank are treated identically. Adjust pH of digested solutions to between 2 and 3 before proceeding to paragraph 6.5.

6.4  Feed all reagents through the system, using demineralized water in the sample line. Allow the heating bath to warm to 95°C.

6.5  Beginning with the most concentrated standard (NOTE 6), place a complete set of standards in the first positions of the first sample tray. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent trays. Fill remainder of each sample tray with unknown samples (well mixed).

NOTE 6.  It is best to place two or three samples of the most concentrated standard at the beginning, since the first peak is usually low.
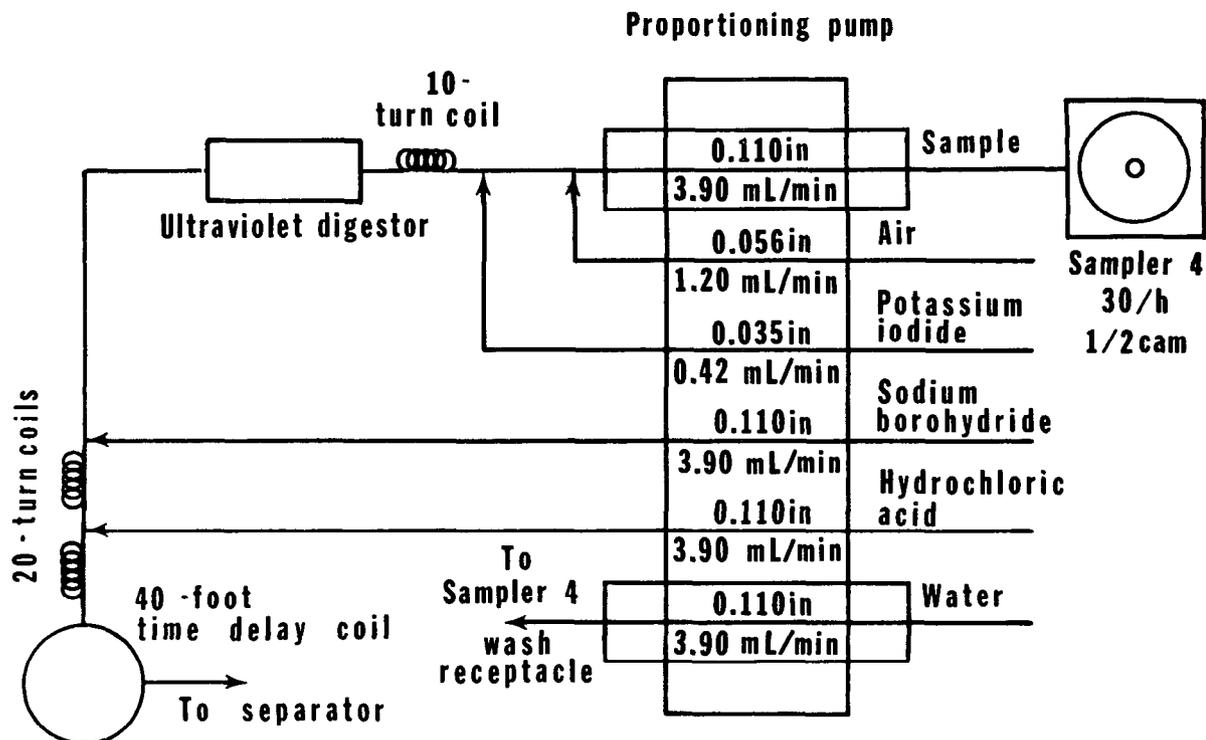
**Proportioning pump**



Figure 14.—Arsenic, ultraviolet radiation manifold

The first standard should not be used in any of the calculations.

6.6   Remove the sample line from the demineralized-water wash solution when the baseline stabilizes and begin the analyses (NOTE 7).
NOTE 7.   When the analyses are complete, the tubes in the manifold and the separator-condensor column should be cleaned if any sediment is present.

6.7   With 10 mV recorder, 20 $\mu g/L$ of arsenic will give a peak approximately 60 percent of full scale. If the sensitivity drops by 30 percent or more, replace or treat the cell by one of the following methods:

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

6.7.2   Grind the cell with silicon carbide as follows: Mount cell with suitable cushioning in a ¾-in. 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 arsenic concentration.

7.2   Determine the concentration of dissolved or total arsenic 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 arsenic, subtract dissolved-arsenic concentration from total-arsenic concentration.

7.4   To determine the concentration of arsenic in bottom-material samples, first determine the micrograms per liter of arsenic in each sample as in paragraph 7.2, then

$$\text{As } (\mu g/g) = \frac{\mu g/L \text{ As} \times 0.1}{\text{wt of sample (g)}}$$

## 8. Report

8.1   Report arsenic, dissolved (01000), total (01002), and suspended-total (01001), concentrations as follows: less than 10 $\mu$g/L, nearest microgram per liter; 10 $\mu$g/L and above, two significant figures.

8.2   Report arsenic, total-in-bottom-material (01003), concentrations as follows: less than 10 $\mu$g/g, nearest microgram per gram; 10 $\mu$g/g and above, two significant figures.

## 9. Precision

9.1   Acid-persulfate digestion: Precision, for dissolved arsenic for replicate analysis by one operator expressed in terms of percent relative standard deviation, is as follows:

| Mean ($\mu$g/L) | Relative standard deviation (percent) |
|---|---|
| 5.8 | 5 |
| 10.4 | 5 |
| 15.5 | 5 |

9.2   Ultraviolet radiation: Precision for dissolved arsenic for replicate analysis by one operator expressed in terms of percent relative standard deviation is as follows:

| Mean ($\mu$g/L) | Relative standard deviation (percent) |
|---|---|
| 5.0 | 10 |
| 10.4 | 10 |
| 13.8 | 4 |

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

## References

Fishman, M. J., Spencer, R. R., 1977, Automated atomic absorption spectrometric determination of total arsenic in water and streambed materials: Analytical Chemistry, v. 49, p. 1599–1602.

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.

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. 693–695.

# Arsenic, colorimetric, silver diethyldithiocarbamate

## Parameters and Codes:

Arsenic, dissolved, I-1060-85 ($\mu$g/L as As): 01000
Arsenic, total, I-3060-85 ($\mu$g/L as As): 01002
Arsenic, suspended total, I-7060-85 ($\mu$g/L as As): 01001
Arsenic, total-in-bottom-material, dry wt, I-5060-85 ($\mu$g/g as As): 01003

## 1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing from 5 to 200 $\mu$g/L of arsenic. Samples containing more than 200 $\mu$g/L need to be diluted.

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

1.3 This method may be used to analyze bottom material containing from 5 to 200 $\mu$g/g of arsenic. Usually, a 100-mg sample of prepared bottom material (method P-0520) is taken for analysis. If the sample contains more than 200 $\mu$g/g of arsenic, a smaller sample needs to be used.

1.4 Total arsenic 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.

1.5 Both inorganic and organic forms of arsenic are determined. To determine only inorganic arsenic, omit the strong-acid digestion, paragraphs 6.4 and 6.5 of the procedure.

## 2. Summary of method

2.1 Organic compounds are decomposed by adding sulfuric and nitric acids, and by repeatedly evaporating the samples to fumes of sulfur trioxide. The arsenic (V) so liberated, together with inorganic arsenic originally present, is subsequently reduced to arsenic (III) by potassium iodide and stannous chloride, and finally to gaseous arsine by zinc in hydrochloric acid solution. The resultant mixture of gases is passed through a scrubber consisting of borosilicate glass wool impregnated with lead acetate solution, and into a gas absorber containing silver diethyldithiocarbamate (AgDDC) dissolved in pyridine. Arsine reacts with AgDDC to form a soluble red complex having maximum absorbance at about 535 nm. The absorbance of the solution is measured spectrophotometrically, and arsenic determined by reference to an analytical curve prepared from standards.

2.2 Additional information on the determination is given by Liederman and others (1959); by Ballinger and others (1962); by Stratton and Whitehead (1962); and by Fresenius and Schneider (1964).

## 3. Interferences

3.1 Some samples may contain sulfides; however, small quantities are effectively removed by a lead acetate scrubber. Several metals—cobalt, nickel, mercury, silver, platinum, copper, chromium, and molybdenum—interfere with the evolution of arsine. Antimony salts, under the reducing conditions in the generator, form stibine, which passes into the absorber and causes high results.

3.2 The blank and standards fade slowly on standing, but not enough to influence results significantly during the first 20 min.

## 4. Apparatus

4.1 *Arsine generator, scrubber, and absorber* (fig. 15).

4.2 *Spectrophotometer*, for use at 535 nm.

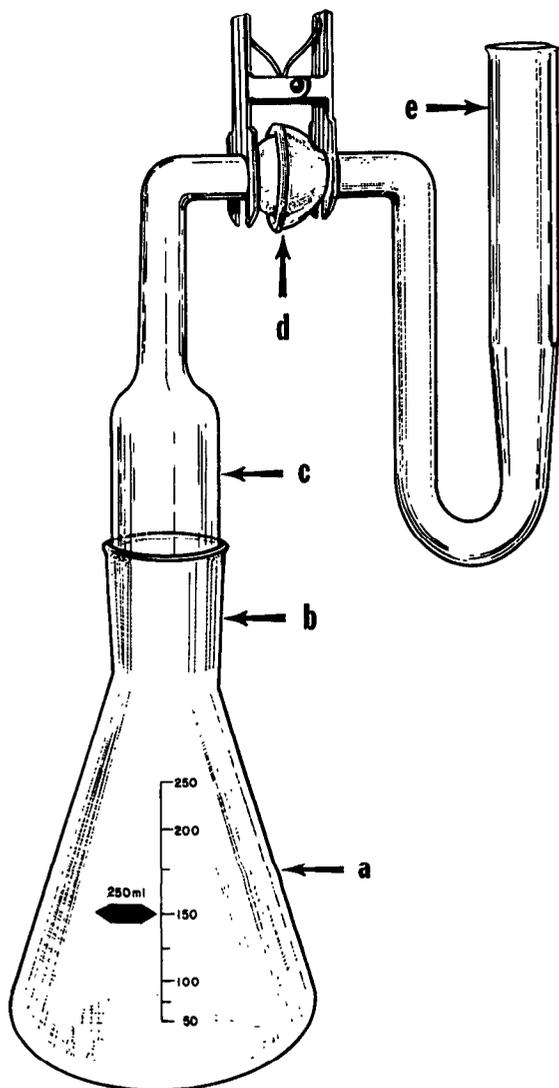4.3 Refer to the manufacturer's manual to optimize instrument.

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Figure 15.—Arsine generator, scrubber, and absorber

## 5. Reagents

5.1  *Arsenic standard solution I*, 1.00 mL= 1.00 mg As: Dissolve 1.320 g $As_2O_3$, dried for 1 h at 110°C, in 10 mL 10$M$ NaOH and dilute to 1,000 mL with demineralized water. This solution is stable. However, it should be prepared fresh every 6 months.

5.2  *Arsenic standard solution II*, 1.00 mL= 10.0 $\mu$g As: Dilute 5.00 mL arsenic standard solution I and 1 mL concentrated $HNO_3$ (sp gr 1.41) to 500.0 mL with demineralized water. Discard after 3 months.

5.3  *Arsenic standard solution III*, 1.00 mL= 1.00 $\mu$g As: Dilute 10.0 mL arsenic standard

solution II and 1 mL concentrated $HNO_3$ (sp gr 1.41) to 100.0 mL with demineralized water. Prepare fresh weekly.

5.4  *Hydrochloric acid*, concentrated (sp gr 1.19): Use analytical-grade acid with arsenic content not greater than $1 \times 10^{-6}$ percent.

5.5  *Lead acetate solution*, 8.6 g/100 mL: Dissolve 10 g $(CH_3COO)_2Pb \cdot 3H_2O$ in 100 mL demineralized water. Keep tightly stoppered.

5.6  *Nitric acid*, concentrated (sp gr 1.41): Use analytical-grade acid with arsenic content not greater than $5 \times 10^{-7}$ percent.

5.7  *Potassium iodide solution*, 15 g/100 mL: Dissolve 15 g KI in 100 mL demineralized water. This solution is stable when stored in an amber bottle.

5.8  *Silver diethyldithiocarbamate (AgDDC) solution*, 0.5 g/100 mL: Dissolve 1 g $(C_2H_5)_2$ NCSSAg in 200 mL pyridine. This solution is stable when stored in an amber bottle.

5.9  *Stannous chloride solution*, 33.6 g/100 mL concentrated HCl: Dissolve 40 g arsenic-free $SnCl_2 \cdot 2H_2O$ in 100 mL concentrated HCl. This solution is unstable. Prepare fresh daily.

5.10 *Sulfuric acid, 9M: Cautiously*, and with constant stirring and cooling, add 250 mL concentrated $H_2SO_4$ (sp gr 1.84) to 250 mL demineralized water.

5.11 *Zinc*: Granular zinc, about 20 mesh, with arsenic content not greater than $1 \times 10^{-6}$ percent.

## 6. Procedure

6.1  Clean all glassware used in this determination with warm, dilute $HNO_3$ (1+4) and rinse with demineralized water immediately before each use. The absorbers must also be rinsed with acetone and air-dried or briefly oven-dried.

6.2  Follow instructions in paragraph 6.2.1 for water or water-suspended sediment and in paragraph 6.2.2 for bottom material.

6.2.1  Pipet a volume of well-mixed sample containing less than 20 $\mu$g As (100 mL max) into the flask of an arsine generator. Rinse the pipet with demineralized water to remove adhering particles and combine with the sample. Dilute the sample to approx 100 mL if less than 100 mL is used.

6.2.2  Weigh a portion (NOTE 1) of prepared bottom-material sample (method P-0520)

containing less than 20 $\mu$g As and transfer to the flask of an arsine generator. Add approx 100 mL demineralized water.

NOTE 1. The sample weight must not exceed 100 mg; otherwise severe bumping and loss of arsenic may occur.

6.3 Prepare a blank and sufficient standards (20 $\mu$g As max), and adjust the volume of each to approx 100 mL with demineralized water.

6.4 To each flask, add 7 mL $9M$ $H_2SO_4$ and 5 mL concentrated $HNO_3$. Add a small boiling chip and carefully evaporate to fumes of $SO_3$. Cool, add 25 mL demineralized water, and again evaporate to fumes of $SO_3$ to expel oxides of nitrogen. Maintain excess of $HNO_3$ until all organic matter is destroyed. This prevents darkening of the solution and possible reduction and loss of arsenic.

6.5 Cool, and adjust the volume to approx 100 mL. (NOTE 2).

NOTE 2. If only inorganic arsenic is to be determined, omit steps 6.4 and 6.5.

6.6 To each flask add successively, with thorough mixing after each addition, 10 mL concentrated HCl, 4 mL KI solution, and 1 mL $SnCl_2$ solution. Allow about 15 min for reduction of the arsenic to the tervalent state.

6.7 Place in each scrubber a plug of borosilicate glass wool that has been impregnated with lead acetate solution. Assemble the generator, scrubber, and absorber, making certain that all parts fit and are correctly adjusted. Add 3.00 mL silver diethyldithiocarbamate-pyridine solution to each absorber. Add glass beads to the absorbers until the liquid just covers them.

6.8 Disconnect each generator, add 6 g granular zinc, and reconnect immediately.

6.9 Allow 30 min for complete evolution of the arsine. Warm the generator flasks for a few minutes to make sure that all the arsine is released, and then pour the solutions from the absorbers directly into the spectrophotometer's cells. Determine the absorbances of the standards and samples against the blank without unnecessary delay, as the color developed is not permanent.

## 7. Calculations

7.1 Determine the micrograms arsenic in the sample from a plot of absorbances of standards.

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

$$\text{As } (\mu g/L) = \frac{1000}{\text{mL sample}} \times \mu g \text{ As in sample}$$

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

7.4 Determine the concentration of arsenic in bottom-material samples as follows:

$$\text{As } (\mu g/g) = \frac{\mu g \text{ As per sample}}{\text{wt of sample (g)}}$$

## 8. Report

8.1 Report arsenic, dissolved (01000), total (01002), and suspended-total (01001), concentrations as follows: less than 10 $\mu$g/L, nearest microgram per liter; 10 $\mu$g/L and above, two significant figures.

8.2 Report arsenic, total-in-bottom-material (01003), concentrations as follows: less than 100 $\mu$g/g, to the nearest 10 $\mu$g/g; 100 $\mu$g/g and above, two significant figures.

## 9. Precision

9.1 Precision for dissolved arsenic for 22 samples within the range of 2.7 to 109 $\mu$g/L may be expressed as follows:

$$S_T = 0.225X + 2.426$$

where

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

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

The correlation coefficient is 0.9430.

9.2 Precision for dissolved arsenic for five of the 22 samples expressed in terms of the percent relative standard deviation is as follows:

| Number of laboratories | Mean ($\mu$g/L) | Relative standard deviation (percent) |
|---|---|---|
| 3 | 2.7 | 85 |
| 12 | 9.8 | 42 |
| 7 | 21.0 | 26 |
| 10 | 40.0 | 40 |
| 16 | 109 | 24 |

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

## References

Ballinger, D. G., Lishka, R. J., and Gales, M. E., 1962, Application of the silver diethyldithiocarbamate method to the determination of arsenic: American Water Works Association Journal, v. 54, p. 1424–1428.

Fresenius, W., and Schneider, W., 1964, Determination of slight amounts of arsenic with silver diethyldithiocarbamate in water analysis: Journal of Analytical Chemistry, v. 203, p. 417–422.

Liederman, D., Bowen, J. E., and Milner, O. I., 1959, Determination of arsenic in petroleum stocks and catalysts by evolution of arsine: Analytical Chemistry, v. 31, p. 2052–5.

Stratton, G., and Whitehead, H. E., 1962, Colorimetric determination of arsenic in water with silver diethyldithiocarbamate: American Water Works Association Journal, v. 54, p. 861–4.

# Arsenic, total-in-sediment, atomic absorption spectrometric, hydride

## 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. Arsenic is determined on the resulting solution by atomic absorption spectrometry. See method I–5475, metals, minor, total-in-sediment, atomic absorption spectrometric, hydride.

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# Barium, atomic absorption spectrometric, direct

## Parameters and Codes:

Barium, dissolved, I-1084-85 ($\mu$g/L as Ba): 01005 Barium, total recoverable, I-3084-85 ($\mu$g/L as Ba): 01007
Barium, suspended recoverable, I-7084-85 ($\mu$g/L as Ba): 01006
Barium, recoverable-from-bottom-material, dry wt, I-5084-85 ($\mu$g/g as Ba): 01008

## 1. Application

1.1   This method may be used to analyze water and water-suspended sediment containing at least 100 $\mu$g/L of barium. Sample solutions containing more than 5000 $\mu$g/L need to be diluted.

1.2   Suspended recoverable barium is calculated by subtracting dissolved barium from total-recoverable barium.

1.3   This method may be used to analyze bottom material containing at least 5 $\mu$g/g of barium.

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

## 2. Summary of method

Barium is determined by atomic absorption spectrometry. Sodium chloride is added to control ionization of barium in the flame.

## 3. Interferences

The use of a nitrous oxide-acetylene flame virtually eliminates chemical interferences in the determination of barium. However, barium is easily ionized in the nitrous oxide-acetylene flame; to control this effect, sodium chloride solution must be added to each sample and standard.

## 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 -------- 553.6 nm
Source (hollow-cathode
 lamp) ------------ Barium
Burner ------------ Nitrous oxide
Oxidant ------------ Nitrous oxide
Fuel ---------------- Acetylene
Type of flame ------- Fuel-rich

## 5. Reagents

5.1   *Barium standard solution*, 1.00 mL = 100 $\mu$g Ba: Dissolve 0.1516 g $BaCl_2 \cdot 2H_2O$, dried at 180 °C for 1 h, in demineralized water and dilute to 1,000 mL.

5.2   *Barium working standards*: Prepare a series of at least six working standards containing from 100 to 5,000 $\mu$g/L of barium by appropriate dilution of barium standard solution. Add 1.00 mL NaCl solution for each 10 mL of working standard. Similarly prepare a demineralized water blank. Prepare fresh daily.

5.3   *Sodium chloride solution*, 25.4 g/L: Dissolve 25.4 g NaCl in demineralized water and dilute to 1 L.

## 6. Procedure

6.1   Add 1.0 mL NaCl solution to 10.0 mL sample solution and mix thoroughly.

6.2   Aspirate the blank to set the automatic zero control. Use the automatic concentration control to set 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

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

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

7.3   To determine micrograms per gram of barium in bottom-material samples, first determine the micrograms per liter of barium in each sample as in paragraph 7.1, then:

$$Ba\ (\mu g/g) = \frac{\mu g/L\ Ba \times \dfrac{mL\ of\ original\ digest}{1,000}}{wt\ of\ sample\ (g)}$$

## 8. Report

8.1   Report barium, dissolved (01005), total-recoverable (01007), and suspended-recoverable (01006), concentrations as follows: less than 1,000 $\mu g/L$, nearest 100 $\mu g/L$; 1,000 $\mu g/L$ and above, two significant figures.

8.2   Report barium, recoverable-from-bottom-material (01008), concentration as follows: less than 100 $\mu g/g$, nearest 10 $\mu g/g$; 100 $\mu g/g$ and above, two significant figures.

## 9. Precision

9.1   The standard deviation for dissolved barium within the range of 43 to 800 $\mu g/L$ for 17 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 93.5 $\mu g/L$ ranged from 85.3 to 103.2 $\mu g/L$.

9.2   Precision for dissolved barium for five of the 17 samples expressed in terms of the percent relative standard deviation is as follows:

| Number of laboratories | Mean (µg/L) | Relative standard deviation (percent) |
|---|---|---|
| 13 | 43 | 70 |
| 17 | 112 | 53 |
| 18 | 294 | 32 |
| 9 | 756 | 7 |
| 6 | 800 | 0 |

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

9.4   Precision expressed in terms of percent relative standard deviation for total recoverable barium for two water-suspended sediments is as follows:

| Number of laboratories | Mean (µg/L) | Relative standard deviation (percent) |
|---|---|---|
| 12 | 91.7 | 86 |
| 10 | 172 | 40 |

# Barium, atomic emission spectrometric, ICP

**Parameter and Code:**
Barium, dissolved, I-1472-85 (µg/L as Ba): 01005

## 2. Summary of method

Barium 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.

# Beryllium, atomic absorption spectrometric, direct

## Parameters and Codes:
Beryllium, dissolved, I–1095–85 ($\mu$g/L as Be): 01010
Beryllium, total recoverable, I–3095–85 ($\mu$g/L as Be): 01012
Beryllium, suspended recoverable, I–7095–85 ($\mu$g/L as Be): 01011
Beryllium, recoverable-from-bottom-material, dry wt, I–5095–85 ($\mu$g/g as Be): 01013

## 1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 10 $\mu$g/L of beryllium. Sample solutions containing more than 200 $\mu$g/L need to be diluted.

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

1.3 This method may be used to analyze bottom material containing at least 0.5 $\mu$g/g of beryllium.

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

## 2. Summary of method

Beryllium is determined by atomic absorption spectrometry. Calcium chloride is added to control ionization of beryllium in the flame.

## 3. Interferences

3.1 Beryllium is slightly ionized in the nitrous oxide-acetylene flame; to control this effect, calcium chloride solution must be added to each standard and sample.

3.2 Bicarbonate ion interferes; however, this interference is of no consequence if samples preserved by the addition of acid are used for the analysis.

3.3 Aluminum at concentrations greater than 500 $\mu$g/L has been reported to depress the beryllium absorbance.

3.4 Sodium and silicon at concentrations in excess of 1000 mg/L have been reported to severely depress the beryllium absorbance (Environmental Protection Agency, 1979).

## 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 --------- 234.9 nm
Source (hollow-cathode
    lamp) ------------ Beryllium
Burner ------------ Nitrous oxide
Oxidant ------------ Nitrous oxide
Fuel ---------------- Acetylene
Type of flame ------- Fuel-rich

## 5. Reagents

CAUTION: Beryllium compounds and samples with high concentrations of beryllium should be handled with care; they may be carcinogenic.

5.1 *Beryllium standard solution I*, 1.00 mL= 100 $\mu$g Be: Dissolve 0.1000 g Be flakes in a minimum of aqua regia. Heat to increase rate of dissolution. Add 10.0 mL of concentrated $HNO_3$ (sp gr 1.41) and dilute to 1000 mL with demineralized water.

5.2 *Beryllium standard solution II*, 1.00 mL=10.0 $\mu$g Be: Dilute 100.0 mL beryllium standard solution I to 1,000 mL with demineralized water.

5.3 *Beryllium working standards*: Prepare a series of at least six working standards

containing from 10 to 200 $\mu$g/L beryllium by appropriate dilution of beryllium standard solution II. Add 1.0 mL CaCl$_2$ solution for each 10.0 mL of working standard. Similarly prepare a demineralized water blank. Prepare fresh daily.

5.4 *Calcium chloride solution*, 27.8 g/L: Suspend 25 g CaCO$_3$ in demineralized water and dissolve with a minimun of dilute HCl. Dilute to 1 L with demineralized water.

## 6. Procedure

6.1 Add 1.0 mL CaCl$_2$ solution to 10.0 mL sample solution and mix thoroughly.

6.2 Aspirate the blank to set the automatic zero control. Use the automatic concentration control to set 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

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

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

7.3 To determine micrograms per gram of beryllium in bottom-material samples, first determine the micrograms per liter of beryllium in each sample as in paragraph 7.1, then:

$$\text{Be }(\mu g/g) = \frac{\mu g/L \text{ Be} \times \dfrac{\text{mL of original digest}}{1,000}}{\text{wt of sample (g)}}$$

## 8. Report

8.1 Report beryllium, dissolved (01010), total-recoverable (01012), and suspended-recoverable (01011), concentrations as follows: less than 1,000 $\mu$g/L to the nearest 10 $\mu$g/L.

8.2 Report beryllium, recoverable-from-bottom-material (01013), as follows: less than 10 $\mu$g/g, nearest microgram per gram; 10 $\mu$g/g and above, two significant figures.

## 9. Precision

9.1 The standard deviation for dissolved beryllium within the range of 5.4 to 70 $\mu$g/L for 17 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 4.11 $\mu$g/L ranged from 3.6 to 4.9 $\mu$g/L.

9.2 Precision for dissolved beryllium for four of the 17 samples expressed in terms of the percent relative standard deviation is as follows:

| Number of laboratories | Mean ($\mu$g/L) | Relative standard deviation (percent) |
|---|---|---|
| 8 | 5.4 | 54 |
| 8 | 20.8 | 19 |
| 11 | 47.7 | 9 |
| 3 | 70.0 | 0 |

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

9.4 Precision for total recoverable beryllium expressed in terms of percent relative standard deviation for two water-suspended sediments is as follows:

| Number of laboratories | Mean ($\mu$g/L) | Relative standard deviation (percent) |
|---|---|---|
| 4 | 22.5 | 27 |
| 5 | 64.2 | 7 |

## Reference

U.S. Environmental Protection Agency, 1979, Methods for chemical analysis of water and wastes, Cincinnati, p. 210.1-1.

# Beryllium, atomic emission spectrometric, ICP

## Parameter and Code:
Beryllium, dissolved, I-1472-85 (µg/L as Be): 01010

### 2. Summary of method

Beryllium 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.

# Boron, atomic emission spectrometric, d-c plasma

Parameter and Code:
Boron, dissolved, I-1114-85 (µg/L as B): 01020

## 1. Application

This method may be used to analyze finished water, natural water, and industrial water containing from 10 to 1000 µg/L of boron. Samples containing more than 1000 µg/L boron and/or with specific conductances greater than 10,000 µS/cm need to be diluted.

## 2. Summary of method

Boron is determined by a direct-reading emission spectrometer that utilizes a d-c argon plasma as an excitation source (Johnson and others, 1979a, b, 1980). A mixture of lithium chloride, sulfuric acid, and glycerin is added to samples and standards to provide a common background matrix and to compensate for viscosity changes. The liquid mixture is then converted by a ceramic nebulizer into a fine aerosol and introduced into the plasma via a plastic spray chamber and Pyrex injection tube. Boron is determined on the basis of the average of two replicate exposures, each of which is performed on a 10 second integrated intensity. Calibration is performed by standardization with a high- standard solution and a blank.

## 3. Interferences

Stray-light effects in a high-resolution, single-element, d-c argon plasma emission spectrometer are found to be negligible.

## 4. Apparatus

4.1 *Spectrometer*, Spectrometrics, Spectrospan IV with d-c argon plasma or equivalent, with Echelle optics, printer, autosampler, and peristaltic pump.

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

| | |
|---|---|
| Plasma viewing position | -1 (fig. 16) |
| Gas | Argon |
| Sleeve pressure | 50 psi |
| Nebulizer pressure | 25 psi |
| Entrance slit | 25×300 µm |
| Exit slit | 50×300 µm |
| Voltage | 1000 V |
| Wavelength | 249.773 nm |
| Signal amplification | 40- to 60-percent full-scale (1000 µg/L) |

## 5. Reagents

5.1 *Boron standard solution I*, 1.00 mL=100 µg B: Dissolve 0.5720 g high-purity $H_3BO_3$, dried over desiccant for 24 h, in demineralized water and dilute to 1000 mL. Store in plastic bottle.

5.2 *Boron standard solution II*, 1.00 mL=10.0 µg B: Dilute 100.0 mL boron standard solution I to 1000 mL with demineralized water. Store in plastic bottle.

5.3 *Boron working standard*, 1.00 mL=1.00 µg B: Dilute 100.0 mL boron standard solution II to 1000 mL with demineralized water. Store in plastic bottle.

5.4 *Glycerin*, USP.

5.5 *Lithium chloride*, LiCl, reagent-grade.

5.6 *Matrix modifier*: Dissolve 367 g LiCl in 1000 mL demineralized water. Transfer to a Teflon beaker and add, with stirring, 10.0 mL concentrated $H_2SO_4$. Heat the solution to 75 to 80 °C on a hotplate (asbestos padded) and slowly add 25 mL methyl alcohol. Stir rapidly for one hour to volatilize of excess methyl alcohol and any trimethyl borate that forms. Repeat the
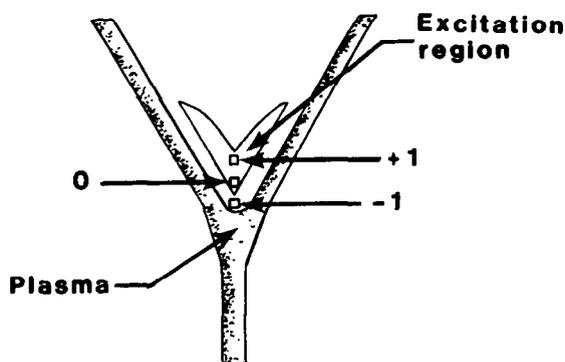
Figure 16.—Plasma position on entrance slit for ooron

process two more times. Allow the solution to cool, transfer to a 4-L polyethylene container, and add with stirring 2000 mL glycerin. In a Teflon beaker slowly add, with stirring, 400 mL concentrated $H_2SO_4$ to 400 mL demineralized water. With stirring and cooling, add 50 mL methyl alcohol. The heat generated should be sufficient to volatilize excess methyl alcohol and any trimethyl borate. When the acid has reached room temperature, add the acid slowly, with stirring (in a hood), to the glycerin-LiCl mixture. Dilute to 4,000 mL with demineralized water.

5.7  *Methyl alcohol,* reagent-grade.

5.8  *Sulfuric acid,* concentrated (sp gr 1.84), Ultrex or equivalent.

## 6.  Procedure

6.1  Pipet 10.0 mL sample into a disposable plastic test tube.

6.2  Pipet 100 mL demineralized-water blank and working standard into plastic bottles.

6.3  Add 2.0 mL matrix modifier to the sample and 20.0 mL to the blank and working standard.

6.4  Place plastic caps on the tube and bottles and mix well.

6.5  Refer to manufacturer's manual for computer-operating procedure. Use the prepared blank and working standard for instrument calibration and all subsequent recalibrations.

6.6  Refer to manufacturer's manual for auto-sampler-operating procedures. Pour samples in autosampler tray, positioning a blank and working standard after every five samples for recalibration. Begin analysis (NOTE 1).

NOTE 1. Because of thermal instability inherent with the high-resolution spectrometer, repeak the analytical line if the boron standard drifts more than 3 percent.

## 7.  Calculations

The computer system is designed so that the blank and the 1000 $\mu$g/L of boron working standard are used to establish a two-point calibration curve. The system will convert instrument-intensity readings to analytical concentrations. The printer display includes the blank and working-standard instrument intensity readings, blank and standard concentrations, sample instrument intensity readings, sample concentrations, average of sample concentrations, and standard deviation.

## 8.  Report

Report boron, dissolved (01020), concentrations as follows: less than 100 $\mu$g/L, nearest 10 $\mu$g/L; 100 $\mu$g/L and above, two significant figures.

## 9.  Precision

Precision based on 12 determinations by a single operator expressed in terms of standard deviation and percent relative standard deviation is as follows:

| Mean ($\mu$g/L) | Standard deviation ($\mu$g/L) | Relative standard deviation (percent) |
|---|---|---|
| 30.8 | 1.8 | 5.8 |
| 40.8 | 1.8 | 4.4 |
| 215 | 5.0 | 2.3 |
| 425 | 1.3 | 0.3 |

## References

Johnson, G. W., Taylor, H. E., and Skogerboe, R. K., 1979a, Determination of trace elements in natural waters by the D.C. Argon-plasma, multielement atomic emission spectrometer (DCP-MAES) technique: Spectrochimica Acta, v. 34B, p. 197–212.

_____1979b, Evaluation of spectral interferences associated with a direct current plasma-multielement atomic emission spectrometer (DCP-MAES) system: Applied Spectroscopy, v. 33, p. 451–456.

_____1980, Characterization of an interelement enhancement effect in a dc plasma atomic emission spectrometry system: Applied Spectroscopy, v. 34, p. 19–24.

# Boron, colorimetric, azomethine H, automated-segmented flow

Parameter and Code:
Boron, dissolved I-2115-85 ($\mu$g/L as B): 01020

## 1. Application

This method may be used to determine concentrations of boron in unacidified water in the range of 10 to 400 $\mu$g/L. Sample solutions containing more than 400 $\mu$g/L boron need to be diluted.

## 2. Summary of method

The condensation product of H-acid (8-amino-1-napthol-3,6-disulphonic acid) and salicylaldehyde is azomethine H, which forms a yellow complex with boron. The absorbance of this complex is measured colorimetrically at 410 nm (Basson and others, 1969; Basson and others, 1974; Spencer and Erdmann, 1979). Interferences from iron and zinc are minimized by addition of diethylenetriamine pentaacetic acid (DTPA). Interferences from bicarbonate are eliminated by careful acidification to pH 3 to 5.

## 3. Interferences

Iron, zinc, and bicarbonate interfere at concentrations above 400 $\mu$g/L, 2000 $\mu$g/L, and 150 mg/L, respectively in the absence of pretreatment with DTPA and acidification.

## 4. Apparatus

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

4.2 With this equipment the following operating conditions have been found satisfactory for the range 10 to 400 $\mu$g/L:

Absorption cell ----- 50 mm
Wavelength -------- 410 nm
Cam --------------- 30/h(2/1)

## 5. Reagents

5.1 *Ammonium acetate buffer:* Dissolve 300 g $NH_4C_2H_3O_2$ in 1,000 mL of demineralized water. Adjust the pH to 6.35 with $6N$ sulfuric acid and filter.

5.2 *Azomethine H synthesis:* Dissolve 18 g H-acid (8-amino-1-naphthol-3,6-disulphonic acid) in 1,000 mL of demineralized water with gentle heating. Filter, with suction, through Whatman No. 40 filter paper. Neutralize the solution to pH 7 with $2M$ KOH. While stirring continuously, add concentrated HCl (sp gr 1.19) until the pH is about 1.5. To the resulting mixture, add 20 mL salicylaldehyde and stir vigorously overnight (12 h). Centrifuge (2,000 rpm, 20 min) to separate the azomethine H (orange product) and wash 2 to 3 times with ethanol. Dry to constant weight at 100° C for 3 h and store in a desiccator.

5.3 *Azomethine H reagent:* Dissolve 4.5 g azomethine H and 10 g ascorbic acid (analytical grade) in 500 mL of demineralized water with gentle heating. Filter, with suction, through Whatman No. 40 filter paper. Store in a dark plastic bottle. Hydrolysis of this compound, and, consequently, of baseline drift, is minimized by placing this reagent bottle in a beaker containing a mixture of ice and water during analysis. This reagent should be prepared daily for optimal results.

5.4 *Boron standard solution I*, 1.00 mL= 0.100 mg B: Dissolve 0.5720 g high-purity $H_3BO_3$, dried over desiccant for 24 h, in demineralized water and dilute to 1000 mL. Store in plastic bottle.

5.5 *Boron standard solution II*, 1.00 mL= 0.010 mg B: Dilute 100.0 mL boron standard solution I to 1,000 mL with demineralized water. Store in plastic bottle.

5.6 *Boron standard solution III*, 1.00 mL= 0.001 mg B: Dilute 100.0 mL boron standard

solution II to 1,000 mL with demineralized water. Store in plastic bottle.

5.7 *Boron working standards*: Prepare a blank and 500 mL each of a series of boron working standards by appropriate quantitative dilution of the boron standard solutions (II and III) as follows:

| Boron standard solutions (mL) | Boron concentration (μg/L) |
|---|---|
| 0.0 | 0.0 |
| 5.0 of III | 10.0 |
| 15.0 of III | 30.0 |
| 25.0 of III | 50.0 |
| 50.0 of III | 100.0 |
| 100.0 of III | 200.0 |
| 15.0 of II | 300.0 |
| 20.0 of II | 400.0 |

5.8 *Brij-35 solution*, 30-percent aqueous solution (Baker Cat. No. C706 or equivalent).

5.9 *DTPA reagent*, 0.05M: Suspend 19.7 g DTPA in approx 900 mL demineralized water. Add 5M NaOH until pH is 5 to 6, and continue stirring until all the DTPA dissolves. Add 6 mL 30-percent Brij-35 solution; dilute to 1 liter and filter.

## 6. Procedure

6.1 Set up manifold (fig. 17).

6.2 Initially feed reagents with demineralized water in the sample line through the system and allow approx 30 min for stabilization of the baseline and instrument warmup. Adjust baseline to read 5 chart divisions on the recorder (25 μg/L on printer). It is necessary to include the reference channel in the manifold to compensate for baseline drift due to hydrolysis of the azomethine H.

6.3 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 every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with samples. Use plastic sample cups to avoid possible boron contamination from glass containers.

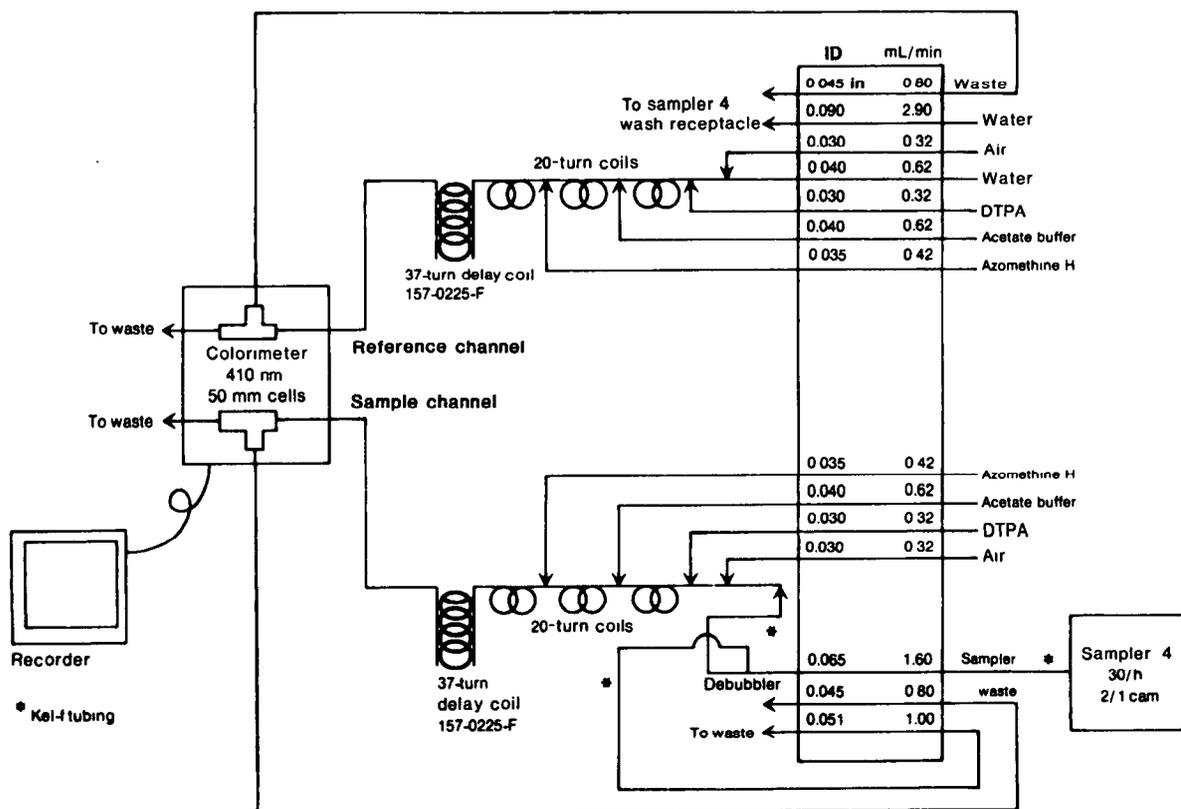6.4 Begin analysis. When the peak from the highest standard appears on the recorder,



Figure 17.—Boron, azomethine H manifold

adjust the STD CAL control until the printer reads 425 $\mu$g/L on the 0- to 500-$\mu$g/L range.

## 7. Calculations

7.1 Obtain concentration of sample directly from the printer and correct for the baseline reading.

7.2 Alternatively, prepare an analytical curve by plotting the height of each standard peak, minus the baseline drift, versus the respective boron concentration. Obtain the boron concentration of each sample by comparing its corrected reading to the analytical curve.

## 8. Report

8.1 Report boron, dissolved (01020), concentrations as follows: less than 100 $\mu$g/L, nearest 10 $\mu$g/L; 100 $\mu$g/L and above, two significant figures.

## 9. Precision

9.1 Analysis of 12 replicates of two test samples by a single laboratory resulted in mean values of 16 and 329 $\mu$g/L and standard deviations of 3 and 5 $\mu$g/L respectively.

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

| Number of replicates | Mean ($\mu$g/L) | Relative standard deviation (percent) |
|---|---|---|
| 12 | 16 | 19 |
| 12 | 329 | 2 |

## References

Basson, W. D., Bohmer, R. G., and Stanton, D. A., 1969, Automated procedure for the determination of boron in plant tissue: Analyst, v. 94, p. 1135-1141.

Basson, W. D., Pille, P. P., and DuPreez, A. L., 1974, Automated in situ preparation of azomethine H and the subsequent determination of boron in aqueous solution: Analyst, v. 99, p. 168-170.

Spencer, R. R., and Erdmann, D. E., 1979, Azomethine H colorimetric method for determining dissolved boron in water: Environmental Science and Technology, v. 13, p. 954-56.

# Boron, colorimetric, curcumin

## 1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 100 $\mu$g/L of boron. The optimum range for the method on undiluted or unconcentrated samples is from 100 to 1,000 $\mu$g/L.

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

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

## 2. Summary of method

2.1 When a sample of water containing boron is acidified and evaporated in the presence of curcumin, a red-colored product, called rosocyanine, is formed. The rosocyanine is extracted into a suitable solvent and the red color, which has a maximum absorbance at 540 nm, is measured spectrometrically.

2.2 The method is identical to that found in "Standard Methods for the Examination of Water and Wastewater" (American Public Health Association and others, 1980).

## 3. Interferences

3.1 Nitrate-nitrogen concentrations greater than 20 mg/L interfere.

3.2 Significantly high results are possible when the total of calcium and magnesium hardness exceeds 100 mg/L as calcium carbonate. Moderate hardness levels also can cause a considerable percentage error in the low boron range. The interference arises from the insolubility of the hardness salts in 95-percent ethanol and consequent turbidity in the final solution.

Filter the final solution or pass the original sample through a column of strongly acidic cation-exchange resin in the hydrogen form to remove the interfering cations. The latter procedure enables application of the method to waters and effluents of high hardness or solids content.

## 4. Apparatus

4.1 *Evaporating dish*, 100- to 150-mL capacity, of Vycor glass, platinum, or other suitable material.

4.2 *Ion-exchange column*, 50-cm long by 1.3-cm diameter.

4.3 *Spectrometer*, for use at 540 nm, and cells with a minimun light-path length of 1 cm.

4.4 Refer to manufacturer's manual to optimize instrument.

4.5 *Water bath*, 55±2°C.

## 5. Reagents

5.1 *Boron standard solution I*, 1.00 mL=100 $\mu$g B: Dissolve 0.5720 g high-purity $H_3BO_3$, dried over desiccant for 24 h, in demineralized water and dilute to 1000 mL. Store in plastic bottle.

5.2 *Boron standard solution II*, 1.00 L=1.00 $\mu$g B: Dilute 10.0 mL boron standard solution I to 1,000 mL with demineralized water. Store in plastic bottle.

5.3 *Cation-exchange resin*: Load the column with a strongly acidic cation-exchange resin. Backwash the column with demineralized water to remove entrained air bubbles. Henceforth, make certain the resin remains covered with liquid at all times. Pass 50 mL 2$M$ HCl through the column at a rate of 0.2 mL/min of acid per milliliter of resin in column and then wash it free of acid with demineralized water. The frequency

of regeneration depends on the mineral content of the samples.

5.4  *Curcumin reagent*: Dissolve 40 mg finely ground curcumin (Eastman No. 1179 or equivalent) and 5.0 g oxalic acid in 80 mL 95-percent ethanol. Add 4.2 mL concentrated HCl (sp gr 1.19) and dilute to 100 mL with ethanol. The reagent is stable for several days if stored in a refrigerator.

5.5  *Ethanol*, 95-percent.

5.6  *Hydrochloric acid, 2M*: Mix 166 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L.

## 6. Procedure

6.1  *Precautions*: Exercise close control of variables, such as volumes and concentrations of samples, standards, and, reagents, as well as time and temperature of drying. Use evaporating dishes identical in shape, size, and composition ·to insure equal evaporation time. Increasing the time of evaporation results in intensification of the resulting color.

6.2  For samples having high hardness (100 mg/L $CaCO_3$ or more), proceed as follows (NOTE 1): Pipet 25 mL of sample solution or of a smaller sample of known high boron content diluted to 25 mL onto the resin column. Adjust the rate of flow through the column to about 2 drops per second and collect the effluent in a 50-mL volumetric flask. Wash the column with small portions of demineralized water until the flask is full to the mark and mix.

NOTE 1. For samples containing less than 100 mg/L hardness as $CaCO_3$, start with paragraph 6.3.

6.3  Pipet 1.00 mL of sample solution containing less than 1.0 $\mu$g B into an evaporating dish (NOTE 2).

NOTE 2. If the sample contains more than 1,000 $\mu$g/L B, make an appropriate dilution with demineralized water, so that a 1.00-mL portion contains approx 0.50 $\mu$g B.

6.4  Prepare in evaporating dishes a blank and sufficient standards (1.0 $\mu$g B max) and adjust the volume of each to exactly 1.0 mL with demineralized water.

6.5  Add 4.0 mL curcumin reagent to each and swirl each dish gently to mix contents.

6.6  Float the dishes on a water bath set at 55±2°C and let them remain for 80 min, a time usually sufficient for complete drying and removal of HCl. Keep drying time constant for standards and samples.

6.7  After the dishes cool to room temperature, add 10.0 mL 95-percent ethanol to each dish, stirring gently with a polyethylene rod to ensure complete dissolution of the red-colored product.

6.8  Wash the contents of each dish into a 25-mL volumetric flask using 95-percent ethanol and adjust to volume with ethanol. Mix by repeated inversion (NOTE 3).

NOTE 3. If the final sample solution is turbid, filter through No. 30 Whatman filter paper or equivalent.

6.9  Determine the absorbance of samples and standards against the blank. Complete all absorbance readings within 1 h of drying the samples.

## 7. Calculations

7.1  Determine the micrograms boron in the sample solution from a plot of absorbances of standards.

7.2  Determine the dissolved or total-recoverable boron concentration in micrograms per liter as follows:

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

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

## 8. Report

Report boron, dissolved (01020), total-recoverable (01022), and suspended-recoverable (01021), concentrations as follows: less than 1,000 $\mu$g/L, nearest 100 $\mu$g/L; 1,000 $\mu$g/L and above, two significant figures.

## 9. Precision

9.1  The standard deviation for dissolved boron within the range of 65 to 643 $\mu$g/L for 16 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 63.4 $\mu$g/L ranged from 54.2 to 76.3 $\mu$g/L.

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

| Number of laboratories | Mean ($\mu$g/L) | Relative standard deviation (percent) |
|---|---|---|
| 4 | 65 | 37 |
| 5 | 98 | 60 |
| 4 | 320 | 20 |
| 6 | 643 | 10 |

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

## Reference

American Public Health Association and others, 1980, Standard methods for the examination of water and wastewater (15th ed.): Washington, D.C., p. 257.

# Boron, colorimetric, dianthrimide

## Parameters and Codes:
Boron, dissolved, I–1110–85 ($\mu$g/L as B): 01020
Boron, total recoverable, I–3110–85 ($\mu$g/L as B): 01022
Boron, suspended recoverable, I–7110–85 ($\mu$g/L as B): 01021
Boron, recoverable-from-bottom-material, dry wt, I–5110–85 ($\mu$g/g as B): 01023

## 1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing between 20 and 1,000 $\mu$g/L of boron. Sample solutions containing more than 1,000 $\mu$g/L need to be diluted.

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

1.3 This method may be used to analyze bottom material containing at least 10 $\mu$g/g of boron. If the sample solution prepared for analysis contains more than 250 $\mu$g boron, a portion of it needs to be diluted before analysis.

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

1.5 This method is not suitable for samples containing high concentrations of oxidizing or reducing materials or dissolved organic matter. However, it is not affected by buffering materials or high concentrations of total salts.

## 2. Summary of method

Boron, when heated with 1,1'-dianthrimide in concentrated sulfuric acid, gives a colored complex (Ellis and others, 1949; Rainwater, 1959). The color change ranges from greenish yellow to blue. The reaction producing the blue color depends on the temperature and duration of heating and on the concentrations of reagent and of boron. Maximum color development is achieved after the reaction has proceeded for 3 h at 90 °C.

## 3. Interferences

3.1 Traces of moisture will precipitate the reagent and interfere in the determination; therefore, precautionary measures given in the procedure must be followed precisely. Nitrate and bicarbonate interfere with color development and must be removed by volatilization as nitric acid and carbon dioxide in the presence of sulfuric acid. Organic matter in high concentrations chars and causes a discoloration of the complex, but this interference is easily recognized; small quantities of organic material cause no trouble. Some success in removal of the organic-material interference has been obtained by heating the sample in the presence of hydrogen peroxide for 1 to 2 h, but all nascent oxygen *must* be volatilized before the dianthrimide is added to the sample. When peroxide digestion is used, the final color complex should be compared with standard boron solutions similarly treated. Oxidizing and reducing constituents also interfere. Do not use glassware cleaned with chromic-sulfuric acid.

3.2 Some boric acid is probably volatilized during evaporation of the sample in the presence of sulfuric acid. Prolonged heating or temperatures higher than that recommended volatilize an excessive amount of boron and decrease the sensitivity of the test. The loss of boron is proportional to the boron content of the sample or standard; hence, such loss in no way affects the linearity of the color development if the heating is uniform. Nonlinearity of the concentration-versus-absorbance curve can result from weak reagents. The standards in step 6.2 of the procedure act as a check on linearity of the reaction and on the suitability of the working reagent.

## 4. Apparatus

4.1 *Oven*, 90°C: Uniformity of temperature throughout the oven is imperative.

4.2 *Spectrometer*, for use at 620 nm.

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

## 5. Reagents

5.1 *Boron standard solution I*, 1.00 mL=100 μg B: Dissolve 0.5720 g high-purity $H_3BO_3$, dried over desiccant for 24 h, in demineralized water and dilute to 1000 mL. Store in plastic bottle.

5.2 *Boron standard solution II*, 1.00 mL= 1.0 μg B: Dilute 10.0 mL boron standard solution I to 1,000 mL with demineralized water. Store in plastic bottle.

5.3 *1,1'-Dianthrimide (or 1,1'-iminodianthra-quinone) solution I*, 200 mg per 50 mL concentrated $H_2SO_4$: Dissolve 200 mg 1,1'-dianthrimide in 50 mL concentrated $H_2SO_4$ (sp gr 1.84). The reagent is stable for a long period if the container is sealed and refrigerated. Store in Teflon bottle.

5.4 *1,1'-Dianthrimide solution II*, (1 + 19): Dilute 1 volume of 1,1'-dianthrimide solution I with 19 volumes of concentrated $H_2SO_4$ (sp gr 1.84). The reagent is stable for a long period if the container is sealed and refrigerated. Store in Teflon bottle.

5.5 *Sulfuric acid*, concentrated (sp gr 1.84).

## 6. Procedure

6.1 Pipet a volume of sample solution containing less than 5.0 μg B (5.0 mL max) into a Pyrex test tube, and adjust volume to 5.0 mL.

6.2 Prepare a blank of demineralized water and sufficient standards, and adjust the volume of each to 5.0 mL.

6.3 *Cautiously* add 1.0 mL concentrated $H_2SO_4$ and mix by swirling the contents of the tube. Use of a test-tube-vibrating mixer is helpful.

6.4 Evaporate for at least 40 h in an oven at 90°C. At the end of the evaporation, the solution volume should be between 1.0 and 0.5 mL.

6.5 Add 5.0 mL 1,1'-dianthrimide solution II and mix by swirling.

6.6 Heat in oven for 3 h at 90°C.

6.7 Immediately after cooling, *with caution*

add 10.0 mL concentrated $H_2SO_4$. Mix carefully with a stirring rod or test-tube mixer.

6.8 Determine the absorbance of each sample and standard against the blank.

## 7. Calculations

7.1 Determine the micrograms boron in each sample solution from a plot of absorbances of standards.

7.2 Determine the dissolved or total-recoverable-boron concentration in micrograms per liter as follows:

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

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

7.4 Determine the boron concentration in micrograms per gram in bottom material as follows:

$$B(\mu g/g) = \frac{\mu g\ B\ in\ sample \times mL\ of\ original\ digest}{wt\ of\ sample\ (g) \times mL\ sample}$$

## 8. Report

8.1 Report boron, dissolved (01020), total-recoverable (01022), and suspended-recoverable (01021), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

8.2 Report boron, recoverable-from-bottom-material (01023), concentrations as follows: less than 100 μg/g, nearest 10 μg/g; 100 μg/g and above, two significant figures.

## 9. Precision

9.1 The standard deviation for dissolved boron within the range of 20 to 530 μg/L for 16 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 37.2 μg/L ranged from 31.2 to 46.1 μg/L.

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

| Number of laboratories | Mean ($\mu$g/L) | Relative standard deviation (percent) |
|---|---|---|
| 5 | 20 | 105 |
| 6 | 101 | 17 |
| 5 | 222 | 24 |
| 3 | 423 | 3 |
| 4 | 530 | 12 |

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

### References

Ellis, G. H., Zook, E. G., and Baudisch, Oskar, 1949, Colorimetric determination of boron using 1,1'-dianthrimide: Analytical Chemistry, v. 21, p. 1345-8.

Rainwater, F. H., 1959, Determination of boron with 1,1'-dianthrimide: American Water Works Association Journal, v. 51, p. 1046-50.