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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

By Marvin J. Fishman and Linda C. Friedman, Editors

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Book 5
LABORATORY ANALYSIS

Sample Preparation and Pretreatment

To determine the total concentrations of metals (dissolved plus suspended forms), the unfiltered sample (water-suspended sediment mixture) must be completely digested with a strong mineral acid or mixture of acids to bring the metals into solution. Digestion is also necessary for analyses of samples of bottom material. In addition, the organic matter, which is nearly always present, must be removed by oxidation and volatization. On samples of bottom material, analytical data are reported on a dry-weight basis. However, if there is a possibility of volatilizing any of the constituents during air or oven drying, the analysis must be made on a weighed portion of the as-received (wet) sample. The percent of moisture is then determined on a separate portion. The concentration values obtained on the wet sample are then converted and reported on a dry-weight basis.

The proper subsampling of bulk samples of bottom material presents unique problems. For most samples, splitting the sample using a Jones-type splitter is satisfactory. Alternatively, subsamples may be conveniently extracted with a small-diameter coring device, commonly glass tubing, to minimize the risk of metal contamination of the sample. Ordinarily, bottom-material samples are sieved before analysis, and only the portion passing through a 2-mm screen is taken for analysis. The use of an all-plastic screen eliminates the risk of introducing metals into the sample.

Sample preparation, bottom-material

(P-0520-85)

1. Application

This method may be used to air-dry samples of bottom material for subsequent analysis.

2. Summary of method

2.1 The sample is sieved, using a 2-mm plastic sieve, and the material passing through this sieve saved for analysis. A portion of the sample is then air-dried.

2.2 The percent moisture remaining in the air-dried sample is determined by heating at 105 °C. This permits computation of all constituents determined to an oven-dried basis if desired.

3. Interferences

None.

4. Apparatus

4.1 *Desiccator*, charged with "Drierite" or its equivalent.

4.2 *Drying oven*, 105 °C, uniform temperature throughout.

4.3 *Sieve*, plastic, with 2.00-mm openings.

4.4 *Tray*, drying, white-enameled, size 34 cm (13-1/2 in.) by 24.5 cm (9-5/8 in.) by 2 cm (3/4 in.) or equivalent.

4.5 *Weighing bottle*, cylindrical, 12-mL capacity.

5. Reagents

None required.

6. Procedure

6.1 Transfer the entire sample to a plastic sieve having 2.00-mm openings. Shake and tip the sieve firmly but gently, washing with minimal amount of demineralized water necessary to sieve all material less than 2-mm diameter. Discard material retained on the sieve.

6.2 Air-dry the sample. Spread a representative portion of the sample in a thin layer on a flat enamelware tray or glass watchglass, and allow it to stand exposed for 24 h, or until dry.

The drying must be conducted in a place free of potential contamination.

6.3 Portions of the resulting air-dried and well-mixed sample are taken for subsequent analyses.

6.4 Determine the percent moisture on a portion of sieved and air-dried sample. Weigh between 1 and 2 g, to nearest 0.1 mg, into a tared weighing bottle. Place the weighing bottle containing the accurately weighed sample in a drying oven and heat for 2 h at 105 °C. Cool in a desiccator for 30 min and immediately weigh.

7. Calculations

7.1 Compute the loss in weight of the sample, in grams, on heating at 105 °C.

7.2 Compute the percent moisture of the sieved and air-dried sample as follows:

$$\text{Percent moisture} = \frac{\text{loss in weight (g)}}{\text{sample weight (g)}} \times 100$$

8. Report

Report percentage of moisture to two significant figures.

9. Precision

Precision data are not available for this method.

Subsampling, bottom-material, coring

(P-0810-85)

1. Application

1.1 This method may be used to subsample wet bottom-material samples for subsequent analysis.

1.2 If the amount of material less than 2 mm in size is insufficient for adequate coring, a Jones-type teflon splitter may be used (method P-0811).

2. Summary of method

2.1 The entire wet sample is sieved, using a 2-mm plastic sieve. The material passing through the sieve is subsampled by coring.

2.2 The percent moisture is determined by drying a suitable portion of the sieved wet sample (method P-0590) in order to compute all constituents determined on an oven-dried basis (105 °C).

2.3 Care must be taken that the sieved sample is well-mixed and that the percent moisture determined on the separate subsample reflects the moisture content of the subsample analyzed.

2.4 In general, when peat-like material composes the majority of a sample, it should be considered as part of the sample even though it will not pass easily through a 2-mm sieve. (Such samples are not to be confused with samples consisting almost solely of leaves and twigs.)

3. Interferences

None.

4. Apparatus

4.1 *Glass tubes*, both 10-mm ID and 20-mm ID have been found satisfactory.

4.2 *Sieve*, plastic, with 2-mm openings.

5. Reagents

None.

6. Procedure

6.1 Transfer the entire sample to the plastic sieve. Shake the sieve firmly, washing with a minimal amount of demineralized water as necessary to sieve all material less than 2-mm diameter.

6.2 Thoroughly mix the sieved portion, returning it to the sample container in which it was received.

6.3 Core the sample, using either a 10-mm or a 20-mm glass tube, and place the core material (subsample) in a tared container. In some cases it may be necessary to withdraw more than one core in order to have sufficient bottom material for the particular determination to be made (NOTE 1).

NOTE 1. The type of container and the amount of bottom material required will depend on the individual method for which the subsample will be used.

6.4 Weigh the subsample to determine its wet weight.

6.5 At the same time as the other subsamplings, use the small-bore (10-mm) tube to withdraw a separate subsample for a moisture determination (method P-0590).

7. Calculations

Compute the dry weight of a subsample as follows:

$$\text{Sample, dry weight (g)} = W\frac{(100-M)}{100}$$

where

W= wet weight of the sample, grams,

and

M= percent of moisture as determined by method P-0590.

8. Report

See individual determination for the number of significant figures to be reported.

9. Precision

Precision data are not available for this method.

Subsampling, bottom-material, splitting

(P-0811-85)

1. Application

1.1 This method may be used to subsample wet bottom-material samples for subsequent analysis if the amount of material that is less than 2 mm in size is insufficient for adequate coring (method P-0810).

1.2 Samples that clog the splitter may be subsampled by coring (method P-0810).

2. Summary of method

2.1 The entire wet sample is sieved, using a 2-mm plastic sieve. The material passing through the sieve is subsampled with a Jones-type Teflon splitter.

2.2 The percent moisture is determined by drying a suitable portion of the sieved wet sample (method P-0590) in order to compute all constituents determined on an oven-dried basis (105 °C).

2.3 Care must be taken that the sieved sample is well mixed and that the percent moisture determined on the separate subsample reflects the moisture content of the subsample analyzed.

2.4 In general, when peat-like material composes the majority of a sample, it should be considered as part of the sample even though it will not pass easily through a 2-mm sieve. (Such samples are not to be confused with samples consisting almost solely of leaves and twigs).

3. Interferences

Certain samples, especially those with a large proportion of sand-size material, may clog the Jones-type splitter, which results in an uneven split.

4. Apparatus

4.1 *Sieve*, plastic, with 2-mm openings.

4.2 *Splitter*, Teflon, Jones-type.

5. Reagents

None.

6. Procedure

6.1 Thoroughly mix the sieved portion and determine the percent moisture (method P-0590) of a subsample obtained by coring with a 10-mm tube (NOTE 1).

NOTE 1. Alternatively, the moisture content may be determined on one of the last splits; however, since samples do not split into equal-weight subsamples, the amount of wash water used in each split is extremely critical and must be calculated accurately.

6.2 Accurately weigh the rest of the sample.

6.3 Pass the sample through a Jones-type Teflon splitter.

6.4 Accurately weigh the split subsample.

6.5 Using one of the split subsamples, repeat steps 6.3 and 6.4 until a sufficient number of subsamples is available.

7. Calculations

Compute the dry weight of a split subsample as follows:

$$\text{Sample, dry weight (g)} = \frac{W_1}{W_1+W_2}W_0\frac{(100-M)}{100}$$

where

W_1= wet weight, grams, of the split subsample,

W_2= wet weight, grams of the other subsample produced by the splitting,

W_0= weight, grams, of the sample before splitting,

and,

M= percent moisture as determined by Method P-0590.

8. Report

See each individual determination for the number of significant figures to be reported.

9. Precision

Precision data are not available for this method.

Percent moisture, total in-bottom-material, gravimetric

(P-0590-85)

1. Application

1.1 This method may be used to determine the percent moisture in bottom material less than 2 mm in size that has not been air-dried (method P-0810 or P-0811). To determine percent moisture of air-dried bottom-material samples, see method P-0520.

1.2 Information obtained by this method is used to compute the dry weight of subsamples used for analysis of bottom material. The result obtained is not applicable to bottom material in situ.

2. Summary of method

A portion of well-mixed sample less than 2 mm in size is dried at 105 °C. The loss of weight on drying is computed as a percentage of the total wet weight and represents the percent moisture of the sample.

3. Interferences

None.

4. Apparatus

4.1 *Crucible*, platinum or porcelain.

4.2 *Desiccator.*

4.3 *Oven*, 105 °C.

5. Reagents

None.

6. Procedure

6.1 Place a subsample of sieved bottom material, between 1 and 2 g, into a crucible that has been dried in an oven for 1 h at 105 °C, cooled, and weighed to the nearest 0.1 mg.

6.2 Weigh sample and crucible to the nearest 0.1 mg.

6.3 Place the crucible containing sample in an oven and dry to constant weight at 105 °C.

7. Calculations

$$\text{Moisture (percent)} = \frac{W-D}{W} \times 100$$

where

W= total wet weight of sample, grams,

and

D= dry weight of sample, grams.

8. Report

Report percentage of moisture to two significant figures.

9. Precision

Precision data are not available for this method.

Extraction procedure, bottom-material

(I-5485-85)

1. Application

This method must be used as preliminary treatment of bottom-material samples to destroy organic matter and to desorb and solubilize metals. If it has been determined that greater than 95 percent of the substance is solubilized, the results should be reported as "total." If less than 95 percent is solubilized, the results should be reported as "total recoverable." Only that portion of bottom material that passes a 2-mm sieve is taken for analysis.

2. Summary of method

2.1 The determination of acid-soluble metals occurring in or associated with sediment and

bottom material involves (1) destruction and removal of all organic matter, followed by (2) treatment to dissolve acid-soluble substances, and (3) measurement of the concentration of constituents in the resulting solution.

2.2 Removal or destruction of organic matter is a necessary preliminary treatment when acid-soluble metals are to be determined in samples of bottom material. This is conveniently accomplished with a strong oxidizing agent that has only a minimal effect on the mineral composition of the particulate material. The following procedure, employing hydrogen peroxide (H_2O_2), is generally satisfactory for destroying organic matter present in samples of bottom material prior to extraction of acid-soluble metals.

2.3 The procedure also provides for a hot, dilute hydrochloric acid digestion of the sample after destruction of organic matter. The digestion is designed to ensure dissolution of all sorbed metals, as well as of all readily acid-soluble components of the bottom-material mixture, without appreciably attacking the mineral structure of the sediment. The treatment is comparable to the procedure used to desorb and dissolve soluble metals associated with particulate material present in water-suspended sediment samples (method I-3485).

3. Interferences

There are no interferences in the acid digestion.

4. Apparatus

Filter paper, Whatman No. 41 or equivalent.

5. Reagents

5.1 *Hydrochloric acid*, double-distilled, 6*M*: Add a specified volume of reagent-grade concentrated HCl (sp gr 1.19) to an equal volume of demineralized water. Purify this acid by double distillation, retaining only the middle one-half of the total volume of acid being distilled in each case. Collect the distillate in a clean polyethylene or Teflon reagent bottle and protect the purified acid from contamination. The concentration of the distillate will be approx 6*M*. Double distillation of HCl may be omitted if each lot of acid is analyzed prior to use and is determined to yield a negligible blank for all metals of interest.

5.2 *Hydrochloric acid*, double-distilled, 1*M*: Add 17 mL of 6*M* HCl (double-distilled) to demineralized water and dilute to 100 mL with demineralized water.

5.3 *Hydrochloric acid*, double-distilled, 0.3*M*: Add 50 mL of 6*M* HCl (double-distilled) to 950 mL demineralized water.

5.4 *Hydrogen peroxide solution*, (H_2O_2), 30-percent w/v.

5.5 *Nitric acid*, dilute (1+4): Add 1 volume of concentrated HNO_3 (sp gr 1.42) to 4 volumes of demineralized water.

6. Procedure

6.1 Immediately before each use, clean all glassware used in this determination by rinsing, first with warm dilute HNO_3 (1+4), and then with demineralized water.

6.2 Weigh, to the nearest milligram, between 4 and 10 g of thoroughly homogenized, undried sample that has passed a 2-mm nonmetallic sieve (method P-0810 or P-0811). Compute the dry weight of the sample by determining the percent moisture on a *separate* subsample (method P-0590).

6.3 Quantitatively transfer each sample to a 600-mL beaker. Add sufficient demineralized water to provide a volume ratio of water to sample between 1:1 and 2:1. Cover the beaker with a ribbed watchglass.

6.4 Check the acidity of the solution with litmus paper. Make acidic by the dropwise addition of 1*M* HCl, if necessary.

6.5 Add 30-percent H_2O_2 in increments of about 5 mL, stir the suspension, and allow time for any strong effervescence or frothing to subside. Continue adding H_2O_2 in small amounts until the sample ceases to froth.

NOTE 1. A demineralized water blank must be carried through the procedure. Add equivalent amounts of 30-percent H_2O_2 and acid to the blank.

6.6 Place the sample beaker on a steam bath or hotplate at low heat (65 to 70 °C), and observe it closely until certain that all danger of further strong reaction has passed. Continue to add small increments of H_2O_2 until all organic matter is destroyed, as evidenced by absence of any dark-colored material and lack of noticeable frothing. Evaporate excess liquid between additions of H_2O_2 to keep the water-to-sediment

ratio between 1:1 and 2:1. Do not allow the mixture to evaporate to dryness at any time.

6.7 Dilute the mixture to 200 mL with demineralized water.

6.8 Add 10 mL double-distilled HCl, 6*M*, mix thoroughly, and heat on a hotplate to just below boiling. Continue heating for 30 min.

6.9 Filter the hot mixture (Whatman No. 41 filter paper, or equivalent) and collect the filtrate in a 250-mL volumetric flask. Wash the residue on the filter paper at least three times with hot 0.3*M* HCl.

6.10 Cool the filtrate to room temperature, and dilute to volume with demineralized water, and mix thoroughly.

6.11 Use appropriate aliquots of this solution to determine acid-soluble metals as required.

7. Calculations

See individual method for each metal.

8. Report

See individual method for significant figures to be reported.

9. Precision

See individual method for each metal.

Extraction procedure, water-suspended sediment

(I-3485-85)

1. Application

This method must be used as preliminary treatment of samples of water-suspended sediment to desorb and solubilize metals associated with the suspended sediment phase of the sample. If it has been determined that greater than 95 percent of the substance to be determined is solubilized, the results should be reported as "total." If less than 95 percent is solubilized, the results should be reported as "total recoverable."

2. Summary of method

2.1 The sample is digested by heating with dilute hydrochloric acid. Following digestion, the sample is filtered to remove particulate matter, and aliquots of the filtrate are analyzed for metals by atomic absorption spectrophotometric or other appropriate methods.

2.2 For additional information on principles of the methods, see individual methods for each of the substances.

3. Interferences

There are no interferences in the acid digestion.

4. Apparatus

Filter paper, Whatman No. 41 or equivalent.

5. Reagents

5.1 *Hydrochloric acid*, double-distilled, 6*M*: Add a specified volume of reagent-grade concentrated HCl (sp gr 1.19) to an equal volume of demineralized water. Purify this acid by double distillation, retaining only the middle one-half of the total volume of acid being distilled in each case. Collect the distillate in a clean polyethylene or Teflon reagent bottle and protect the purified acid from contamination. The concentration of the distillate will be approx 6*M*. Double distillation of HCl may be omitted if each lot of acid is analyzed prior to use and is determined to yield a negligible blank for all metals of interest.

5.2 *Hydrochloric acid*, double-distilled, 0.3*M*: Add 50 mL of 6*M* HCl (double-distilled) to 950 mL demineralized water.

5.3 *Nitric acid*, dilute (1+4): Add 1 volume of concentrated HNO_3 (sp gr 1.42) to 4 volumes of demineralized water.

6. Procedure

6.1 Immediately before each use, clean all glassware used in this procedure by rinsing, first with warm dilute HNO_3 (1+4) and then with demineralized water.

6.2 Mark the level of the sample on the bottle and determine the volume by weight.

6.3 Transfer the entire contents of the sample bottle to a beaker or fleaker.

6.4 Add 5 mL double-distilled 6*M* HCl to the sample bottle for each 100 mL of original sample. Shake vigorously and add this solution to the beaker. Heat solution in beaker to just below boiling and continue heating until the volume is reduced approximately 20 percent (NOTE 1).

NOTE 1. A demineralized water blank must be carried through the procedure. Add an equivalent amount of acid to the blank.

6.5 Filter the hot mixture (Whatman No. 41 filter paper or equivalent) into the original sample bottle. Wash the residue on the filter paper three times with 5-mL portions of hot 0.3*M* HCl.

6.6 Cool to room temperature, and dilute to the original volume with demineralized water. Mix thoroughly.

6.7 Use appropriate aliquots of this solution to determine acid-soluble metals as required.

7. Calculations

See individual method for each metal.

8. Report

See individual method for significant figures to be reported.

9. Precision

See individual method for each metal.

Total decomposition, sediment

(I-5473-85)
(I-5474-85)
(I-5475-85)

1. Application

1.1 These methods may be used to analyze suspended and bottom sediment for the determination of total concentration of constituents present.

1.2 Analyses must be performed on dried and ground samples that either have been fused with a lithium metaborate-lithium tetraborate flux with the resulting bead dissolved in acidified deionized water or have been solubilized with a combination of nitric, hydrofluoric, and perchloric acids heated in open teflon beakers.

2. Summary of method

2.1 See method I-5473, metals, major, total in sediment; method I-5474, metals, major and minor, total in sediment; and method I-5475, metals, minor, total in sediment, for complete solubilization procedures.

2.1 After solubilization the solutions are analyzed by atomic absorption spectrometry.

Analytical methods

Acidity, electrometric titration

Parameters and Codes:
Acidity, I-1020-85 (mg/L as H^{+1}): 71825 (mg/L as $CaCO_3$): 00435

1. Application

This method is applicable to many acidic samples. When the sample is suspected or known to contain mostly weak acids, however, the construction of a neutralization curve is imperative, and the acidity value is reported and interpreted in terms of the character of the curve obtained.

2. Summary of method

2.1 Acidity is determined by titrating the sample with a standard solution of a strong base to an electrometrically observed end point pH of 8.3. The titration is carried out at room temperature, except that the sample is heated briefly near the end of the titration to increase the rate of hydrolysis of metal ions present.

2.2 For additional information concerning the determination of acidity and for instructions for constructing an electrometric titration curve, see ASTM Method D 1067-82, "Standard Methods of Test for Acidity or Alkalinity of Water," (American Society for Testing and Materials, 1984).

3. Interferences

Dissolved gases that are acidic, such as CO_2 and H_2S, may easily be lost from the sample. If any substantial part of the acidity is due to gaseous solutes, special care must be taken to prevent their escape prior to and during the titration. Gases are less soluble in warm water than in cold; hence, the sample must be kept chilled until analyzed, and even then the analysis must be performed as soon as possible. Stirring and agitation of the sample cause expulsion of dissolved gases; care must be taken to avoid unnecessary agitation of the sample. A tightly capped bottle is essential for storing and transporting samples. The determination should be performed at the time of sampling for greatest accuracy.

4. Apparatus

4.1 *Buret*, 50-mL capacity.
4.2 *Hotplate.*
4.3 *pH meter.*
4.4 *Stirrer*, magnetic.

5. Reagents

5.1 *Sodium hydroxide stock solution*, approx. 2*N*: Dissolve 80 g NaOH in carbon dioxide-free water and dilute to 1 L with carbon dioxide-free water. Store in a tightly capped polyethylene bottle.

5.2 *Sodium hydroxide standard solution*, approx. 0.025*N*: Dilute 12.5 mL 2*N* NaOH with carbon dioxide-free water to approx 1 L. Standardize the solution against primary standard potassium hydrogen phthalate ($KHC_8H_4O_4$) as follows: Lightly crush 3 g of the salt to a fineness of approx 100 mesh and dry for at least 1 h at 110°C. Dissolve about 2 g, accurately weighed to the nearest milligram, in carbon dioxide-free water and dilute to 500.0 mL. Titrate 50.0 mL of the solution with the NaOH standard solution to pH 8.6:

$$\text{Normality of NaOH} = \frac{\text{g } KHC_8H_4O_4 \text{ in 50.0 mL} \times 4.896}{\text{mL NaOH}}$$

6. Procedure

6.1 Samples should be collected in tightly capped polyethylene bottles, with as little agitation as possible, particularly if it is suspected or known that any significant part of the acidity is due to dissolved gases. Chill or otherwise keep the sample cool during transportation to the laboratory and perform the determination as soon as possible. Do not open the sample bottle until ready to determine the acidity, and then perform the determination without delay once the bottle has been opened.

6.2 Carefully pipet an aliquot of sample containing less than 1.0 mg H^{+1} (50.0 mL max) into a 150-mL beaker. Avoid disturbing any sediment in the sample bottle. Do not filter.

6.3 Insert the beaker in the titration assembly and record the pH.

6.4 Titrate the sample with standard NaOH solution to pH 8.3.

6.5 Heat the solution to about 90 °C (do not boil), and maintain this temperature for 2 min.

6.6 Cool to room temperature and resume the titration, titrating again to a final pH of 8.3. Record the total volume of titrant used (mL_b).

7. Calculations

7.1 Determine acidity as me/L as follows:

$$\text{Acidity, me/L} = \frac{mL_b}{mL_s} \times N_b \times 10^3$$

7.2 Determine acidity as hydrogen ion in mg/L as follows:

$$\text{Acidity, mg/L as } H^{+1} = \frac{mL_b}{mL_s} \times N_b \times 1.008 \times 10^3$$

7.3 Determine acidity as $CaCO_3$ in mg/L as follows:

$$\text{Acidity, mg/L as } CaCO_3 = \frac{mL_b}{mL_s} \times N_b \times 10^3 \times 50.05$$

where

mL_b and mL_s = volumes of standard NaOH solution and sample, respectively,

and

N_b = normality of standard NaOH solution.

8. Report

8.1 Report acidity values in milliequivalents per liter or milligrams per liter as hydrogen ion as follows: less than 10 me/L (mg/L), one decimal; 10 me/L (mg/L) and above, two significant figures.

8.2 Report acidity, hydrogen ion (71825), concentrations as milligrams per liter.

8.3 Report acidity, calcium carbonate (00435), concentrations in milligrams per liter as follows: less than 100 mg/L, whole numbers; 100 mg/L and above, two significant figures.

9. Precision

The precision for one sample expressed in both standard deviation and percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L as H^{+1})	Standard deviation (mg/L as H^{+1})	Relative standard deviation (percent)
21	26.0	0.9	3.5

Reference

American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, v. 11.01, p. 125–133.

Alkalinity, electrometric titration

Parameter and Code:
Alkalinity, I-1030-85 (mg/L as $CaCO_3$): 00410

1. Application

This method is suitable for analyzing water with any amount of alkalinity, but aliquots for analysis should be taken to avoid a titration volume of standard acid in excess of 50 mL.

2. Summary of method

2.1 Alkalinity is determined by titrating the water sample with a standard solution of strong acid. The end point of the titration is selected as pH 4.5.

2.2 For waters that contain only small quantities of dissolved mineral matter, the alkalinity determination is likely the largest single source of error in the analysis. Alkalinity is very susceptible to change between time of collection and analysis, with changes occurring more rapidly after the sample bottle is opened. The overall alkalinity value is probably somewhat more stable than the relative values of the common alkalinity components. Unless a gross error is made in the initial determination of alkalinity, it is seldom advisable to try to check the results if several days have elapsed since the bottle was first opened. The alkalinity of some samples may change appreciably in a few hours. The determination should be performed at the time of sampling for highest accuracy.

2.3 Selection of pH 4.5 as the titration end point for determining total alkalinity is arbitrary and corresponds to the true equivalence point only under ideal conditions. The equivalence point of the bicarbonate-carbonic acid titration varies with the concentration of bicarbonate present; the deviation from pH 4.5 is particularly serious at low bicarbonate-ion concentrations. When greater accuracy in the determination is needed, the titration equivalence point may be determined for each sample by adding the titrant in small increments in the vicinity of pH 4.5 and by recording the pH of the solution after each measured addition. The true end point is then determined from either (1) a plot of pH versus total titrant volume, where the end point is the pH corresponding to a change in slope of the curve, or (2) a plot of

$$\frac{\delta \text{pH}}{\Delta \text{mL titrant}} \text{ versus titrant volume}$$

where the end point is that volume at which there occurs a maximum rate of change of pH per volume of titrant added.

2.4 There are other methods for arriving at a more reliable determination of total alkalinity. Barnes (1964) discusses the several factors involved in the accurate measurement of alkalinity, particularly under field conditions. A routine laboratory method for determining total alkalinity with improved accuracy for widely differing types of water has been described by Larson and Henley (1955) and further evaluated by Thomas and Lynch (1960). A rather complete consideration of carbonate equilibria and their analytic considerations may be found in a publication by Stumm and Morgan (1970).

3. Interferences

3.1 Any ionized substance that reacts with a strong acid can contribute to alkalinity if the reaction occurs at a pH above that of the specified end point; examples are salts of weak organic and inorganic acids.

3.2 Oils and greases, if present, may tend to foul the pH-meter electrode and prevent its proper operation.

4. Apparatus

4.1 *Buret*, 50-mL capacity.

4.2 *pH meter.*

4.3 *Stirrer*, magnetic.

5. Reagents

5.1 Sodium carbonate standard solution, 1.0 mL ≙ 1.00 mg HCO_3^{-1}: Dry 1.0 g primary standard Na_2CO_3 at 150 to 160°C for 2 h. Cool in a desiccator and dissolve 0.8685 g in carbon dioxide-free water; dilute to 1,000 mL.

5.2 *Sulfuric acid standard solution*, 0.01639*N*, 1.00 mL ≙ 1.00 mg HCO_3^{-1}: *Cautiously* add 0.5 mL concentrated H_2SO_4 (sp gr 1.84) to 950 mL water. (The titrant is stable for several months if protected from ammonia fumes and is usually prepared in larger quantities.) After the solution has been thoroughly mixed, standardize by titrating 25.00 mL Na_2CO_3 standard solution (1.00 mL ≙ 1.00 mg HCO_3^{-1}) to pH 4.5. Adjust the concentration of the sulfuric acid standard solution to exactly 0.01639*N* by dilution with water or by addition of dilute acid as indicated by the first titration. Confirm the exact normality by restandardization. Although the sulfuric acid standard solution is reasonably stable, its normality should be verified at least monthly (NOTE 1).

NOTE 1. Preparing standard sulfuric acid that is not exactly 0.01639*N* may be more convenient. Standard sulfuric acid that is approximately 0.01639*N* (but the exact normality of which is known) can be used if the appropriate factor is applied in the calculations.

6. Procedure

6.1 Water samples for the determination of alkalinity should not be filtered, diluted, concentrated, or altered in any way. The determination should be performed without delay after the sample bottle has been opened.

6.2 From a settled, unfiltered sample, pipet a volume containing less than 40 mg alkalinity as HCO_3^{-1} (50.0 mL max) into a suitable beaker.

6.3 Titrate immediately with 0.01639*N* H_2SO_4 and record the titrant volume at pH 4.5.

7. Calculations

$$\text{Total alkalinity as } CaCO_3 \text{ in mg/L} = \frac{1{,}000}{mL_s} \times 0.8202 \times (mL_a \text{ to pH } 4.5)$$

where

mL_a and mL_s = volumes of standard acid and sample, respectively.

8. Report

Report alkalinity, total (00410), concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

9.1 Precision for alkalinity for 36 samples within the range of 3.6 to 316 mg/L calcium carbonate may be expressed as follows:

$$S_T = 0.034X + 1.93$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of alkalinity as $CaCO_3$, milligrams per liter.

The correlation coefficient is 0.5308.

9.2 Precision for alkalinity for six of the 36 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L as $CaCO_3$)	Relative standard deviation (percent)
25	3.6	25
14	56.7	11
27	107	13
31	119	3
30	183	6
26	316	2

References

Barnes, Ivan, 1964, Field measurement of alkalinity and pH: U.S. Geological Survey Water-Supply Paper 1535-H, 17 p.

Larson, T. E., and Henley, Laurel, 1955, Determination of low alkalinity or acidity in water: Analytical Chemistry, v. 27, p. 851–2.

Stumm, Werner, and Morgan, J. J., 1970, Aquatic Chemistry: New York, John Wiley and Sons, 583 p.

Thomas, J. F. J., and Lynch, J. J., 1960, Determination of carbonate alkalinity in natural waters: American Water Works Association Journal, v. 52, p. 259–68.

Alkalinity, electrometric titration, automated

Parameter and Code:
Alkalinity, I-2030-85 (mg/L as $CaCO_3$): 00410

1. Application

This method is suitable for analyzing water with any amount of alkalinity. Sample aliquots for analysis and maximum titration volume of standard acid will depend on specifications in the manufacturer's instruction manual.

2. Summary of method

2.1 Alkalinity is determined by titrating the water sample with a standard solution of a strong acid. The end point of the titration is selected as pH 4.5.

2.2 For additional information on the principles of the method see alkalinity (I-1030).

3. Interferences

See alkalinity (I-1030).

4. Apparatus

4.1 *Automatic titrator*, with potentiometric assembly.

4.2 *Combination electrode* (glass and reference). Separate glass and reference electrodes are also satisfactory.

5. Reagents

5.1 *Sodium carbonate standard solution*, 1.00 mL ○ 1.00 mg HCO_3^{-1}: Dry 1 g primary standard Na_2CO_3 at 150 to 160 °C for 2 h. Cool in a desiccator and dissolve 0.8685 g in carbon dioxide-free water; dilute to 1,000 mL.

5.2 *Sulfuric acid standard solution*, 0.01639*N*, 1.00 mL ○ 1.00 mg HCO_3^{-1}: *Cautiously* add 0.5 mL concentrated H_2SO_4 (sp gr 1.84) to 950 mL water. (The titrant is stable for several months if protected from ammonia fumes, and it is usually prepared in larger quantities.) After the solution has been thoroughly mixed, standardize by titrating 25.00 mL Na_2CO_3 standard solution (1.00 mL ○ 1.00 mg HCO_3^{-1}) to pH 4.5. Adjust the concentration of the sulfuric acid standard solution to exactly 0.01639*N* by dilution with water or by addition of dilute acid as indicated by the first titration. Confirm the exact normality by restandardization. Although the sulfuric acid standard solution is reasonably stable, its normality should be verified at least monthly (NOTE 1).

NOTE 1. Preparing standard sulfuric acid that is not exactly 0.01639*N* may be more convenient. Standard sulfuric acid that is approximately 0.01639*N* (but the exact normality of which is known) can be used if the appropriate factor is applied in the calculations.

6. Procedure

6.1 Water samples for the determination of alkalinity should not be filtered, diluted, concentrated, or altered in any way. The determination should be performed without delay after the sample bottle has been opened.

6.2 Set up the automatic titrator according to the directions given in the instruction manual.

6.3 From a settled, unfiltered sample, transfer or pipet a volume of sample to the vessel specified by the manufacturer.

6.4 Set the end point to pH 4.5 following the instructions provided with the instrument.

6.5 Place the samples in position in the titration assembly and activate the automatic potentiometric titration, using 0.01639*N* H_2SO_4 as titrant. Continue titrations until all samples have been titrated.

7. Calculations

Total alkalinity as $CaCO_3$ (mg/L)=

$$\frac{1{,}000}{mL_s} \times 0.8202 \times (mL_a \text{ to pH } 4.5)$$

where

mL_a and mL_s= volumes of standard acid and sample, respectively.

8. Report

Report alkalinity, total (00410), concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

9.1 The standard deviation for alkalinity within the range of 18.4 to 303 mg/L for 17 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 6.7 mg/L ranged from 5.8 to 7.9 mg/L.

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

Number of laboratories	Mean (mg/L as $CaCO_3$)	Relative std. deviation (percent)
7	18.4	13
3	101	17
3	101	2
5	151	12
10	303	2

Aluminum, atomic emission spectrometric, d-c plasma

Parameters and Codes:

Aluminum, dissolved, I-1054-85 (μg/L as Al): 01106
Aluminum, total recoverable, I-3054-85 (μg/L as Al): 01105
Aluminum, suspended recoverable, I-7054-85 (μg/L as Al): 01107

1. Application

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

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

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

2. Summary of method

Aluminum is determined by a direct-reading emission spectrometer which utilizes a d-c argon plasma as an excitation source (Johnson and others, 1979 a,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. Aluminum 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 negligible.

4. Apparatus

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

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

Plasma viewing position	+1 (fig. 9)
Gas	Argon
Sleeve pressure	50 psi
Nebulizer pressure	25 psi
Entrance slit	25×300 μm
Exit slit	50×300 μm
Voltage	1000 V
Wavelength	308.215 nm
Signal amplification	40- to 60-percent full-scale (1000 μg/L)

5. Reagents

5.1 *Aluminum standard solution I*, 1 mL= 100 μg Al: Dissolve 0.100 g aluminum powder in a minimun of 6*M* HCl using a Teflon beaker. Heat to increase rate of dissolution. Add 10.0 mL 6*M* HCl and dilute to 1,000 mL with demineralized water. Store in plastic bottle.

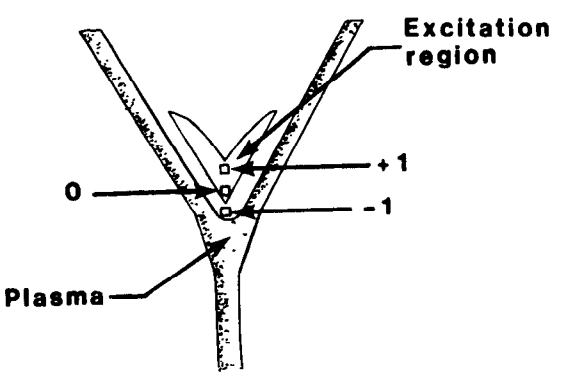

Figure 9.—Plasma position on entrance slit for aluminum

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

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

5.4 *Glycerin*, USP.

5.5 *Hydrochloric acid*, concentrated (sp gr 1.19), Ultrex or equivalent.

5.6 *Hydrochloric acid*, 6*M*: Add 500 mL concentrated HCl (sp gr 1.19) to 400 mL demineralized water and dilute to 1 L with demineralized water.

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

5.8 *Matrix modifier:* Dissolve 367 g LiCl in 1,000 mL demineralized water. Allow the solution to cool. Transfer to a 4-L polyethylene container, and add with stirring 2,000 mL of glycerin. In a Teflon beaker slowly add with stirring 400 mL concentrated H_2SO_4 to 400 mL demineralized water. When the dilute acid has reached room temperature, add the acid slowly, with stirring, to the glycerin-LiCl mixture. Dilute to 4,000 mL with demineralized water.

5.9 *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 and wavelength-optimization procedures. Use the prepared blank and aluminum working standard for instrument calibration and all subsequent recalibrations.

6.6 Refer to manufacturer's manual for autosampler-operating procedures. Pour samples in autosampler tray, positioning a blank and working standard after every 3 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 aluminum standard drifts more than 3 percent.

7. Calculations

The computer system is designed so that the blank and the 1,000 μg/L of aluminum 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 aluminum, dissolved (01106), total-recoverable (01105), and suspended-recoverable (01107), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

9. Precision

9.1 Precision, based on 14 to 18 determinations by a single operator during a 47-day period, expressed in terms of standard deviation and percent relative standard deviation, is as follows:

Number of determinations	Mean (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)
17	12.9	1.9	14.7
14	30.5	3.0	9.8
14	73.1	8.9	12.2
15	132	11	8.3
18	221	6.0	2.7
18	437	18	4.1
18	763	32	4.2

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

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.

Aluminum, atomic absorption spectrometric, chelation-extraction

Parameters and Codes:

Aluminum, dissolved, I-1052-85 (μg/L as Al): 01106
Aluminum, total recoverable, I-3052-85 (μg/L as Al): 01105
Aluminum, suspended recoverable, I-7052-85 (μg/L as Al): 01107

1. Application

1.1 This method may be used to analyze water, brines, and water-suspended sediment containing from 10 to 1,000 μg/L of aluminum. Samples containing more than 1,000 μg/L should either be diluted prior to chelation-extraction or be analyzed by the atomic absorption spectrometric direct method.

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

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

1.4 If the iron concentration of the sample exceeds 10,000 μg/L, determine aluminum by the atomic absorption spectrometric direct method.

2. Summary of method

2.1 Aluminum is determined by atomic absorption spectrometry following chelation with 8-hydroxyquinoline and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into the nitrous oxide-acetylene flame of the spectrometer.

2.2 Additional information about the principles of the method may be found in Snell and Snell (1959), and in Fishman (1972).

3. Interferences

3.1 Concentrations of iron greater than 10,000 μg/L interfere by suppressing aluminum absorption.

3.2 Manganese concentrations as great as 80,000 μg/L do not interfere if the turbidity in the MIBK extract is allowed to settle (preferably overnight).

3.3 Magnesium, as little as 25 mg/L, forms an insoluble chelate with 8-hydroxyquinoline at pH 8.0 and tends to coprecipitate aluminum 8-hydroxyquinolate. However, the magnesium 8-hydroxyquinolate forms rather slowly (approx 4 to 6 min); its interference can be avoided if the aluminum 8-hydroxyquinolate is extracted with MIBK immediately after the sample is buffered to pH 8.

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	309.3 nm
Source (hollow-cathode lamp)	Aluminum
Burner	Nitrous oxide
Oxidant	Nitrous oxide
Fuel	Acetylene
Type of flame	Fuel-rich

5. Reagents

5.1 *Aluminum standard solution I*, 1.00 mL=100 μg Al: Dissolve 0.100 g Al powder in a minimun of 6*M* HCl. Heat to increase rate of dissolution. Add 10.0 mL 6*M* HCl and dilute to 1000 mL with demineralized water.

5.2 *Aluminum standard solution II*, 1.00 mL=1.00 μg Al: Dilute 10.0 mL aluminum standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water. This standard is used to prepare working standards at the time of analysis.

5.3 *Ammonium hydroxide-ammonium acetate buffer solution*: Dissolve 200 g $NH_4C_2H_3O_2$ and 70 mL concentrated NH_4OH (sp gr 0.90) in water, and dilute to 1 L with demineralized water.

5.4 *8-Hydroxyquinoline solution*: Dissolve 20 g 8-hydroxyquinoline in 57 mL glacial acetic acid (sp gr 1.06) and in 200 mL demineralized water, and dilute to 1 L with demineralized water.

5.5 *Methyl isobutyl ketone* (MIBK).

6. Procedure

6.1 Clean all glassware used in this determination with warm, dilute HNO_3 (1+9) and rinse with demineralized water immediately before use.

6.2 Pipet a volume of sample solution containing less than 100 μg Al (100 mL max) into a 200-mL volumetric flask and adjust the volume to approx 100 mL.

6.3 Prepare a blank and at least six standards and adjust the volume of each to approx 100 mL with demineralized water.

6.4 Add 2 mL 8-hydroxyquinoline solution and mix (NOTE 1).

NOTE 1. Proceed to paragraph 6.5 if only dissolved aluminum is to be determined. If total recoverable aluminum is to be determined, add 2.2 mL concentrated NH_4OH (sp gr 0.90) to the sample solutions that undergo digestion-solubilization (paragraph 1.3), and then proceed to paragraph 6.5.

6.5 Add 10 mL NH_4OH-$NH_4C_2H_3O_2$ buffer solution to *one* sample and *immediately* add 10.0 mL MIBK. Shake vigorously for 15 sec. Each sample must be treated individually to avoid interference from magnesium. Each remaining sample, blank, and standard is treated in a like manner.

6.6 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask (NOTE 2).

NOTE 2. If the layers do not separate, allow to stand overnight.

6.7 Aspirate the ketone layer of 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 aluminum in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing concentrations of aluminum that exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factors.

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

8. Report

Report aluminum, dissolved (01106), total-recoverable (01105), and suspended-recoverable (01107), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

9. Precision

9.1 The standard deviation for dissolved aluminum within the range of 74 to 793 μg/L for 10 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 58.5 μg/L ranged from 47.8 to 77.0 μg/L.

9.2 Precision for dissolved aluminum for six of the 10 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
6	74	15
4	82	37
4	195	9
4	252	29
5	650	23
3	793	3

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

References

Fishman, M. J., 1972, Determination of aluminum in water: Atomic Absorption Newsletter, v. 11, p. 46–47.

Snell, F. D., and Snell, C. T., 1959, Colorimetric methods of analysis: Princeton, D. Van Nostrand Company, p. 181–183.

Aluminum, atomic absorption spectrometric, direct

Parameters and Codes:

Aluminum, dissolved, I-1051-85, (μg/L as Al): 01106
Aluminum, total recoverable, I-3051-85 (μg/L as Al): 01105
Aluminum, suspended recoverable I-7051-85 (μg/L as Al): 01107
Aluminum, recoverable-from-bottom-material, dry wt, I-5051-85 (μg/g as Al): 01108

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 100 μg/L of aluminum. Sample solutions containing more than 5,000 μg/L need either to be diluted or to be read on a less expanded scale. Sample solutions containing less than 100 μg/L and brines need to be analyzed by the atomic absorption spectrometric chelation-extraction method, provided that the interference limits discussed in that method are not exceeded.

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

1.3 This method may be used to analyze bottom material containing at least 5 μg/g of aluminum.

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

2. Summary of method

Aluminum is determined by atomic absorption spectrometry by direct aspiration of the sample into a nitrous oxide-acetylene flame without preconcentration or pretreatment of the sample other than the addition of sodium chloride to control ionization of aluminum, and bis(2-ethoxyethyl)ether to enhance the analytical sensitivity (Ramakrishna and others, 1967).

3. Interferences

3.1 Aluminum ionizes slightly in the nitrous oxide-acetylene flame; to control this effect, adjust the sodium-ion concentration of each standard and sample to at least 850 mg/L.

3.2 Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), calcium (4,000 mg/L), magnesium (4,000 mg/L), sulfate (9,000 mg/L), chloride (9,000 mg/L), nitrate (9,000 mg/L), and iron (9×10^6 μg/L) do not interfere. Greater concentrations of each constituent were not investigated.

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	309.3 nm
Source (hollow-cathode lamp)	Aluminum
Burner	Nitrous oxide
Oxidant	Nitrous oxide
Fuel	Acetylene
Type of flame	Fuel-rich

5. Reagents

5.1 *Aluminum standard solution*, 1.00 mL= 100 μg Al: Dissolve 0.100 g Al powder in a minimum of 6*M* HCl. Heat to increase rate of dissolution. Add 10.0 mL 6*M* HCL and dilute to 1,000 mL with demineralized water.

5.2 *Aluminum working standards*, Prepare at least six working standards containing from 100 to 5,000 μg/L of Al by appropriate dilution

of aluminum standard solution. Add 1.0 mL NaCl solution and 1.0 mL bis(2-ethoxyethyl)-ether for each 10 mL of working standard. Prepare fresh daily.

5.3 *Bis(2-ethoxyethyl)ether*: Eastman Kodak Co. Chemical No. 4738 or equivalent.

5.4 *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 and 1.0 mL bis(2-ethoxyethyl)ether to 10.0 mL of 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 aluminum in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing concentrations of aluminum 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 aluminum, subtract dissolved-aluminum concentration from total-recoverable-aluminum concentration.

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

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

8. Report

8.1 Report aluminum, dissolved (01106), total-recoverable (01105), and suspended-recoverable (01107), concentrations as follows: less than 10,000 μg/L, nearest 100 μg/L; 10,000 μg/L and above, two significant figures.

8.2 Report aluminum, recoverable from bottom material (01108), concentrations as follows: less than 1,000 μg/g, nearest 10 μg/g; 1,000 μg/g and above, two significant figures.

9. Precision

9.1 Precision for dissolved aluminum for 17 samples within the range of 40 to 811 μg/L, may be expressed as follows:

$$S_T = 0.253X + 9.84$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of aluminum, micrograms per liter.

The correlation coefficient is 0.7779.

9.2 Precision for dissolved aluminum for six 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)
7	40	135
7	40	85
5	138	79
8	144	31
15	513	19
7	811	9

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

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

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
12	4450	13
7	5530	33

References

Ramakrishna, T. V., West, P. W., and Robinson, J. W., 1967, The determination of aluminum and beryllium by atomic absorption spectroscopy: Analytica Chimica Acta, v. 39, p. 81–87.

Aluminum, total-in-sediment, atomic absorption spectrometric, direct

Parameters and Codes:
Aluminum, total, I-5473-85 (mg/kg as Al): none assigned
Aluminum, total, I-5474-85 (mg/kg as Al): none assigned

2. Summary of method

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

2.1.1 The sample is fused with a mixture of lithium metaborate and lithium tetraborate in a graphite crucible in a muffle furnace at 1000 °C. The resulting bead is dissolved in acidified, boiling, demineralized water, and aluminum is determined by atomic absorption spectrometry. See method I-5473, metals, major, total-in-sediment, atomic absorption spectrometric, direct.

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

Antimony, atomic absorption spectrometric, hydride

Parameters and Codes:

Antimony, dissolved, I-1055-85 (μg/L as Sb): 01095
Antimony, total, I-3055-85 (μg/L as Sb): 01097
Antimony, suspended total, I-7055-85 (μg/L as Sb): 01096
Antimony, total-in-bottom material, dry wt, I-5055-85 (μg/g as Sb): 01098

1. Application

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

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

1.3 This method may be used to analyze bottom material containing at least 1 μg/g of antimony. Ordinarily, a 100-mg sample of prepared bottom material (method P-0520) is taken for analysis. However, if the sample contains more than 15 μg/g of antimony, a smaller sample needs to be used.

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

2. Summary of method

Organic antimony-containing compounds are decomposed by adding sulfuric and nitric acids and by repeatedly evaporating the sample to fumes of sulfur trioxide. The antimony so liberated, together with inorganic antimony originally present, is subsequently reacted with potassium iodide and stannous chloride, and finally with sodium borohydride to form stibine. The stibine 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 217.6 nm.

3. Interferences

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

3.2 Selenium and arsenic, which also form gaseous hydrides, do not interfere at concentrations of 100 μg/L. Greater concentrations were not tested.

4. Apparatus

4.1 *Atomic absorption spectrometer* and recorder.

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

Wavelength	217.6 nm
Source (electrodeless discharge lamp)	Antimony
Burner	Three-slot
Fuel	Hydrogen
Diluent	Nitrogen
Carrier	Nitrogen

4.3 *Stibine vapor analyzer* (fig. 10) consisting of _____

4.3.1 *Beaker*, Berzelius, 200-mL capacity.

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

4.3.3 *Medicine dropper*, 2-mL capacity, minimum, or automatic pipettor, 5-mL capacity.

5. Reagents

5.1 *Antimony standard solution I*, 1.00 mL= 100 μg Sb: Dissolve 0.100 g Sb metal in a minimum amount of aqua regia. Add demineralized water to increase rate of dissolution and dilute to 1000 mL with demineralized water.

5.2 *Antimony standard solution II*, 1.00 mL=10.0 μg Sb: Dilute 50.0 mL antimony standard solution I to 500.0 mL with demineralized water.

5.3 *Antimony standard solution III*, 1.0 mL= 0.10 μg Sb: Dilute 5.0 mL antimony standard

solution II to 500.0 mL with demineralized water. Prepare fresh before each use.

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

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

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*, 4.2 g/100 mL concentrated HCl: Dissolve 5 g $SnCl_2 \cdot 2H_2O$ in 100 mL concentrated HCl (sp gr 1.19). 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 Follow instructions in paragraph 6.1.1 for water or water-suspended sediment and in paragraph 6.1.2 for bottom material.

6.1.1 Pipet a volume of well-mixed sample containing less than 1.5 μg Sb (100 mL max) into a 200-mL Berzelius beaker and dilute to 100 mL with demineralized water.

6.1.2 Weigh a portion of the prepared bottom-material sample containing less than 1.5 μg Sb (100 mg max); transfer to a 200-mL Berzelius beaker and add 100 mL demineralized water (NOTE 1).

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

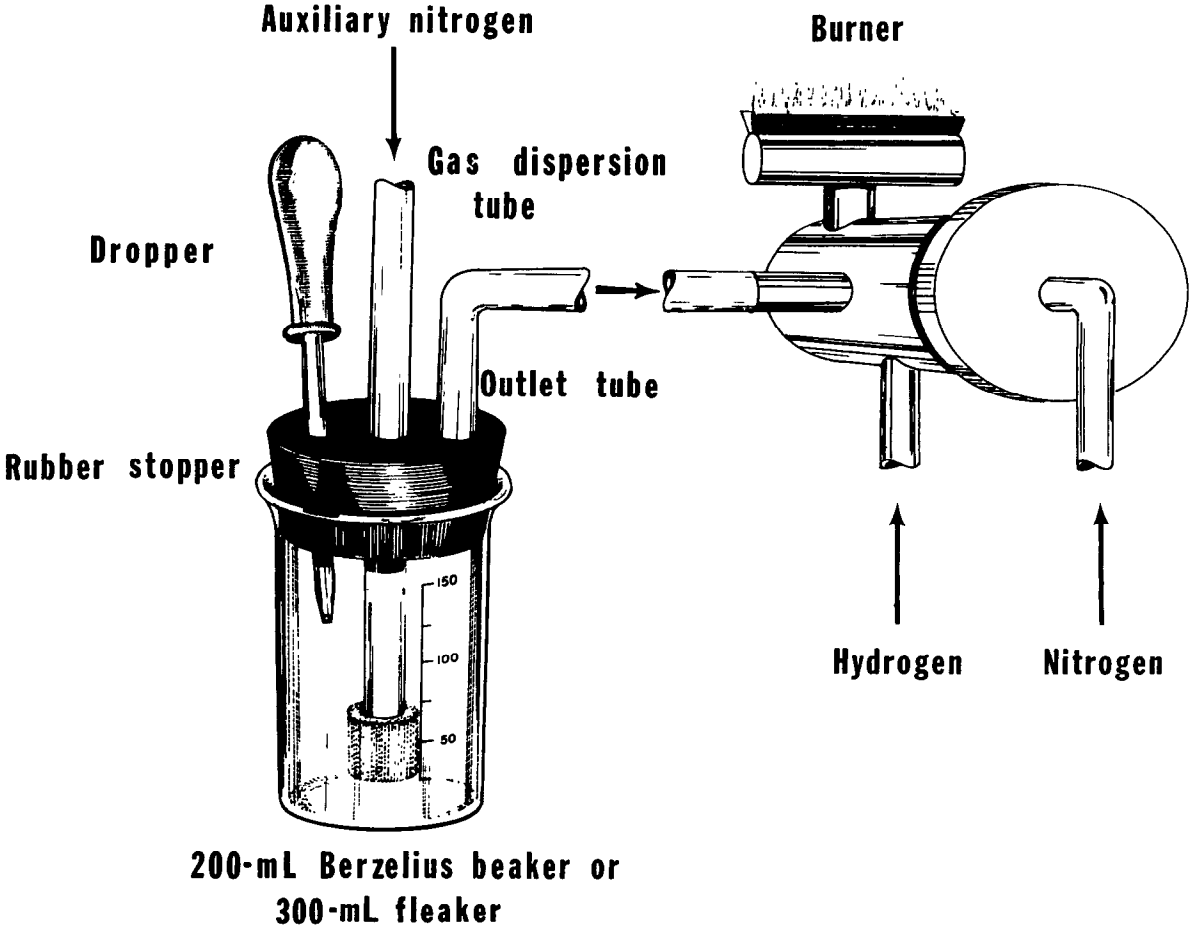

Figure 10.—Stibine vapor analyzer

6.2 Prepare, in 200-mL Berzelius beakers, a blank and sufficient standards containing from 0.1 to 1.5 μg Sb by diluting 1.0 to 15.0 mL portions of antimony standard solution III to 100 mL with demineralized water.

6.3 To each beaker, add 7 mL 9*M* H_2SO_4 and 5 mL concentrated HNO_3. Add a small boiling chip 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 antimony. Cool, add 25 mL demineralized water, and again evaporate to fumes of SO_3 to expel oxides of nitrogen.

6.4 Cool, and adjust the volume of each beaker to approx 100 mL with demineralized water.

6.5 To each beaker, add successively, with thorough mixing after each addition, 8 mL concentrated HCl, 1 mL KI solution, and 0.5 mL $SnCl_2$ solution. Allow about 15 min for reaction to proceed.

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

6.7 Fill the medicine dropper with 2 mL $NaBH_4$ solution and insert into hole in rubber stopper.

6.8 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 the next sample. Treat each succeeding sample, blank, and standard in a like manner.

7. Calculations

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

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

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

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

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

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

8. Report

8.1 Report antimony, dissolved (01095), total (01097), and suspended-total (01096), concentrations as follows: less than 100 μg/L, nearest microgram per liter; 100 μg/L and above, two significant figures.

8.2 Report antimony, total-in-bottom-material (01098), concentrations as follows: less than 100 μg/g, nearest microgram per gram; 100 μg/g and above, two significant figures.

9. Precision

9.1 Precision for dissolved antimony for seven samples expressed in terms of percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
3	2.0	0
3	2.0	50
3	2.3	26
3	4.3	28
3	4.3	35
3	4.7	13
3	8.0	0

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

Antimony, total-in-sediment, atomic absorption spectrometric, hydride

Parameter and Code:
Antimony, total, I-5475-85 (mg/kg as Sb): none assigned

2. Summary of method

A sediment sample is dried, ground, and homogenized. The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200 °C. Antimony is determined on the resulting solution by atomic absorption spectrometry. See method I-5475, metals, minor, total-in-sediment, atomic absorption spectrometric, hydride.