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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

Strontium, atomic absorption spectrometric, direct

Parameters and Codes:
Strontium, dissolved, I-1800-85 (µg/L as Sr): 01080
Strontium, total recoverable, I-3800-85 (µg/L as Sr): 01082
Strontium, suspended recoverable, I-7800-85 (µg/L as Sr): 01081
Strontium, recoverable-from-bottom-material, dry wt, I-5800-85 (µg/g as Sr): 01083

1. Application

1.1 This method may be used to analyze water, brines, and water-suspended sediment containing from 10 to 5000 µg/L of strontium. Samples containing more than 5,000 µg/L need to be diluted.

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

1.3 This method may be used to analyze bottom material containing at least 1.0 µg/g of strontium. If the sample solution contains more than 5,000 µg/L of strontium, it must be diluted.

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

1.5 Samples containing more than 2,500 mg/L of total solutes need first to be diluted. If the strontium concentration in the diluted sample is below detection, the undiluted sample needs to be analyzed by the standard-addition method.

2. Summary of method

2.1 Strontium is determined by atomic absorption spectrometry. Lanthanum chloride and excess potassium chloride are added to mask interferences and control ionization of strontium in the flame (Fishman and Downs, 1966).

2.2 This procedure may be automated by the addition of a sampler, a proportioning pump, and a strip-chart recorder or a printer or both (fig. 44).

3. Interferences

3.1 Sodium and potassium decrease the strontium ionization in the flame. To control the ionization, 1,000 mg/L of potassium are added to both standards and samples.

3.2 Aluminum, phosphate, and silica interfere but are masked by the addition of lanthanum.

3.3 Nitrate interferes, but in the presence of lanthanum chloride-potassium chloride solution at least 2,000 mg/L can be tolerated. The addition of nitric acid in the field to preserve samples causes no problem.

3.4 Low strontium values result even in the presence of potassium and lanthanum if the dissolved-solids concentration exceeds 2,500 mg/L. For this reason, brines and highly mineralized waters must either be diluted or analyzed by the standard-addition method. For the standard-addition method, the dissolved solids content of the samples must be reduced to less than 20,000 mg/L.

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:

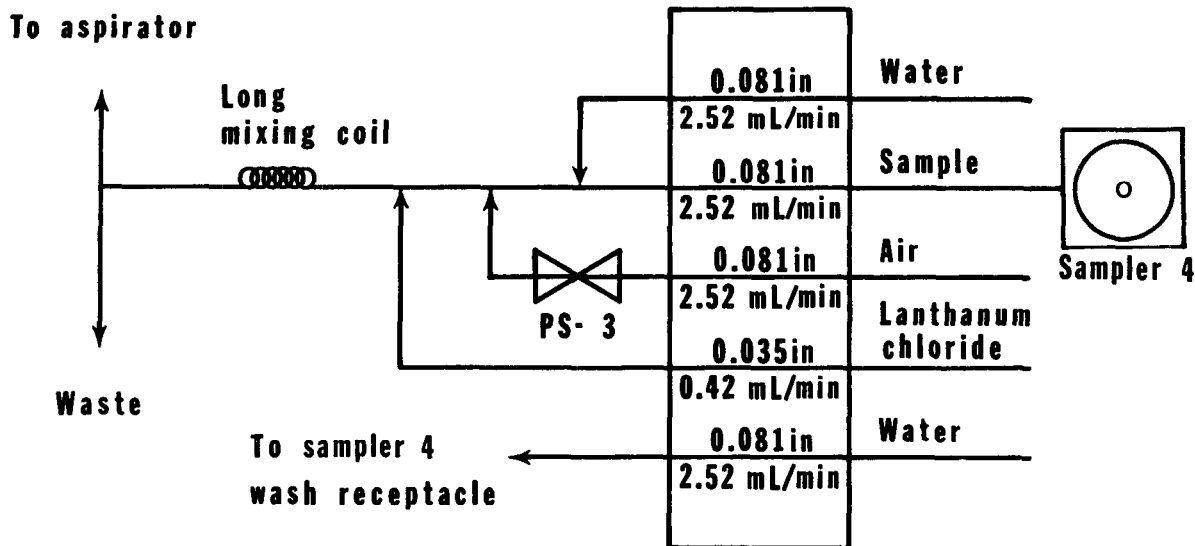|	
Grating ------------	Visible
Wavelength --------	460.7 nm
Source (hollow-cathode lamp) ------------	Strontium
Oxidant ------------	Air
Fuel ---------------	Acetylene
Type of flame -------	Slightly reducing

Figure 44.—Strontium manifold

4.3 The 100-mm (4-in.), single-slot burner allows a working range of 10 to 5,000 μg/L. Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Lanthanum chloride-potassium chloride solution*: Dissolve 117.3 g La_2O_3 in a minimum amount of dilute HCl. Add 19.1 g KCl, and dilute to 1,000 mL with demineralized water.

5.2 *Strontium standard solution*, 1.00 mL = 100 μg Sr: Dissolve 0.1684 g $SrCO_3$ in a minimum amount of dilute HCl, and dilute to 1,000 mL.

5.3 *Strontium working standards*: Prepare a blank and a series of at least six working standards containing from 10 to 5,000 μg/L of Sr by appropriate dilutions of strontium standard solution. Add 1.0 mL of $LaCl_3$-KCl solution to each 10 mL of working standards prepared. For example, to 500 mL of a working standard, add 50 mL $LaCl_3$-KCl solution.

6. Procedure

6.1 Add 1.0 mL $LaCl_3$-KCl solution to 10.0 mL of sample solution.

6.2 Aspirate the blank (10 mL demineralized water plus 1.0 mL $LaCl_3$-KCl solution) to set the automatic zero control. Use the automatic concentration control to set 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 strontium in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing strontium concentrations 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 strontium, subtract dissolved-strontium concentration from total-recoverable-strontium concentration.

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

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

8. Report

8.1 Report strontium, dissolved (01080), total-recoverable (01082), and suspended-recoverable (01081), concentrations as follows:

less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

8.2 Report strontium, recoverable-from-bottom-material (01083), concentrations as follows: less than 10 μg/g, nearest microgram per gram; 10 μg/g and above, two significant figures.

9. Precision

9.1 Precision for dissolved strontium for 39 samples within the range of 55 to 2790 μg/L may be expressed as follows:

$$S_T = 0.119X + 12.886$$

where

S_T = overall precision, micrograms per liter, and

X = concentration strontium, micrograms per liter.

The correlation coefficient is 0.7322.

9.2 Precision for dissolved strontium for eight of the 39 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
8	55.0	22
12	99.2	30
12	583	32
10	592	14
19	818	12
13	1260	24
10	2150	25
9	2790	5

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

Reference

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540-C, p. 41-3.

Strontium, atomic emission spectrometric, ICP

Parameter and Code:
Strontium, dissolved, I-1472-85 (µg/L as Sr): 01080

2. Summary of method

Strontium is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

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

Parameter and Code:
Strontium, total, I-5474-85 (mg/kg as Sr): 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. Strontium 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.

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Sulfate, dissolved, colorimetric, complexometric, methylthymol blue, automated-segmented flow

Parameter and Code:
Sulfate, dissolved, I-2822-85 (mg/L as SO_4): 00945

1. Application

This method can be used to determine concentrations of sulfate in surface, domestic, and industrial water in the range from 5 to 100 mg/L. The range can be extended to 300 mg/L by decreasing the sample-to-water ratio. Samples containing higher concentrations need to be diluted.

2. Summary of method

The sample stream is passed through a cation-exchange column before an acid solution is added containing equimolar quantities of barium chloride and methylthymol blue (MTB). Any sulfate ion is thereby precipitated as barium sulfate. When the mixture is then made basic, the remaining barium ions form a complex with MTB, and the absorbance of the uncomplexed MTB, which is gray, is directly proportional to the amount of sulfate originally present (Lazarus and others, 1968).

3. Interferences

Color is the only significant interference. Interfering cations are removed by a cation-exchange column, which is incorporated into the system.

4. Apparatus

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

4.2 With this equipment the following operating conditions have been found satisfactory for the ranges from 5 to 100 mg/L and from 100 to 300 mg/L:

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Absorption cell -----  15 mm
Wavelength --------  460 nm
Cam ---------------  30/h (6/1)
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5. Reagents

5.1 *Barium chloride stock solution*, 1.301 g/L: Dissolve 1.526 g $BaCl_2 \cdot 2H_2O$ (assay 99.0 percent min) in demineralized water and dilute to 1,000 mL.

5.2 *EDTA solution*: Dissolve 6.75 g NH_4Cl and 40 g disodium ethylenediaminetetra-acetic acid (EDTA) in 500 mL demineralized water and 57 mL concentrated NH_4OH (sp gr 0.90). Dilute to 1 L with demineralized water.

5.3 *Hydrochloric acid, 1M*: Add 83 mL concentrated hydrochloric acid (sp gr 1.19) to demineralized water and dilute to 1 L.

5.4 *Methylthymol blue (MTB) solution*, 0.5417 g/100 mL: Dissolve 0.5417 g MTB (Eastman Kodak No. 8068, M.W. = 866.73) in demineralized water and dilute to 100 mL.

5.5 *MTB-barium chloride reagent*: The purity of MTB may vary from one lot to another; this variation affects the linearity of the analytical curve (Colovos and others, 1976). It is, therefore, necessary to adjust the Ba-MTB ratio by the following calibration procedure in order to achieve a linear relationship between absorbance and sulfate concentration. Add 25.0 mL $BaCl_2$ stock solution to each of several 500-mL volumetric flasks. Then add volumes of MTB solution ranging from 26.0 to 36.0 mL (0.96 to 0.69 Ba-MTB molar ratio), in 2.0-mL increments, to each flask. Add 4.0 mL 1M HCl and an appropriate volume of demineralized water to bring the total volume to 100 mL. Dilute to 500 mL with 95-percent ethanol and

add 1 mL Brij-35 solution. Analyze eight sulfate standards covering the 5- to 100-mg/L operating range (5.0, 10.0, 20.0, 30.0, 40.0, 50.0, 75.0, and 100.0 mg/L) with reagent solutions of varying Ba-MTB molar ratios. Do not vary the instrumental parameters, but adjust the baseline as necessary. Plot an analytical curve of peak height versus known sulfate concentration for each Ba-MTB ratio. Determine least-squares equation and a coefficient of correlation on a programmable calculator or computer. From the coefficient of correlation, determine the optimum Ba-MTB ratio for a particular lot of

MTB. Use this ratio when preparing subsequent solutions of MTB-barium chloride reagent. Repeat this calibration procedure only when a different lot of MTB is used.

5.6 *Sodium hydroxide*, 0.18M: *Cautiously* dissolve 7.2 g NaOH in demineralized water and dilute to 1 L.

5.7 *Sulfate standard solution I*, 1.00 mL = 1.00 mg SO$_4$: Dissolve 1.4787 g Na$_2$SO$_4$, dried for 2 h at 180°C, in demineralized water and dilute to 1,000 mL.

5.8 *Sulfate working standards*: Prepare a blank and 1,000 mL each of a series of sulfate
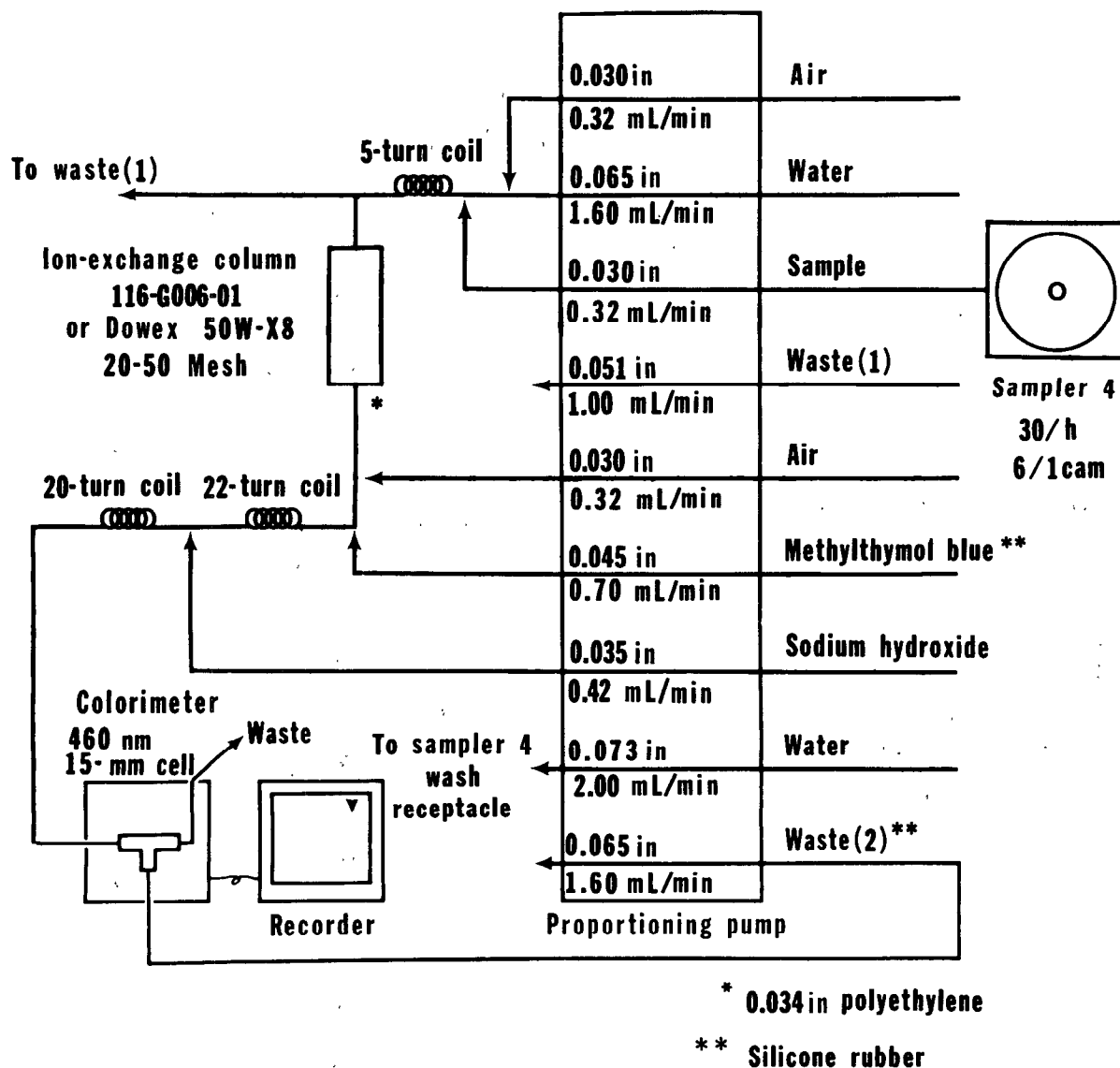

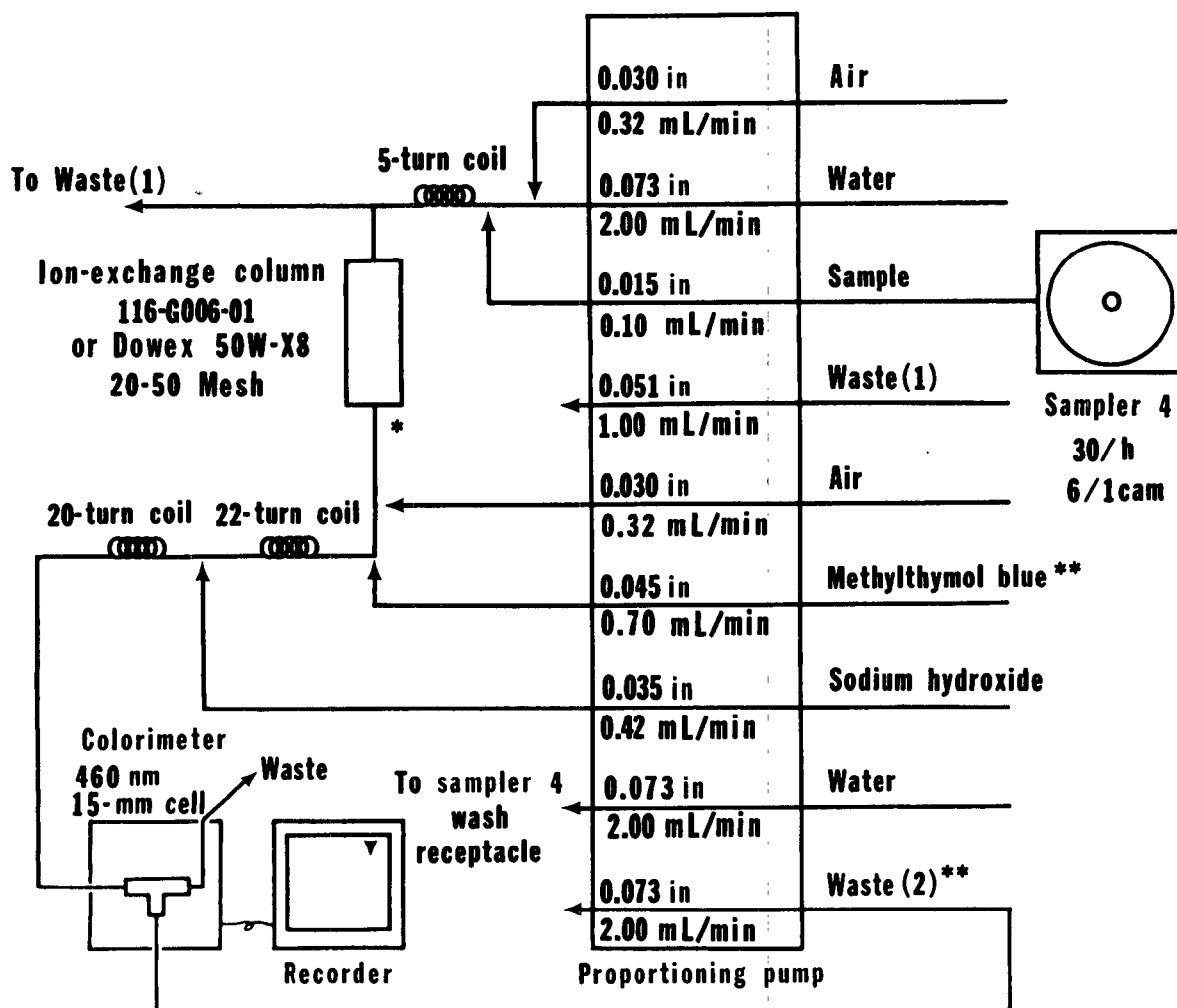Figure 45.—Sulfate, methylthymol blue manifold, low range, 5 to 100 mg/L SO$_4$

working standards by appropriate quantitative dilution of sulfate standard solution I as follows:

Sulfate standard solution I (mL)	Sulfate concentration (mg/L)
0.0	0.0
5.0	5.0
10.0	10.0
20.0	20
30.0	30
40.0	40
50.0	50
75.0	75
100.0	100
150.0	150
200.0	200
300.0	300

6. Procedure

6.1 Set up manifold (fig. 45 or 46, NOTES 1 and 2).

NOTE 1. The manifold includes a cation-exchange column consisting of a 2.0-mm ID Pyrex tube approx 19-cm (7.5-in.) long filled with Dowex 50W-X8 (20 to 50 mesh), or equivalent, cation-exchange resin. The resin is held in place by a loose plug of glass wool on the exit end. Regenerate the resin daily with $1M$ HCl. Tygon transmission tubing may be used in place of the Pyrex tube. The column must be replaced if air bubbles are introduced.

Figure 46.—Sulfate, methylthymol blue manifold, high range, 100 to 300 mg/L SO_4

NOTE 2. At the end of each day wash the system with a solution of EDTA: Place the MTB line and the NaOH line in water for a few minutes and then into the EDTA solution for 10 min. Wash the system with water for 15 min before shutting down.

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

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

6.4 Place a complete set of standards and a blank in the first positions of the first sample tray, beginning with the most concentrated standard. Place individual standards of differing concentrations in approx every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

6.5 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the curve reads full scale.

7. Calculations

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

7.2 Compute the sulfate concentration in milligrams per liter of 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.

8. Report

Report sulfate, dissolved (00945), concentra-

tions as follows: 5-9 mg/L, nearest 1 mg/L; 10 mg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved sulfate for 16 samples within the range of 14 to 943 mg/L may be expressed as follows:

$$S_T = 0.029X + 3.42$$

where
S_T = overall precision, milligrams per liter, and
X = concentration of sulfate, milligrams per liter.

The correlation coefficient is 0.8863.

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

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
7	13.9	12
10	59.2	9
12	143	5
6	526	2
15	943	3

References

Colovos, G., Panesar, M. R., and Parry, E. P., 1976, Linearizing the calibration curve in determination of sulfate by the methylthymol blue method: Analytical Chemistry, v. 48, p. 1693-6.

Lazarus, A., Lorange, E., and Lodge, J. P., Jr., 1968, New automated microanalyses for total inorganic fixed nitrogen and for sulfate ion in water, in Trace inorganics in water: American Chemical Society, Advances in Chemistry Series, No. 73, p. 164-71.

Sulfate, turbidimetric, barium sulfate, automated-discrete

Parameter and Code:

Sulfate, dissolved, I-2823-85 (mg/L as SO$_4$): 00945

1. Application

This method may be used to determine concentrations of sulfate in surface, domestic, and industrial water in the ranges of 0.2 to 1000 mg/L. Samples containing greater concentrations must first be diluted. Three working ranges are provided: from 0.2 to 10.0 mg/L, from 10 to 200 mg/L, and from 200 to 1000 mg/L.

2. Summary of method

Sulfate ion is reacted with barium chloride under acidic conditions to form barium sulfate. The absorbance of the resulting suspension is measured photometrically and is proportional to the sulfate concentration present in the original sample (Santiago and others, 1975).

3. Interferences

Suspended matter in large amounts will interfere. Natural color exceeding 50 platinum cobalt units may interfere. Silica, at concentrations less than 200 mg/L, does not interfere.

4. Apparatus

4.1 *Discrete analyzer system*, American Monitor IQAS or equivalent.

4.2 With this equipment the following operating conditions have been found satisfactory for the ranges: from 0.2 to 10.0 mg/L, from 10 to 200 mg/L, and from 200 to 1000 mg/L.

Wavelength	340 nm for 0.2 to 10.0 mg/L
	410 nm for 10 to 200 mg/L
	458 nm for 200 to 1000 mg/L
Absorption cell -----	1 cm square, temperature-controlled, flow-through quartz cuvette

Reaction temperature –	ambient	
Sample volumes	0.450 mL with 0.050 mL of diluent for 0.2 to 10.0 mg/L	
	0.200 mL with 0.050 mL of diluent for 10 to 200 mg/L	
	0.140 mL with 0.075 mL of diluent for 200-1000 mg/L (NOTE 1)	
Reagent volumes	0.25 mL BaCl$_2$-NaCl-HCl-gelatin solution and 0.25 mL sulfate standard solution IV for 0.2 to 10 mg/L	
	1.0 mL BaCl$_2$-NaCl-HCl-gelatin solution for 10 to 200 mg/L	
	2.0 mL BaCl$_2$-NaCl-HCl-gelatin solution for 200 to 1000 mg/L (NOTE 1)	

NOTE 1. Sample-to-diluent ratio and reagent volumes must be optimized for each individual instrument according to manufacturer's specifications.

5. Reagents

5.1 *Barium chloride-sodium chloride-hydrochloric acid-gelatin solution.*

5.1.1. *Sulfate ranges 0.2 to 10.0 mg/L and 10 to 200 mg/L*: Dissolve 20 g BaCl$_2$·2H$_2$O in 500 mL demineralized water, and add 10 mL concentrated HCl (sp gr 1.19), 0.5 g gelatin (USP) and 20 g NaCl. Mix well, dilute to 1,000 mL with demineralized water, and filter. Prepare fresh weekly.

5.1.2. *Sulfate range, 200 to 1000 mg/L*: Dissolve 10 g $BaCl_2 \cdot 2H_2O$ in 500 mL demineralized water, and add 10 mL concentrated HCl (sp gr 1.19), 0.125 g gelatin (USP) and 20 g NaCl. Mix well, dilute to 1,000 mL with demineralized water, and filter. Prepare fresh weekly.

5.2 *Sulfate standard solution I*, 1.00 mL = 10.0 mg SO_4: Dissolve 14.787 g Na_2SO_4, dried for 2 h at 180°C, in demineralized water and dilute to 1,000 mL.

5.3 *Sulfate standard solution II*, 1.00 mL = 1.00 mg SO_4: Dilute 100 mL standard solution I to 1,000 mL with demineralized water.

5.4 *Sulfate standard solution III*, 1.00 mL = 0.100 mg SO_4: Dilute 100 mL standard solution II to 1,000 mL with demineralized water.

5.5 *Sulfate standard solution IV*, 1.00 mL = 0.010 mg SO_4: Dilute 10.0 mL sulfate standard solution II to 1,000 mL with demineralized water.

5.6 *Sulfate working standards*: Prepare a blank and 1,000 mL each of a series of sulfate working standards by the appropriate dilution of sulfate standard solution I, II, or III as follows:

Standard solution I (mL)	Standard solution II (mL)	Standard solution III (mL)	Sulfate concentration (mg/L)
		5.0	0.5
		10.0	1.0
		50.0	5.0
		100.0	10.0
	20.0		20
	50.0		50
	125.0		125
20.0			200
30.0			300
50.0			500
80.0			800
100.0			1000

6. Procedure

6.1 Set up analyzer and computer-card assignments according to the manufacturer's instructions.

6.2 Place standards, beginning with the lowest concentration, in ascending order (computer-calibration curve) in the first five positions on the sample turntable. For the low range use 0.0, 0.5, 1.0, 5.0, and 10.0 mg/L SO_4; for the mid-range use 10, 20, 50, 125, and 200 mg/L; and for the high range use 200, 300, 500, 800, and 1,000 mg/L. Place samples and quality-control reference samples in the remainder of the sample turntable.

6.3 Begin analysis (NOTE 2).

NOTE 2. The cathode-ray tube (CRT) will acknowledge parameter and concentration range selected, listing each sample-cup number and corresponding concentrations calculated from the working curve. During each run, the CRT display will provide a plot of standards, samples, and list blank and slope calculations. Retain copy of all information obtained from the printer.

7. Calculations

Determine the milligrams per liter of sulfate in each sample from either the CRT display or the computer printout.

8. Report

Report sulfate, dissolved (00945), concentrations as follows: 0.2 to 10.0 mg/L, one decimal, 10 mg/L and above, two significant figures.

9. Precision

Precision expressed in terms of the standard deviation the and percent relative standard deviation for replicates analysis by a single operator is as follows (NOTE 3):

Mean (mg/L)	Number of replicates	Standard deviation (mg/L)	Relative standard deviation (percent)
0.7	22	0.08	11.0
1.3	22	.14	7.6
2.7	22	.14	5.0
4.4	22	.12	2.7
6.2	22	.12	1.9
14.3	21	.11	.5
272	22	1.14	4.2
112	21	.68	3.2
387	10	5.5	1.4
612	10	5.0	.8

NOTE 3. Some imprecision has been observed in the range from 8 to 12 mg/L. More precise data can be obtained by diluting samples within this range and determining sulfate in the 0.2 to 10 mg/L range.

Sulfate, ion-exchange chromatographic, automated

Parameters and Codes:
Sulfate, dissolved, I-2057-85 (mg/L as SO$_4$): 00945
Sulfate, dissolved, I-2058-85 (mg/L as SO$_4$): 00945

2. Summary of method

Sulfate is determined sequentially with six other anions by ion-exchange chromatography. Ions are separated based on their affinity for the exchange sites of the resin. The separated anions in their acid form are measured using an electrical-conductivity cell. See method I-2057, anions, ion-exchange chromatographic, automated and method I-2058, anions, ion-exchange chromatographic, precipitation, automated.

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Sulfate, titrimetric, thorin

Parameter and Code:
Sulfate, dissolved, I-1820-85 (mg/L as SO_4): 00945

1. Application

This method may used to analyze water containing from 0.5 to 200 mg/L of sulfate. Samples with greater concentrations need to be diluted or analyzed by an alternate method.

2. Summary of method

2.1 Thorin and barium react to form a complex that is deep red. The intensity of the color is dependent on pH, indicator concentration, and nature of the solvent. The color is more intense in organic than in aqueous solutions and also varies in intensity with different organic solvents. The color reaction can be utilized to titrate sulfate directly with barium chloride by adding a large volume of organic solvent to the sample and titrating in this mixed medium. When the end point is detected spectrometrically, the preferred titration medium is 80-percent alcohol maintained at pH 5 with a sodium acetate buffer.

2.2 The end point may also be detected by viewing the solution through a didymium glass filter. When visual detection is made, the titration medium should be 66-percent dioxane, adjusted to a pH between 2.2 and 5. The initial yellow color of thorin in the dioxane-water medium changes to pink at the end point.

3. Interferences

Thorin reacts with many metals, including calcium; therefore, all metal ions must be removed by cation exchange prior to titration. Phosphate interferes somewhat by coprecipitation; with 100 mg/L of sulfate, 10 and 20 mg/L of phosphate result in a positive error of about 2 and 3 percent, respectively. Color may interfere with the spectrometric reading and require correction.

4. Apparatus

4.1 *Absorption cells*, 50-mm. The cement in some cells reacts with thorin to produce a red color. Cells should be tested for thorin reaction, and those that produce a red color in 10 to 15 min should be rejected. Alternatively, 100-mL beakers may be used, providing the titration assembly is designed to accept such beakers.

4.2 *Buret*, 10-mL.

4.3 *Cation-exchange column* (fig. 47). The column should be filled to within 5 to 8 cm of the top with Amberlite IR-120 or equivalent,
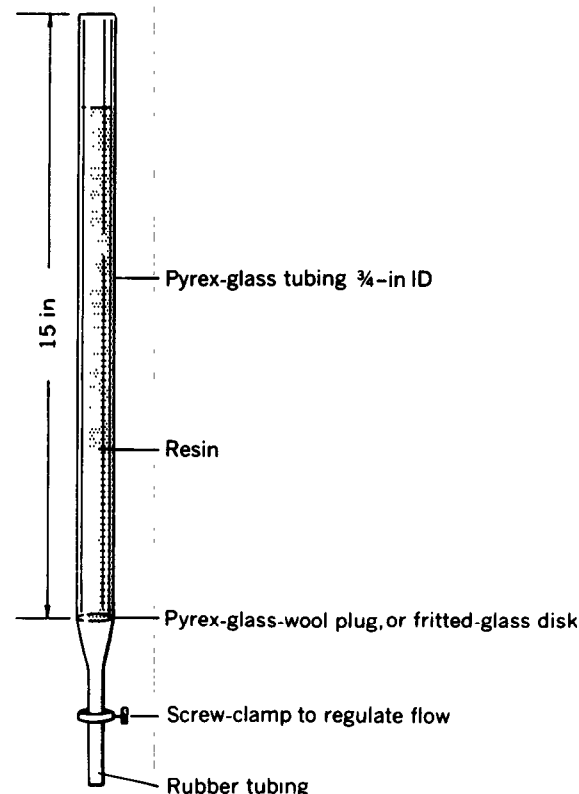

15 in

Pyrex-glass tubing ¾-in ID

Resin

Pyrex-glass-wool plug, or fritted-glass disk

Screw-clamp to regulate flow

Rubber tubing

Figure 47.—Cation-exchange column for sulfate

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operating on the hydrogen cycle. The resin is regenerated with 30-percent (volume-to-volume) HCl solution. The frequency of regeneration depends on the mineral content of the samples. The need for regeneration may be determined by checking a small portion of column effluent for the presence of calcium.

4.4 *Spectrophotometer* with titration assembly for use at 520 nm. Commercial instrumentation is available. Follow manufacturer's instruction for optimizing instrument conditions.

5. Reagents

5.1 *Barium standard solution*, 1.00 mL ♢ 0.20 mg SO_4^{-2}: Dissolve 0.5086 g $BaCl_2 \cdot 2H_2O$ (assay 99.0 percent minimum) in demineralized water and dilute to 1,000 mL. The exact concentration of this standard solution may be verified by titrating a known volume of sulfate standard solution as in the analytical procedure.

5.2 *Solvent indicator solution*: Dissolve 0.025 g thorin and 0.5 g anhydrous sodium acetate in 10 mL water, warming gently if necessary to ensure complete dissolution. Filter the solution through Whatman No. 1 filter paper into 1 L of 95-percent ethanol and discard the filter paper without washing or rinsing. Add 12 mL glacial CH_3COOH (sp gr 1.06) and mix. Difficulty in preparing a clear solution of the indicator is probably due to poor-quality thorin reagent.

5.3 *Sulfate standard solution*, 1.00 mL = 1.00 mg SO_4^{-2}: Dissolve 1.4787 g Na_2SO_4, dried for 2 h at 180 °C, in demineralized water and dilute to 1,000 mL.

6. Procedure

6.1 Rinse the cation-exchange columns with 20 to 30 mL of sample and discard the rinse. (Check a portion for the presence of calcium.)

6.2 Pass sufficient sample through the exchanger to provide at least 10 mL of effluent for the determination.

6.3 Pipet a volume of sample containing less than 2 mg SO_4^{-2} and 10 mg dissolved solids

(10.0 mL max) into a 50-mm absorption cell and adjust the volume to 10.0 mL.

6.4 Add 40 mL solvent indicator solution.

6.5 Insert cell in titration assembly and begin analysis.

6.6 Titrate with $BaCl_2$ (1.00 mL ♢ 0.20 mg SO_4^{-2}).

6.7 Determine a blank correction by titrating demineralized water. The blank is constant throughout the concentration range of the method. A blank of 0.05 mL has been found. Correct for water color when necessary.

7. Calculations

$$SO_4 \text{ in mg/L} = \frac{1,000}{\text{mL sample}} \times$$

$$0.2 \times (\text{mL titrant–mL blank})$$

8. Report

Report sulfate, dissolved (00945), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved sulfate for 11 samples within the range of 9.8 to 394 mg/L may be expressed as follows:

$$S_T = 0.026X + 0.686$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of sulfate, milligrams per liter.

The correlation coefficient is 0.9010.

9.2 Precision for dissolved sulfate for four of the 11 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
13	9.8	6
18	50.8	4
18	141	2
16	394	3

Sulfide, titrimetric, iodometric

Parameter and Code:
Sulfide, total, I-3840-85 (mg/L as S): 00745

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing more than 0.5 mg/L of sulfide.

1.2 Water-suspended sediment may be analyzed by this method if sample is shaken vigorously and a suitable aliquot of well-mixed sample is rapidly withdrawn.

1.3 Water containing dissolved sulfides readily loses hydrogen sulfide, particularly if the pH of the sample is low. Oxygen destroys sulfides by oxidation, particularly if the pH of the sample is high. Aeration and agitation of the sample should, therefore, be avoided. The addition of 2 g of zinc acetate per liter of water will fix the sample for several days. Acidic water must be neutralized before addition of zinc acetate.

2. Summary of method

2.1 This iodometric method does not differentiate the forms of the sulfide ion in solution.

2.2 Sulfide is reacted with an excess of iodine in acid solution, and the remaining iodine is then determined by titration with sodium thiosulfate, using starch as an indicator (Kolthoff and others, 1969).

$$S^{-2} + I_2 \xrightarrow{H^{+1}} S + 2I^{-1}$$

$$I_2 + 2S_2O_3^{-2} \xrightarrow{H^{+1}} S_4O_6^{-2} + 2I^{-1}$$
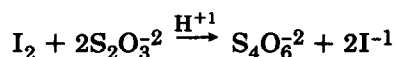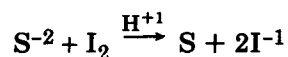
A blank is treated exactly the same as the samples. The sulfide concentration is calculated from the difference between the volume of thiosulfate required for the blank and the volume used for the sample.

2.3 This method is similar to that in an article published by the American Public Health Association (1980).

3. Interferences

Reducing substances such as sulfites and heavy-metal ions react with iodine, which contributes to positive errors. Oxygen and other oxidants may react with hydriodic acid to liberate iodine, which contributes to negative errors.

4. Apparatus

4.1 *Buret*, 10-mL capacity.

4.2 *Flasks*, Erlenmeyer, 250-mL capacity.

5. Reagents

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

5.2 *Iodine standard solution*, 0.010N: Dissolve 6 g iodate-free KI in approx 25 mL water. Add 1.2690 g resublimed I_2. When solution is complete, dilute to 1 L. Standardize with 0.010N $Na_2S_2O_3$, using starch as an indicator.

$$\text{Normality of } I_2 = \frac{0.010 \times \text{mL } Na_2S_2O_3}{\text{mL } I_2}$$

Adjust the normality of the iodine standard solution, if necessary, to 0.010 by addition of small quantities of demineralized water or iodine as indicated by the first titration. Confirm the normality by restandardization.

5.3 *Potassium iodide*, crystals, iodate-free: The KI can be tested for IO_3^{-1} by dissolving about 0.1 g in 5 mL water, acidifying with 1 or

2 drops concentrated H_2SO_4 (sp gr 1.84) and adding 2 to 3 mL starch indicator solution. Immediate appearance of blue color indicates the presence of IO_3^{-1}; slow color formation is caused by atmospheric oxidation.

5.4 *Sodium thiosulfate standard solution*, 0.010*N*: Dissolve 2.482 g $Na_2S_2O_3 \cdot 5H_2O$ in carbon dioxide-free water and dilute 1 L with carbon dioxide-free water. Standardize against KIO_3 as follows: Dry approx 0.5 g KIO_3 for 2 h at 180°C. Dissolve 0.3567 g in water and dilute to 1,000 mL. Pipet 25.0 mL KIO_3 solution into a 250-mL Erlenmeyer flask, then add successively 75 mL deionized water and 0.5 g iodate-free KI. After solution is complete, add 10 mL HCl (sp gr 1.19). Allow the stoppered flask to stand 5 min in the dark and titrate with $Na_2S_2O_3$ solution, adding starch indicator solution as the end point is approached (light-straw color):

$$\text{Normality of } Na_2S_2O_3 = \frac{0.25}{\text{mL } Na_2S_2O_3}$$

Adjust the normality of the thiosulfate standard solution, if necessary, to 0.010 by addition of small quantities of demineralized water or sodium thiosulfate as indicated by the first titration. Confirm the normality by restandardization.

5.5 *Starch indicator solution*, stable (NOTE 1).

NOTE 1. A convenient substitute for starch indicator solution is the product thyodene, sold by Fisher Scientific Co. It can be used in its dry form and produces an end point similar to that of starch.

6. Procedure

6.1 Shake the sample vigorously and immediately pipet a volume of sample with ZnS in suspension containing less than 1.5 mg S^{-2} (100.0 mL max) into a 250-mL Erlenmeyer flask, and adjust the volume to approx 100 mL.

6.2 Prepare a blank of approx 100 mL demineralized water, and carry it through the procedure with the sample.

6.3 Add 10.0 mL 0.010*N* I_2 and mix.

6.4 Without delay add 10 mL concentrated HCl.

6.5 Immediately titrate the excess I_2 with 0.010*N* $Na_2S_2O_3$, adding 2 to 3 mL starch indicator solution as the end point is approached (light-straw color).

7. Calculations

$$S^{-2} \text{ (mg/L)} = \frac{1,000}{\text{mL sample}} \times 0.1603$$

$$\times \text{ (mL blank titrant–mL sample titrant)}$$

8. Report

Report sulfide, total (00745), concentrations as follows: 0.5 to 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

References

American Public Health Association, 1980, Standard methods for the examination of water and wastewater (15th ed.): Washington, D.C., p. 448.

Kolthoff, I. M., Sandell, E. B., Meehan, E. J., and Bruckenstein, S., 1969, Quantitative Chemical Analysis (4th ed.): New York, Macmillan, p. 857.

Thallium, atomic absorption spectrometric, graphite furnace

Parameter and Code:
Thallium, dissolved, I-1866-85 (μg/L as Tl): 01057

1. Application

This method may be used to analyze water containing at least 1 μg/L of thallium. Samples containing more than 9 μg/L need either to be diluted or a smaller volume needs to be used for analysis.

2. Summary of method

2.1 Thallium is determined by atomic absorption spectrometry in conjunction with a graphite furnace and the method of standard additions. The sample is placed in the graphite tube and is then evaporated to dryness, charred, and atomized. The absorbance signal generated during atomization is recorded. Known concentrations of thallium are added to aliquots of the sample in the tube and the technique is repeated. The absorbances are then plotted and the concentration of thallium is determined by extrapolation.

2.2 Pretreatment of the graphite tube with ammonium molybdate and addition of ammonium nitrate to the sample in the graphite tube are employed to reduce background scattering.

2.3 For discussion of standard additions, see this chapter, Analytical techniques, atomic absorption spectrometry.

3. Interferences

False peaks or recorder deflections below the baseline often occur during the atomization cycle because of heavy background scattering in this wavelength region (276.8 nm) and because of the requirement for very close alignment of the deuterium background corrector and source (electrodeless-discharge lamp).

4. Apparatus

4.1 *Atomic absorption spectrometer*, for use at 276.8 nm, equipped with deuterium background correction, graphite furnace, and recorder with 2.5-mv or 5.0-mv range.

4.2 Refer to the manufacturer's manual to optimize instrumental performance.

4.3 *Graphite furnace*, capable of reaching temperatures sufficient to atomize thallium. *CAUTION*: Dial settings frequently are inaccurate and newly conditioned furnaces require temperature calibration. Use the following operating conditions:

Drying temperature ------ 100 °C
Charring temperature ----- 400 °C
Atomizing temperature --- 2400 °C
Drying time ------------- (NOTE 1)
Charring time ----------- 15 s
Atomizing time ---------- 10 s
Purge gas --------------- Argon, 25 cm^3/min normal flow

NOTE 1. Set drying time for as many seconds as the total microliters of sample plus standard injected.

4.4 *Graphite tubes*, compatible with furnace. Standard graphite tubes are preferred.

4.5 *Pipets*, microliter with disposable tips, 1- to 50-μL capacity.

4.6 *Thallium light source*, thallium electrodeless-discharge lamp.

4.7 *Argon*, standard, welder's grade, commercially available. Nitrogen may also be used if recommended by the instrument manufacturer.

5. Reagents

5.1 *Ammonium hydroxide solution, 3M*: Dilute 20 mL concentrated NH$_4$OH (sp gr 0.90) to 100 mL with demineralized water.

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5.2 *Ammonium molybdate solution*, 8.7 g/50 mL: Dissolve 9.2 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 40 mL $3M$ ammonium hydroxide solution and dilute to 50 mL with demineralized water.

5.3 *Ammonium nitrate solution*, 25 g/50 mL: Dissolve 25 g NH_4NO_3 in 50 mL demineralized water.

5.4 *Nitric acid*, concentrated (sp gr 1.41): High-purity, Ultrex or equivalent.

5.5 *Nitric acid solution*, (1 + 499): Mix 1 part concentrated HNO_3 (sp gr 1.41) with 499 parts demineralized water.

5.6 *Thallium standard solution I*, 1.00 mL = 1000 μg Tl: Dissolve 1.303 g $TlNO_3$ in demineralized water. Add 2 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1000 mL with demineralized water.

5.7 *Thallium standard solution II*, 1.00 mL = 20.0 μg Tl: Dilute 20.0 mL thallium standard solution I to 1,000 mL with nitric acid solution (1 + 499).

5.8 *Thallium working standards*: Dilute 50, 100, and 150 μL each of thallium standard solution II to 250 mL with nitric acid solution. These working standards represent concentrations of 4, 8, and 12 pg/μL of thallium. Prepare fresh daily (NOTE 2).

NOTE 2. Clean the 250-mL volumetric flasks with dilute nitric acid (1 + 50) and rinse with demineralized water immediately before use. Rinse the 50-μL micropipet disposable plastic tip twice in a solution of nitric acid (1 + 2), twice in demineralized water, and twice in thallium standard solution II before preparing the working standards.

6. Procedure

6.1 Prior to use, rinse pipet tips twice with a solution of nitric acid (1 + 2) and then twice in demineralized water.

6.2 Pretreat the graphite tube. Inject 25 μL ammonium molybdate solution and cycle as follows: dry for 20 s at 110°C, char for 15 s at 550°C, and atomize for 10 s at 2500°C. Use an argon flow of 12 mL/min in the interrupt mode. Repeat injection and cycle three times.

6.3 Inject 30 μL of sample into the graphite tube and dry, char, and atomize as given in step 4.3.

6.4 From the signal's peak height obtained in paragraph 6.3, choose a sample volume which will give a signal less than 40 percent of full scale on the recorder.

6.5 Choose a volume of thallium working standards that, when added to the sample aliquot, will produce a 50-, 100-, and 150-percent increase in signal peak height (NOTE 3). Inject the same volume of demineralized water to the sample for the blank spike.

NOTE 3. To determine the approx signal (absorbances or peak heights) of the thallium working standards, inject 30 μL of the low working standard, cycle, and record signal. From this information, the volume of standard can be determined.

6.6 Inject in the graphite tube the aliquot of sample and blank as determined in steps 6.4 and 6.5. Cycle as given in paragraph 4.3 and record absorbance or peak height. Repeat process with sample and the standard additions of thallium working standards as determined in steps 6.4 and 6.5. Analyze the sample plus standards twice (NOTE 4).

NOTE 4. If background interferences occur as mentioned in paragraph 2.2, inject 20 μL ammonium nitrate solution to each sample, standard, and blank.

7. Calculations

7.1 Plot absorbances (or peak heights) of sample plus standards on the vertical axis of a graph and the mass, in pg, added on the horizontal axis.

7.2 Fit the points to a straight line by the least-squares method and extrapolate the line to the horizontal axis. The mass of thallium present in the sample is the reading at the horizontal intercept.

7.3 Determine the micrograms per liter of dissolved thallium in each sample as follows:

$$Tl(\mu g/L) = \frac{\text{mass Tl in sample (pg)}}{\text{volume of sample } (\mu L)}$$

8. Report

Report thallium, dissolved (01057), concentrations to the nearest microgram per liter.

9. Precision

9.1 Precision for dissolved thallium for four samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
4	3.2	75
5	3.4	38
6	3.8	39
3	5.0	20

9.2 Analyses of two samples six times each by a single operator resulted in mean values of 5.6 and 10.9 μg/L and relative standard deviations of 10 and 3 percent, respectively.

Tin, atomic absorption spectrometric, hydride, automated

Parameters and Codes:

Tin, dissolved, I-2851-85 (μg/L as Sn): 01100
Tin, total recoverable, I-4851-85 (μg/L as Sn): 01102
Tin, suspended recoverable, I-7851-85 (μg/L as Sn): 01101
Tin, recoverable-from-bottom-material, dry wt, I-6851-85 (μg/g as Sn): 01103

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing from 1 to 10 μg/L of tin. Samples containing more than 10 μg/L need to be diluted.

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

1.3 This method may used to analyze bottom material containing at least 0.1 μg/g of inorganic tin. Sample solutions containing more than 10 μg/L must be diluted.

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

2. Summary of method

2.1 Tin is reduced to tin hydride with sodium borohydride. Interferences from most major and trace elements in the hydride-generation step are reduced to insignificance by addition of EDTA. The tin hydride is stripped from the solution by a stream of nitrogen gas and conveyed to a tube furnace placed in the optical path of an atomic absorption spectrometer, where it is decomposed to atomic tin. The optical absorbance is measured and related to the tin concentration in the original sample.

2.2 For additional information see Vijan and Chan (1976) and Pyen and Fishman (1979).

3. Interferences

3.1 No interferences in the hydride-generation process have been observed from aluminum, iron, barium, beryllium, cadmium, chromium, cobalt, lead, lithium, manganese, mercury, molybdenum, nickel, selenium, and zinc at concentrations to 1 mg/L each, or from calcium, potassium, and sodium at concentrations up to 1,000 mg/L each.

3.2 Antimony, arsenic, copper, and silver concentrations greater than 200 μg/L, 100 μg/L, 300 μg/L and 100 μg/L, respectively, depress the tin absorption. At 300 μg/L of antimony, 200 μg/L of arsenic, 400 μg/L of copper, and 200 μg/L of silver, the depression is approx 16, 15, 8, and 20 percent, respectively.

3.3 Magnesium at concentrations greater than 300 mg/L depresses the tin absorption. At 400 and 1,000 mg/L, the depression is approximately 20 and 24 percent, respectively.

4. Apparatus

4.1 *Atomic absorption spectrometer* and recorder.

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

Grating ------------- Ultraviolet
Wavelength counter --- 286.3 nm
Source (electrodeless-
    discharge lamp) ----- Tin

4.2 *Autotransformer, variable*: Superior Powerstat Type 3 PN 1010 or equivalent.

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

4.4 *Stripping-condensing column*, Pyrex, packed with 3- to 5-mm Pyrex beads (fig. 48). The condensing column need not be cooled. The nitrogen gas flow rate is adjusted for maximum sensitivity by analyzing a series of identical standards. A flow rate of approx 225 mL/min has been found satisfactory.
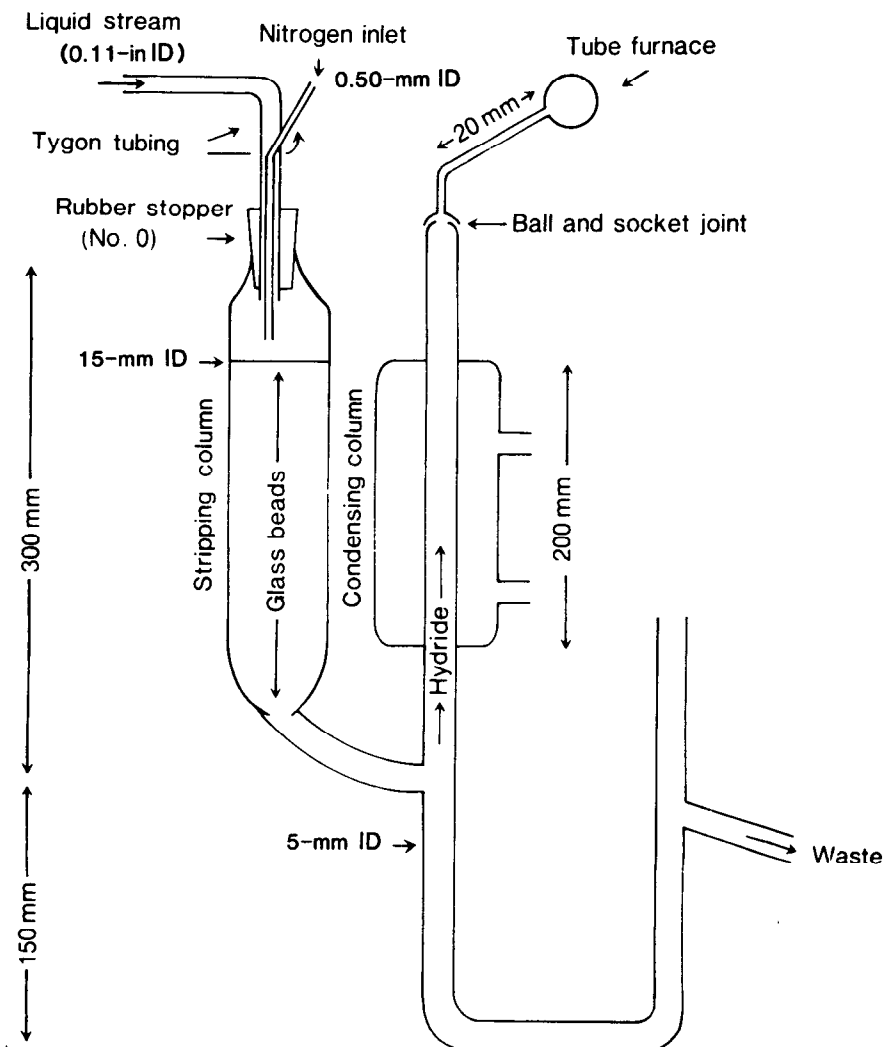
Figure 48.—Stripping-condensing column and quartz tube furnace

4.5 *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.

4.6 *Technicon AutoAnalyzer II*, consisting of sampler, manifold, proportioning pump, and recorder.

Cam ---------------- 20 (2/1)

5. Reagents (NOTE 1)

NOTE 1. Because tin is used extensively in metal products, its occurrence in laboratories is ubiquitous. Extreme care is required in the preparation of reagents to avoid contamination. Wash all glassware, including pipets, with 1:1 HCl just prior to use in the preparation of reagent and standard solutions.

5.1 *(Ethylenedinitrilo) tetraacetic acid, tetrasodium salt solution*, 41.6 g/L: Dissolve 41.6 g Na_4EDTA in demineralized water and dilute to 1 L.

5.2 *Hydrochloric acid*, 3M: Add 250 mL concentrated HCl (sp gr 1.19) to demineralized water and dilute to 1 L.

5.3 *Nitrogen gas*, N_2.

5.4 *Sodium borohydride solution*, 5 g/L: Dissolve 5 g $NaBH_4$ and 40 g NaOH in demineralized water and dilute to 1 L.

5.5 *Tin standard solution I*, 1.00 mL = 1.00 mg Sn: Dissolve 1.0 g tin metal in 15 mL of aqua regia in a beaker. Heat to dissolve the tin metal and evaporate just to dryness. To the residue add 100 mL concentrated HCl (sp gr 1.19). Mix until the residue dissolves. Transfer the solution to a volumetric flask containing demineralized water and dilute to 1,000 mL. Prepare fresh each month.

5.6 *Tin standard solution II*, 1.00 mL = 10.0 μg Sn: Dilute 5.00 mL tin standard solution I and 50 mL concentrated HCl (sp gr 1.19) to 500 mL with demineralized water. Prepare fresh daily.

5.7 *Tin standard solution III*, 1.00 mL = 0.10 μg Sn: Dilute 5.00 mL tin standard solution II and 50 mL concentrated HCl (sp gr 1.19) to 500 mL with demineralized water. Prepare fresh daily.

5.8 *Tin working standards*: Prepare daily a blank and 200 mL each of a series of tin working standards by appropriate quantitative dilution of tin standard solution III and concentrated HCl (sp gr 1.19) as follows:

Tin standard solution III (mL)	Concentrated HCl (mL)	Tin concentration (μg/L)
0.0	2.0	0
2.0	1.8	1
4.0	1.6	2
10.0	1.0	5
20.0	.0	10

6. Procedure

6.1 Set up manifold (fig. 49).

6.2 Set the tube-furnace temperature at 850°C (about 47 V on the autotransformer) and monitor using the portable pyrometer with the thermocouple placed in the center of the tube. Adjust voltage on the autotransformer as appropriate.

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

6.4 Prepare the sample trays as follows: (1) In the first tray, place three tubes of the most concentrated standard followed by one tube each of the remaining standards and the blank in decreasing concentrations; (2) place individual standards of differing concentrations in
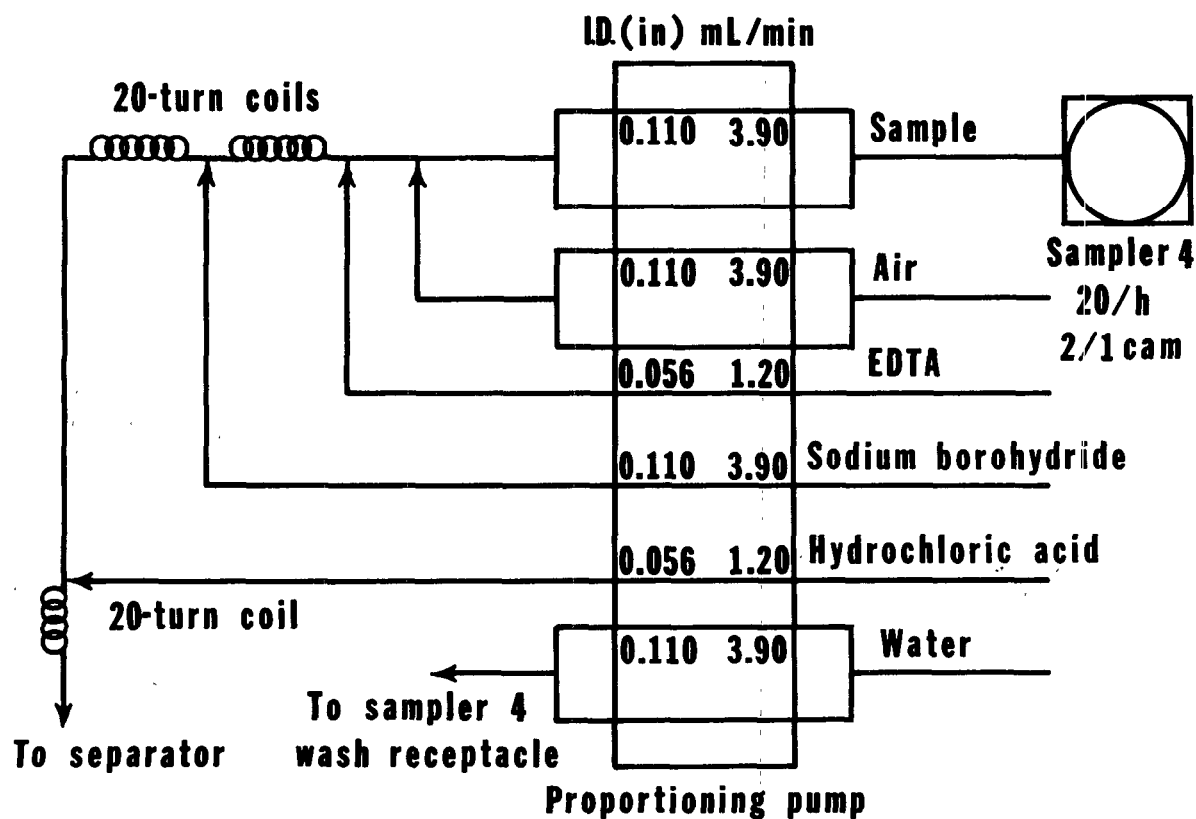

Figure 49.—Tin, hydride manifold

every eighth position of the remainder of this and subsequent trays; (3) fill remainder of each sample tray with unknown samples.

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

6.6   With a 5-mV recorder, 10 μg/L of tin will give a peak approx 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:

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

6.6.2 Grind the cell with silicon carbide as follows: Mount cell with suitable cushioning in a ¾-inch chuck on a slowly-revolving shaft. Wet inside of cell and apply grinding compound such as commercial auto-valve-grinding compound. Using a standard speed drill and an aluminum oxide grinding wheel suitably reduced in diameter to give adequate clearance, and plenty of water, begin grinding cell with a steady movement from inside to outside of cell. Grind one-half of cell at a time and regrind if necessary to achieve an even frosting.

7. Calculations

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

7.2   Determine the concentration of dissolved or total recoverable tin 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 micrograms per liter of suspended recoverable tin, subtract dissolved-tin concentration from total-recoverable-tin concentration.

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

$$Sn \ (\mu g/g) = \frac{\mu g/L \ Sn \times mL \ of \ digest/1000}{wt \ of \ sample \ (g)}$$

8. Report

8.1   Report tin, dissolved (01100), total-recoverable (01102), and suspended-recoverable (01101), concentrations as follows: less than 10 μg/L, nearest μg/L; 10 μg/L and above, two significant figures.

8.2   Report tin, recoverable-from-bottom-material (01103), concentrations as follows: less than 1.0 μg/g, nearest 0.1 μg/g; 1.0 μg/g and above, two significant figures.

9. Precision

9.1   Determination of dissolved tin in four test samples 10 times each by one operator resulted in mean values of 5.1, 9.2, 9.7, and 10.0, μg/L and standard deviations of 0.3, 0.3, 0.4, and 0.1, respectively.

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

Number of replicates	Mean (μg/L)	Relative standard deviation (percent)
10	5.1	6
10	9.2	3
10	9.7	4
10	10.0	1

9.3   Determination of total recoverable tin in five test samples 10 times each by one operator resulted in mean values of 5.3, 9.8, 10.1, 10.5, and 11.7 μg/L and standard deviations of 0.2, 0.4, 0.2, 0.3, and 0.5, respectively.

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

Number of replicates	Mean (μg/L)	Relative standard deviation (percent)
10	5.3	4
10	9.8	4
10	10.1	2
10	10.5	3
10	11.7	4

9.5   Determination of tin in bottom material in four test samples 10 times each by one operator resulted in mean values of 0.36, 0.56, 0.68, and 0.94 μg/g and standard deviations of 0.04, 0.03, 0.03, and 0.02, respectively.

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

Number of replicates	Mean (µg/L)	Relative standard deviation (percent)
10	0.36	11
10	0.56	5
10	0.68	4
10	0.94	2

References

Pyen, G., and Fishman, M. J., 1978, Automated determination of tin in water: Atomic Absorption Newsletter, v. 18, p. 34–26.

Vijan, P. N., and Chan, C. Y., 1976, Determination of tin by gas phase atomization atomic absorption spectrometry: Analytical Chemistry, v. 48, p. 1788–92.

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

Parameter and Code:
Titanium, total, I-5474-85 (mg/kg as Ti): 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 hot plate at 200 °C. Titanium 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.

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Turbidity, nephelometric

1. Application

This method is generally applicable to any water that does not contain coarse material that settles rapidly. Samples having greater than 100 nephelometric turbidity units (NTU) must be diluted prior to analysis.

2. Summary of method

2.1 The method presented below is based upon a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension under the same conditions. The greater the intensity of scattered light, the greater the turbidity. Formazin polymer, which has gained acceptance as the turbidity standard reference suspension in the brewing industry, is also used as the turbidity standard reference suspension for water. It is easy to prepare and is more reproducible in its light-scattering properties than is clay or turbid, natural-water standards. The turbidity of a particular concentration of Formazin suspension is defined as 40 NTU. This same suspension of Formazin has a turbidity of approximately 40 units when measured on the Jackson candle turbidimeter; therefore, turbidity units based on the Formazin preparation will closely approximate those derived from the Jackson candle turbidimeter but may not always be identical to them.

2.2 For additional information on the turbidity measurement and its significance, see American Public Health Association and others (1980), California State Water Quality Control Board (1963), and U.S. Public Health Service (1962).

3. Interferences

The presence of colored solutes causes measured turbidity values to be low. Precipitation of dissolved constituents (for example, Fe) causes measured turbidity values to be high.

4. Apparatus

Hach turbidimeter, Model No. 2100 or 2100A.

5. Reagents

5.1 *Hexamethylenetetramine solution*, 10 g/100 mL: Dissolve 10.0 g hexamethylenetetramine in demineralized water and dilute to 100.0 mL.

5.2 *Hydrazine sulfate solution*, 1 g/100 mL: Dissolve 1.000 g $(NH_2)_2 \cdot H_2SO_4$ in demineralized water and dilute to 100.0 mL.

5.3 *Turbidity standard suspension I* (Formazin): In a 100-mL volumetric flask mix 5.0 mL hydrazine sulfate solution with 5.0 mL hexamethylenetetramine solution. After 24 h standing at $25 \pm 3\,°C$, dilute to 100.0 mL with demineralized water and mix well. Prepare fresh monthly (NOTE 1).

NOTE 1. Prepared standards of several ranges are available from the instrument manufacturer. These have a reliable shelf life of 4 to 6 months, thereby making more frequent preparation unnecessary.

5.4 *Turbidity standard suspension II*: Dilute 10.0 mL turbidity standard suspension I to 100.0 mL with demineralized water. The turbidity of this suspension is defined as 40 nephelometric turbidity units (NTU). Prepare fresh weekly. This suspension may be diluted

as required to prepare more dilute turbidity standards.

6. Procedure

6.1 *Turbidimeter calibration*: The manufacturer's operating instructions should be followed. Measure the standards on the turbidimeter covering the range of 0 to 100 NTU. If the instrument is already calibrated in standard turbidity units, this procedure will check the accuracy of the calibration. At least one standard should be included for each instrument range to be used. Some instruments permit adjustment of sensitivity so that scale values will correspond to turbidities. *Reliance on a manufacturer's solid-scattering standard for setting overall instrument sensitivity for all ranges is not an acceptable practice unless the turbidimeter has been shown to be free of drift on all ranges.* If a pre-calibrated scale is not supplied, then a calibration graph should be prepared for each range of the instrument.

6.2 *Turbidity less than 100 NTU*: Shake the sample to disperse the solids thoroughly. Wait until air bubbles disappear; then pour the sample into the turbidimeter tube. Read the turbidity directly from the instrument scale or from the appropriate calibration curve.

6.3 *Turbidity exceeding 100 NTU*: Dilute the sample with one or more volumes of nonturbid water until the turbidity falls below 100 NTU.

7. Calculations

Turbidity (NTU) =

$$\text{observed turbidity} \times \frac{\text{final dilution volume}}{\text{original sample volume}}$$

8. Report

Report turbidity (00076) as follows: less than 10 NTU, one decimal; 10 NTU and above, two significant figures.

9. Precision

According to data reported by the U.S. Environmental Protection Agency, the precision of data from a single laboratory expressed in terms of the percent relative standard deviation is as follows:

Mean (NTU)	Relative standard deviation (percent)
0.26	2

References

American Public Health Association and others, 1980, Standard methods for the examination of water and wastewater 15th ed. : Washington, D.C., p. 132–4.

California State Water Quality Control Board, 1963, Water quality criteria: Publication 3-A, p. 290.

U.S. Environmental Protection Agency, 1979, Methods for chemical analysis of water and wastes: Cincinnati, p. 180.1–1.

U.S. Public Health Service, 1962, Drinking water standards: Public Health Service Publication 956, p. 6.