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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

Cobalt, atomic absorption spectrometric, chelation-extraction

Parameters and Codes:

Cobalt, dissolved, I-1240-85 (μg/L as Co): 01035
Cobalt, total recoverable, I-3240-85 (μg/L as Co): 01037
Cobalt, suspended recoverable, I-7240-85 (μg/L as Co): 01036

1. Application

1.1 This method may be used to analyze water, brines, and water-suspended sediment containing from 1 to 50 μg/L of cobalt. Sample solutions containing more than 50 μg/L need either to be diluted prior to chelation-extraction or to be analyzed by the atomic absorption spectrometric direct method.

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

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

1.4 If the iron concentration of the sample solution exceeds 25,000 μg/L, determine cobalt by atomic absorption spectrometric direct method.

2. Summary of method

Cobalt is determined by atomic absorption spectrometry following chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into an air-acetylene flame of the spectrometer (Fishman and Midgett, 1968).

3. Interferences

Concentrations of iron greater than 25,000 μg/L interfere by suppressing the cobalt absorption.

4. Apparatus

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

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

Grating	Ultraviolet
Wavelength	240.7 nm
Source (hollow-cathode lamp)	Cobalt
Oxidant	Air
Fuel	Acetylene
Type of flame	Oxidizing

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

5. Reagents

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

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

5.3 *Cobalt standard solution I*, 1.00 mL = 100 μg Co: Dissolve 0.1407 g Co_2O_3 in a minimum amount of dilute HNO_3. Add 10 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1000 mL with demineralized water.

5.4 *Cobalt standard solution II*, 1.00 mL = 2.0 μg Co: Dilute 20.0 mL cobalt standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water.

5.5 *Cobalt standard solution III*, 1.00 mL = 0.2 μg Co: Immediately before use, dilute 10.0 mL cobalt standard solution II to 100.0 mL with acidified water. This standard is used to prepare working standards at the time of analysis.

5.6 *Methyl isobutyl ketone (MIBK).*

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

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

NOTE 1. Alternatively, a 2.5*M* NH_4OH solution may be used. Add 167 mL concentrated NH_4OH (sp gr 0.90) to 600 mL demineralized water. Cool, and dilute to 1 L.

5.9 *Water, acidified*: Add 1.5 mL concentrated HNO_3 (sp gr 1.41) to 1 L of demineralized water.

6. Procedure

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

6.2 Pipet a volume of sample solution containing less than 5.0 μg Co (100 mL max) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

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

6.4 With a pH meter, adjust the pH of each solution to 2.7 with 2.5*M* KOH (NOTES 2 and 3). Shake for 3 min.

NOTE 2. For water-suspended sediment samples that have been digested, add 1 to 2 mL 10*M* KOH or concentrated NH_4OH (sp gr 0.90) before pH adjustment.

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

6.5 Add 2.5 mL APDC solution and mix.

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

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

6.8 Aspirate the ketone layer within 1 h. 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 cobalt in each sample from the digital display or printer. Dilute those samples containing cobalt concentrations that exceed the working range of the method; repeat the chelation-extraction, and multiply by the proper dilution factors.

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

8. Report

Report cobalt, dissolved (01035), total-recoverable (01037), and suspended-recoverable (01036), concentrations as follows: less than 100 μg/L, nearest microgram per liter; 100 μg/L and above, two significant figures.

9. Precision

9.1 The standard deviation for dissolved cobalt within the range of 2.0 to 14.0 μg/L for 17 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 1.6 μg/L ranged from 1.4 to 1.9 μg/L.

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

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
3	2.0	0
6	2.2	79
9	5.3	23
5	11.4	13
8	14.0	14

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

Reference

Fishman, M. J., and Midgett, M. R., 1968, Extraction techniques for the determination of cobalt, nickel, and lead in fresh water by atomic absorption, *in* Trace inorganics in water: American Chemical Society, Advances in Chemistry Series, no. 73, p. 230-5.

Cobalt, atomic absorption spectrometric, direct

Parameters and Codes:

Cobalt, dissolved, I-1239-85 (μg/L as Co): 01035
Cobalt, total recoverable, I-3239-85 (μg/L as Co): 01037
Cobalt, suspended recoverable, I-7239-85 (μg/L as Co): 01036
Cobalt, recoverable-from-bottom-material, dry wt, I-5239-85, (μg/g as Co): 01038

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 50 μg/L of cobalt. Samples solutions containing more than 1,000 μg/L need either to be diluted or to be read on a less expanded scale. Sample solutions containing less than 50 μg/L need to be analyzed by the atomic absorption spectrometric chelation-extraction method, providing the interference limits discussed in that method are not exceeded.

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

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

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

2. Summary of method

Cobalt is determined by atomic absorption spectrometry by direct aspiration of the sample into an air-acetylene flame without additional treatment of the sample other than the addition of ammonium chloride to mask certain interferences.

3. Interferences

3.1 Nitrate at 1 mg/L interferes by suppressing the absorption of the cobalt. This interference is eliminated in solutions containing about 18,000 mg/L of ammonium chloride. Samples adjusted to this concentration of ammonium chloride show no interference from 800 mg/L of nitrate.

3.2 Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), calcium (4,500 mg/L), magnesium (4,500 mg/L), sulfate (9,000 mg/L), chloride (15,000 mg/L), iron (4×10^6 μg/L), and cadmium, nickel, copper, zinc, lead, and chromium (10,000 μg/L) do not interfere. Higher 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 -------- 240.7 nm
Source (hollow-cathode lamp) ------------ Cobalt
Oxidant ------------ Air
Fuel --------------- Acetylene
Type of flame ------- Oxidizing

4.3 The Perkin-Elmer, flathead, single-slot burner allows a working range of 50 to 1,000 μg/L. Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Ammonium chloride solution*, 200 g/L: Dissolve 200 g NH_4Cl in demineralized water and dilute to 1 L with demineralized water.

5.2 *Cobalt standard solution I*, 1.00 mL= 100 µg Co: Dissolve 0.1407 g Co_2O_3 in a minimum amount of dilute HNO_3. Add 10 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1000 mL with demineralized water.

5.3 *Cobalt standard solution II*, 1.00 mL= 10 µg Co: Dilute 100.0 mL cobalt standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water.

5.4 *Cobalt standard working solutions*: Prepare a series of at least six standard working solutions containing from 50 to 1,000 µg/L cobalt by appropriate dilution of cobalt standard solution II with acidified water. Add 1.0 mL NH_4Cl solution for each 10 mL standard working solution. Similarly, prepare an acidified water blank. Prepare fresh daily.

5.5 *Water, acidified*: Add 1.5 mL concentrated HNO_3 (sp gr 1.41) to a liter of demineralized water.

6. Procedure

6.1 Add 1.0 mL NH_4Cl solution to 10.0 mL sample solution and mix thoroughly.

6.2 Aspirate the blank to set the automatic zero control. Use the automatic concentration control to set 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 cobalt in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing cobalt concentrations that exceed the working range of the method and multiply by the proper dilution factors.

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

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

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

8. Report

8.1 Report cobalt, dissolved (01035), total-recoverable (01037), and suspended-recoverable (01036), concentrations to the nearest 50 µg/L.

8.2 Report cobalt, recoverable-from-bottom-material (01038), concentrations as follows: 50 to 100 µg/g, the nearest 10 µg/g; 100 µg/g and above, two significant figures.

9. Precision

9.1 The standard deviation for dissolved cobalt within the range of 6.2 to 19.3 µg/L (NOTE 1) for six samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 4.4 µg/L ranged from 3.4 to 6.4 µg/L.

NOTE 1. Precision data for cobalt are below the reporting level of 50 µg/L. Samples that contained greater cobalt concentrations were not available; however, precision should improve at greater concentrations.

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

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
5	6.2	57
4	15.8	27
3	19.3	11

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

Cobalt, atomic absorption spectrometric, graphite furnace

Parameter and Code:

Cobalt, dissolved, I-1241-85 (μg/L as Co): 01035

1. Application

1.1 This method may be used to determine cobalt in low ionic-strength water and precipitation. With deuterium background correction and a 20-μL sample, the method is applicable in the range from 0.5 to 100 μg/L. With Zeeman background correction and a 20-μL sample, the method is applicable in the range from 0.5 to 65 μg/L. Sample solutions that contain cobalt concentrations exceeding the upper limits must be diluted or preferably be analyzed by the atomic absorption spectrometric direct or chelation-extraction method, or by the atomic emission spectrometric ICP method.

1.2 The analytical range and detection limits can be increased or possibly decreased by varying the volume of sample injected or the instrumental settings. Purification of reagents and use of ASTM Type 1 water (Method D-1193, American Society for Testing and Materials, 1984) may result in lower detection limits.

2. Summary of method

Cobalt is determined by atomic absorption spectrometry in conjunction with a graphite furnace containing a graphite platform (Hinderberger and others, 1981). A sample is placed on the graphite platform, then evaporated to dryness, charred, and atomized using high-temperature ramping. The absorption signal generated during atomization is recorded and compared with standards.

3. Interferences

3.1 Interferences in low ionic-strength samples, such as precipitation, normally are quite low. In addition, the use of the graphite platform reduces the effects of many interferences. Calcium (60 mg/L), magnesium (14 mg/L), sodium (55 mg/L), sulfate (110 mg/L), and chloride (45 mg/L) do not interfere. Higher concentrations of these constituents were not investigated.

3.2 Precipitation samples usually contain very low concentrations of cobalt. Special precautionary measures must be employed during both sample collection and laboratory determination to prevent contamination.

4. Apparatus

4.1 *Atomic absorption spectrometer*, for use at 240.7 nm and equipped with background correction, digital integrator to quantitate peak areas, graphite furnace with temperature programmer, and automatic sample injector. The programmer must have high temperature ramping and stopped-flow capabilities.

4.1.1 Refer to the manufacturer's manual to optimize instrumental performance. The analytical ranges reported in paragraph 1.1 are for a 20-μL sample (NOTE 1).

NOTE 1. A 20-μL sample generally requires 30 s to dry. Samples that have a complex matrix may require a longer drying and charring time.

4.1.2 *Graphite furnace*, capable of reaching temperatures sufficient to atomize the element of interest. Warning: dial settings frequently are inaccurate and newly conditioned furnaces require temperature calibration.

4.1.3 *Graphite tubes and platforms*. Pyrolytically coated graphite tubes and solid pyrolytic graphite platforms are recommended.

4.2 *Labware*. Many trace metals at very low concentrations have been found to sorb very rapidly to glassware. To preclude this, fluorinated ethylene propylene (FEP) or Teflon labware may be used. Alternately, glassware, particularly flasks and pipets, may be treated with silicone anti-wetting agent such as Surfacil (Pierce Chemical Co., Rockford, IL, 61105) according to the manufacturer's instructions. Autosampler cups must be checked for contamination. Lancer (1831 Olive St., St. Louis, MO, 63103) polystyrene disposable cups have been found to be satisfactory after acid rinsing. Alternately, reuseable Teflon or FEP cups may be used.

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

5. Reagents

5.1 *Cobalt standard solution I*, 1.00 mL= 1,000 µg Co: Dissolve 1.4070 g Co_2O_3 in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10 mL high-purity, concentrated HNO_3 (sp gr 1.41), Ultrex or equivalent, and dilute to 1,000 mL with Type 1 water.

5.2 *Cobalt standard solution II*, 1.00 mL= 10.0 µg Co: Dilute 10.0 mL cobalt standard solution I to 1,000 mL (NOTE 2).

NOTE 2. Use acidified Type 1 water (paragraph 5.6) to make dilutions. All standards must be stored in sealed Teflon or FEP containers. Each container must be rinsed twice with a small volume of standard before being filled. Standards stored for 6 months in FEP containers yielded values equal to those of freshly prepared standards.

5.3 *Cobalt standard solution III*, 1.00 mL= 1.00 µg Co: Dilute 100.0 mL cobalt standard solution II to 1,000 mL. This standard is used to prepare working standards serially at time of analysis.

5.4 *Cobalt standard solution IV*, 1.00 mL=0.010 µg Co: Dilute 10.0 mL cobalt standard solution III to 1,000 mL. This standard also is used to prepare working standards serially at time of analysis.

5.5 *Nitric acid, concentrated*, high-purity, (sp gr 1.41): J. T. Baker "Ultrex" brand HNO_3 has been found to be adequately pure; however, each lot must be checked for contamination. Analyze acidified Type 1 water for cobalt. Add an additional 1.5 mL of concentrated HNO_3/liter of water, and repeat analysis. Integrated signal should not increase by more than 0.001 absorbance-seconds.

5.6 *Water, acidified*, Type 1: Add 1.5 mL high-purity, concentrated HNO_3(sp gr 1.41) to each liter of water.

5.7 *Water, Type 1.*

6. Procedure

6.1 Systematically clean and rinse work areas with deionized water on a regular schedule. Use a laminar flow hood or a "clean room" environment during sample transfers. Ideally, the autosampler and the graphite furnace should be in a clean environment.

6.2 Soak autosampler cups at least overnight in a 1+1 solution of Type 1 water and high-purity nitric acid.

6.3 Rinse the sample cups twice with sample before filling. Place cups in sample tray and cover. Adjust sampler so that only the injection tip contacts the sample.

6.4 In sequence, inject 20-µL aliquots of blank and working standards and analyze. Analyze the blank and working standards twice. Construct the analytical curve from the integrated peak areas (absorbance-seconds). Generally, the curve should be linear to a peak-absorbance (peak-height) value of 0.40 absorbance units.

6.5 Similarly, inject and analyze the samples twice. Every tenth sample cup should contain either a standard or a reference material.

6.6 Restandardize as required. Minor changes of values for known samples usually indicate deterioration of the furnace tube, contact rings, and (or) platform. A major variation usually indicates either autosampler malfunction or residue buildup from a complex matrix in a previous sample.

7. Calculations

Determine the micrograms per liter of cobalt in each sample from the digital display or printer output. Dilute those samples containing concentrations of cobalt that exceed the working range of the method; repeat the analysis, and multiply by the proper dilution factors.

8. Report

Report cobalt, dissolved (01035), concentrations as follows: less than 10.0 µg/L, nearest 0.1 µg/L; 10 µg/L and above, two significant figures for both deuterium background correction and Zeeman background correction.

9. Precision

9.1 Analysis of one sample 13 times each by a single operator using deuterium background correction is as follows:

Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
9.05	0.67	7.4

9.2 Analysis of four samples six times each by a single operator using Zeeman background correction is as follows:

Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
5.75	0.24	4.2
20.52	.26	1.3
32.27	.38	1.2
64.20	.20	.3

9.3 The precision and bias for the Zeeman background correction were tested on deionized water and tap water (specific conductance 280 µS/cm). A known amount of cobalt was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (µg/L)	Amount found (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
8.5	8.67	0.88	10.1	102
9.5	9.92	.97	9.8	104
15	15.00	1.10	7.3	100
17	17.00	1.52	8.9	100
30	29.50	1.41	4.8	98
Tap water				
8.5	8.58	1.07	12.5	101
9.5	9.58	.58	6.1	101
15	14.92	1.36	9.1	99
17	16.67	1.66	10.0	98
30	28.33	1.99	7.0	94

9.4 The precision and bias for the deuterium background method were tested on deionized water and tap water (specific conductance 280 µS/cm). A known amount of cobalt was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (µg/L)	Amount found (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
8.5	8.61	0.97	11.3	101
9.5	10.96	.58	5.3	115
15	14.34	.70	4.9	96
17	17.25	1.42	8.2	101
30	29.03	2.76	9.5	97
Tap water				
8.5	8.27	0.85	10.3	97
9.5	10.89	.86	7.9	115
15	15.12	1.73	11.7	101
17	15.88	.49	3.1	93
30	28.43	2.68	9.4	95

9.5 The standard deviation from interlaboratory data, without regard to type of background correction and use of matrix modifiers, if any, for dissolved cobalt within the range of 2.3 to 18.3 µg/L for 14 samples, was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 3.2 µg/L ranged from 2.7 to 3.8 µg/L.

References

American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, v. 11.01, p. 39-41.

Cooksey, M., and Barnett, W. B., 1979, Matrix modification and the method of additions in flameless atomic absorption: Atomic Absorption Newsletter, v. 18, p. 101-5.

Fernandez, F. J., Beatty, M. M., and Barnett, W. B., 1981, Use of the L'vov platform for furnace atomic absorption applications: Atomic Spectroscopy, v. 2, p. 16-21.

Hinderberger, E. J., Kaiser, M. L., and Koirtyohann, S. R., 1981, Furnace atomic absorption analysis of biological samples using the L'vov platform and matrix modification: Atomic Spectroscopy, v. 2, p. 1-11.

Manning, D. C., and Slavin, W., 1983, The determination of trace elements in natural waters using the stabilized temperature platform furnace: Applied Spectroscopy, v. 37, p. 1-11.

Ottaway, J. M., 1982, A revolutionary development in graphite furnace atomic absorption: Atomic Spectroscopy, v. 3, p. 89-92.

Slavin, W., Carnrick, G. R., and Manning, D. C., 1982, Magnesium nitrate as a matrix modifier in the stabilized temperature platform furnace: Analytical Chemistry, v. 54, p. 621-4.

Cobalt, atomic emission spectrometric, ICP

Parameter and Code:

Cobalt, dissolved, I-1472-85 (µg/L as Co): 01035

2. Summary of method

Cobalt 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.

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

Parameter and Code:

Cobalt, total, I-5474-85 (mg/kg as Co): 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. Cobalt 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.

Color, electrometric, visual comparison

Parameter and Code:

Color, I-1250-85 (platinum-cobalt units): 00080

1. Application

This method may be used to measure the color of water whose color reasonably matches from 1 to 70 units of the Hazen scale (Hazen, 1892) and that contains no excessive amount of sediment. Samples that have a color unit value greater than 70 must first be diluted.

2. Summary of method

The color of the water is compared to that of colored glass disks that have been calibrated to correspond to the platinum-cobalt scale of Hazen (1892). The unit of color is that produced by 1 mg/L of platinum. A small amount of cobalt may be added to aid in color matching. The Hazen scale (platinum-cobalt units) is usually satisfactory for most waters, but the hues and shades of some waters may not easily be compared with standards. If the hue of the water does not compare with that of the standard, very little can be done except to visually compare the absorbances of the sample and standard. Highly colored waters should not be diluted more than necessary because the color of the diluted sample often is not proportional to the dilution.

3. Interferences

Turbidity generally causes the observed color value to be greater than the true color value, but there is some disagreement as to the magnitude of the effect of turbidity. The removal of turbidity is a recurrent problem in the determination of color. Color is removed by absorption on suspended material. Filtration of samples to remove turbidity frequently removes some of the color-imparting solutes by absorption on the sediments or on the filter medium. Centrifuging is preferable to filtration, but centrifuging may not be completely effective in removing very finely divided particles. Flocculation of the dispersed particles with a strong electrolyte has been proposed (Lamar, 1949) and is sometimes effective. The process of flocculation decolorizes some waters and is, therefore, not suitable in all cases.

4. Apparatus

Color comparator, with standard color disks, covering the range 0 to 70 color units.

5. Reagents

None required.

6. Procedure

6.1 Fill one instrument tube with the sample of water, level the tube, insert the glass plug, making sure that no air bubbles are trapped, and insert the tube into the comparator.

6.2 Use demineralized water as a blank in the second tube.

6.3 The color comparison is made by revolving the disk until the colors of the two tubes match. Samples having color values greater than 70 must first be diluted.

7. Calculations

Read the color directly from the matching color standard; apply the proper dilution if required.

8. Report

Report color (00080) (platinum-cobalt units) as follows:

Color unit	Record units to nearest
1-49	1
50-99	5
100-249	10
250-500	20

9. Precision

Precision data are not available for this method.

References

Hazen, Allen, 1892, A new color standard for natural waters: American Chemical Society Journal, v. 12, p. 427.

Lamar, W.L., 1949, Determination of color of turbid waters: Analytical Chemistry, v. 21, p. 726-27.

Copper, atomic absorption spectrometric, chelation-extraction

Parameters and Codes:

Copper, dissolved, I-1271-85 (μg/L as Cu): 01040
Copper, total recoverable, I-3271-85 (μg/L as Cu): 01042
Copper, suspended recoverable, I-7271-85 (μg/L as Cu): 01041

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing from 1 to 50 μg/L of copper. Sample solutions containing more than 50 μg/L need either to be diluted prior to chelation-extraction or to be analyzed by the atomic absorption spectrometric direct method.

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

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

1.4 If the iron concentration of the sample exceeds 25,000 μg/L, determine copper by the atomic absorption spectrometric direct method.

2. Summary of method

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

3. Interferences

Concentrations of iron greater than 25,000 μg/L interfere by suppressing the copper absorption.

4. Apparatus

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

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

Grating ------------ Ultraviolet
Wavelength -------- 324.7 nm
Source (hollow-cathode lamp) ------------ Copper
Oxidant ------------ Air
Fuel ---------------- Acetylene
Type of flame ------- Oxidizing

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

5. Reagents

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

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

5.3 *Copper standard solution I*, 1.00 mL=100 μg Cu: Dissolve 0.1252 g CuO in a minimum amount of dilute HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.4 *Copper standard solution II*, 1.00 mL=1.00 μg Cu: Dilute 10.0 mL copper 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.

5.5 *Methyl isobutyl ketone (MIBK).*

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

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

NOTE 1. Alternatively, a 2.5*M* NH_4OH solution may be used. Add 167 mL concentrated NH_4OH (sp gr 0.90) to 600 mL demineralized water. Cool, and dilute to 1 L.

5.8 *Water, acidified*: Add 1.5 mL concentrated HNO_3 (sp gr 1.41) to 1 L of demineralized water.

6. Procedure

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

6.2 Pipet a volume of sample solution containing less than 5.0 μg Cu (100 mL max) into a 200-mL volumetric flask and adjust the volume to approx 100 mL.

6.3 Prepare a blank with 1.5 mL concentrated HNO_3 per liter of acidified water and sufficient standards, and adjust the volume of each to approx 100 mL with acidified water.

6.4 With a pH meter, adjust the pH of each solution to 2.4 with 2.5*M* KOH (NOTE 2 and NOTE 3). Shake for 3 min.

NOTE 2. For water-suspended sediment samples that have been digested, add 1 to 2 mL 10*M* KOH or concentrated NH_4OH (sp gr 0.90) before pH adjustment.

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

6.5 Add 2.5 mL APDC solution and mix.

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

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

6.8 Aspirate the ketone layer within 1 h. 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 copper in each sample from the digital display or printer. Dilute those samples containing copper concentrations that exceed the working range of the method; repeat the chelation-extraction, and multiply by the proper dilution factors.

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

8. Report

Report copper, dissolved (01040), total-recoverable (01042), and suspended-recoverable (01041), concentrations as follows: less than 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved copper for eight samples within the range of 18.5 to 403 μg/L may be expressed as follows:

$$S_T = 0.084X + 2.57$$

where

S_T= overall precision, micrograms per liter, and

X= concentration of copper, micrograms per liter.

The correlation coefficient is 0.8156.

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

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
4	18.5	14
3	100	0
3	153	21
3	403	8

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

Copper, atomic absorption spectrometric, direct

Parameters and Codes:

Copper, dissolved, I-1270-85 (μg/L as Cu): 01040
Copper, total recoverable, I-3270-85 (μg/L as Cu): 01042
Copper, suspended recoverable, I-7270-85 (μg/L as Cu): 01041
Copper, recoverable-from-bottom-material, dry wt, I-5270-85 (μg/g as Cu): 01043

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 10 μg/L of copper. Sample solutions containing more than 1,000 μg/L need either to be diluted or to be read on a less expanded scale. Brines need to be analyzed by the atomic absorption spectrometric chelation-extraction method, providing that the interference limits discussed in that method are not exceeded.

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

1.3 This method may be used to analyze bottom material containing at least 1 μg/g of copper. Prepared sample solutions containing more than 1,000 μg/L need either to be diluted or to be read on a less expanded scale.

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

2. Summary of method

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

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

3. Interferences

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 (2,000 mg/L), iron (4×10^6μg/L), lead, cadmium, zinc, and chromium (10,000 μg/L each) do not interfere. Higher concentrations of each constituent were not investigated. Nickel and cobalt concentrations greater than 8,000 μg/L suppress the copper absorption.

4. Apparatus

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

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

Grating	Ultraviolet
Wavelength	324.7 nm
Source (hollow-cathode lamp)	Copper
Oxidant	Air
Fuel	Acetylene
Type of flame	Oxidizing

4.3 The 100-mm (4-in.), flathead, single-slot burner allows a working range of 10 to 1,000 μg/L. Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Copper standard solution I*, 1.00 mL= 1000 μg Cu: Dissolve 1.252 g CuO in a minimum amount of dilute HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1000 mL with demineralized water.

5.2 *Copper standard solution II*, 1.00 mL= 5.00 μg Cu: Dilute 5.0 mL copper 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 time of analysis.

5.3 *Copper working standards*: Prepare a series of at least six working standards containing from 10 to 1,000 µg/L of copper by appropriate dilution of copper standard solution II with acidified water. Prepare fresh daily.

5.4 *Water, acidified*: Add 1.5 mL concentrated HNO_3 (sp gr 1.41) to 1 L of demineralized water.

6. Procedure

Aspirate the blank (acidified water) 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 copper in each sample solution from the digital display or printer while aspirating each sample. Dilute those samples containing copper concentrations that exceed the working range of the method and multiply by proper dilution factors.

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

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

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

8. Report

8.1 Report copper, dissolved (01040), total-recoverable (01042), and suspended- recoverable (01041), concentrations as follows: less than 100 µg/L, nearest 10 µg/L; 100 µg/L and above, two significant figures.

8.2 Report copper, recoverable-from-bottom-material (01043), 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 copper for 28 samples within the range of 10 to 595 µg/L may be expressed as follows:

$$S_T = 0.057X + 7.13$$

where

S_T= overall precision, micrograms per liter, and

X= concentration of copper, micrograms per liter.

The correlation coefficient is 0.8007.

9.2 Precision for dissolved copper for five of the 28 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
9	10.0	90
30	60.3	14
22	100	16
28	245	11
23	595	9

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

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

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
17	21.1	39
23	131	16

References

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. 28-30.

Copper, atomic absorption spectrometric, graphite furnace

Parameter and Code:

Copper, dissolved, I-1272-85 (μg/L as Cu): 01040

1. Application

1.1 This method may be used to determine copper in low ionic-strength water and precipitation. With deuterium background correction and a 20-μL sample, the method is applicable in the range from 0.2 to 10 μg/L. With Zeeman background correction and a 20-μL sample, the method is applicable in the range from 0.5 to 35 μg/L. Sample solutions that contain copper concentrations exceeding the upper limits must be diluted or preferably be analyzed by the atomic absorption spectrometric direct or chelation-extraction method, or by the atomic emission spectrometric ICP method.

1.2 The analytical range and detection limits can be increased or possibly decreased by varying the volume of sample injected or the instrumental settings. Purification of reagents and use of ASTM Type 1 water (Method D-1193, American Society for Testing and Materials, 1984) may result in lower detection limits.

2. Summary of method

Copper is determined by atomic absorption spectrometry in conjunction with a graphite furnace containing a graphite platform (Hinderberger and others, 1981). A sample is placed on the graphite platform, and the sample is then evaporated to dryness, charred, and atomized using high-temperature ramping. The absorption signal generated during atomization is recorded and compared with standards.

3. Interferences

3.1 Interferences in low ionic-strength samples, such as precipitation, normally are quite low. In addition, the use of the graphite platform reduces the effects of many interferences. Calcium (60 mg/L), magnesium (10 mg/L), sodium (50 mg/L), sulfate (100 mg/L), and chloride (40 mg/L) do not interfere. Higher concentrations of these constituents were not investigated.

3.2 Precipitation samples usually contain very low concentrations of copper. Special precautionary measures must be employed during both sample collection and laboratory determination to prevent contamination.

4. Apparatus

4.1 *Atomic absorption spectrometer*, for use at 324.7 nm and equipped with background correction, digital integrator to quantitate peak areas, graphite furnace with temperature programmer, and automatic sample injector. The programmer must have high-temperature ramping and stopped-flow capabilities.

4.1.1 Refer to the manufacturer's manual to optimize instrumental performance. The analytical ranges reported in paragraph 1.1 are for a 20-μL sample (NOTE 1).

NOTE 1. A 20-μL sample generally requires 30 s to dry. Samples that have a complex matrix may require a longer drying and charring time.

4.1.2 *Graphite furnace*, capable of reaching temperatures sufficient to atomize the element of interest. Warning: dial settings frequently are inaccurate and newly conditioned furnaces require temperature calibration.

4.1.3 *Graphite tubes and platforms*. Pyrolytically coated graphite tubes and solid pyrolytic graphite platforms are recommended.

4.2 *Labware*. Many trace metals at very low concentrations have been found to sorb very rapidly to glassware. To preclude this, fluorinated ethylene propylene (FEP) or Teflon labware may be used. Alternately, glassware, particularly flasks and pipets, may be treated with silicone anti-wetting agent such as Surfacil (Pierce Chemical Co., Rockford, IL, 61105) according to the manufacturer's instructions. Autosampler cups must be checked for contamination. Lancer (1831 Olive St., St. Louis, MO, 63103) polystyrene disposable cups have been found to be satisfactory after acid rinsing. Alternately, reuseable Teflon or FEP cups may be used.

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

5. Reagents

5.1 *Copper standard solution I*, 1.00 mL= 1,000 μg Cu: Dissolve 1.2518 g CuO in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10 mL high-purity, concentrated HNO_3 (sp gr 1.41) Ultrex or equivalent and dilute to 1,000 mL with Type 1 water.

5.2 *Copper standard solution II*, 1.00 mL= 10.0 μg Cu: Dilute 10.0 mL copper standard solution I to 1,000 mL (NOTE 2).

NOTE 2. Use acidified Type 1 water (paragraph 5.6) to make dilutions. All standards must be stored in sealed Teflon or FEP containers. Each container must be rinsed twice with a small volume of standard before being filled. Standards stored for 6 months in FEP containers yielded values equal to those of freshly prepared standards.

5.3 *Copper standard solution III*, 1.00 mL= 1.00 μg Cu: Dilute 100.0 mL copper standard solution II to 1,000 mL. This standard is used to prepare working standards serially at time of analysis.

5.4 *Copper standard solution IV*, 1.00 mL= 0.010 μg Cu: Dilute 10.0 mL copper standard solution III to 1,000 mL. This standard also is used to prepare working standards serially at time of analysis.

5.5 *Nitric acid, concentrated*, high-purity, (sp gr 1.41): J. T. Baker "Ultrex" brand HNO_3 has been found to be adequately pure; however, each lot must be checked for contamination. Analyze acidified Type 1 water for copper. Add an additional 1.5 mL of concentrated HNO_3 per liter of water, and repeat analysis. The integrated signal should not increase by more than 0.001 absorbance-seconds.

5.6 *Water, acidified*, Type 1: Add 1.5 mL high-purity, concentrated HNO_3 (sp gr 1.41) to each liter of water.

5.7 *Water, Type 1.*

6. Procedure

6.1 Systematically clean and rinse work areas with deionized water on a regular schedule. Use a laminar flow hood or a "clean room" environment during sample transfers. Ideally, the autosampler and the graphite furnace should be in a clean environment.

6.2 Soak autosampler cups at least overnight in a 1+1 solution of Type 1 water and high-purity nitric acid.

6.3 Rinse the sample cups twice with sample before filling. Place cups in sample tray and cover. Adjust sampler so that only the injection tip contacts the sample.

6.4 In sequence, inject 20-μL aliquots of blank and working standards, and analyze. Analyze the blank and working standards twice. Construct the analytical curve from the integrated peak areas (absorbance-seconds). Generally, the curve should be linear to a peak-absorbance (peak-height) value of 0.40 absorbance units.

6.5 Similarly, inject and analyze the samples twice. Every tenth sample cup should contain either a standard or a reference material.

6.6 Restandardize as required. Minor changes of values for known samples usually indicate deterioration of the furnace tube, contact rings, and (or) platform. A major variation usually indicates either autosampler malfunction or residue buildup from a complex matrix in a previous sample.

7. Calculations

Determine the micrograms per liter of copper in each sample from the digital display or printer output. Dilute those samples containing concentrations of copper that exceed the working range of the method; repeat the analysis, and multiply by the proper dilution factors.

8. Report

Report copper, dissolved (01040), concentrations as follows: less than 10.0 μg/L, nearest 0.1 μg/L; 10 μg/L and above, two significant figures for both deuterium background correction and Zeeman background correction.

9. Precision

9.1 Analysis of six samples six times each by a single operator using deuterium background correction is as follows:

Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
0.60	0.04	7.2
1.38	.11	8.1
2.31	.10	4.2
4.11	.15	3.6
5.58	.25	4.4
10.25	.40	3.9

9.2 Analysis of four samples by a single operator using Zeeman background correction is as follows:

Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
3	3.93	0.55	14
4	12.85	1.23	9.6
9	17.76	.36	2.0
6	34.88	1.13	3.2

9.3 The precision and bias for the Zeeman background correction were tested on deionized water and tap water (specific conductance 280 µS/cm). A known amount of copper was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (µg/L)	Amount found (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
4.35	4.57	0.29	6.3	105
8.0	8.23	.46	5.6	103
8.7	9.23	.57	6.2	106
9.0	8.40	.40	4.8	93
16	16.10	.98	6.1	101
Tap water (NOTE 3)				
4.35	6.45	4.00	7.0	148
8.0	8.28	3.47	5.9	103
8.7	12.97	4.15	6.6	149
9.0	9.49	1.73	5.0	105
16	14.17	4.43	6.9	89

NOTE 3. The tap water contained approx 50 µg/L of copper, and the standard deviation and percent relative standard deviation were calculated prior to subtraction of copper originally present.

9.4 The precision and bias for the deuterium background method were tested on deionized water and tap water (specific conductance 280 µS/cm). A known amount of copper was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (µg/L)	Amount found (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
4.35	4.38	0.13	3.0	101
8.0	7.45	.34	4.6	93
8.7	8.42	.52	6.2	97
9.0	8.68	.57	6.5	96
16	15	.75	5.0	94
Tap water (NOTE 3)				
4.35	9.40	.72	1.1	216
8.0	7.37	2.17	3.5	92
8.7	16.75	1.99	2.8	193
9.0	18.83	5.41	12	209
16	22.88	2.76	3.6	143

9.5 Interlaboratory precision for dissolved copper for 12 samples within the range of 21.8 to 490 µg/L without regard to type of background correction and use of matrix modifiers, if any, may be expressed as follows:

$$S_T = 0.184X + 2.04$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of copper, micrograms per liter.

The correlation coefficient is 0.9246.

References

American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, v. 11.01, p. 39–41.

Cooksey, M., and Barnett, W. B., 1979, Matrix modification and the method of additions in flameless atomic absorption: Atomic Absorption Newsletter, v. 18, p. 101–5.

Fernandez, F. J., Beatty, M. M., and Barnett, W. B., 1981, Use of the L'vov platform for furnace atomic absorption applications: Atomic Spectroscopy, v. 2, p. 16–21.

Hinderberger, E. J., Kaiser, M. L., and Koirtyohann, S. R., 1981, Furnace atomic absorption analysis of biological samples using the L'vov platform and matrix modification: Atomic Spectroscopy, v. 2, p. 1–11.

Manning, D. C., and Slavin, W., 1983, The determination of trace elements in natural waters using the stabilized temperature platform furnace: Applied Spectroscopy, v. 37, p. 1-11.

Ottaway, J. M., 1982, A revolutionary development in graphite furnace atomic absorption: Atomic Spectroscopy, v. 3, p. 89-92.

Slavin, W., Carnrick, G. R., and Manning, D. C., 1982, Magnesium nitrate as a matrix modifier in the stabilized temperature platform furnace: Analytical Chemistry, v. 54, p. 621-4.

Copper, atomic emission spectrometric, ICP

Parameter and Code:

Copper, dissolved, I-1472-85 (μg/L as Cu): 01040

2. Summary of method

Copper 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.

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

Parameter and Code:

Copper, total, I-5474-85 (mg/kg as Cu): 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. Copper 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.

Cyanide, colorimetric, barbituric acid, automated-segmented flow

Parameters and Codes:

Cyanide, dissolved, I-2302-85 (mg/L as CN): 00723
Cyanide, total recoverable, I-4302-85 (mg/L as CN): 00720
Cyanide, recoverable-from-bottom-material, dry wt, I-6302-85 (mg/kg as CN): 00721

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing from 0.01 to 0.30 mg/L cyanide. Samples containing more than 0.30 mg/L need to be diluted.

1.2 Total recoverable cyanide in water-suspended sediment can be determined if each sample is shaken vigorously and a suitable aliquot of well-mixed sample withdrawn.

1.3 This method may be used to determine cyanide in bottom material containing at least 0.5 mg/kg.

2. Summary of method

This method is based on the chlorination of cyanide with chloramine-T and on the subsequent reaction with a pyridine-barbituric acid reagent (Goulden and others, 1972). This method detects simple cyanides only; therefore, any complex cyanides must first be broken down by passing the acidified sample solution through an ultraviolet digestion-distillation procedure. The distillation step also removes certain interferences.

3. Interferences

3.1 Chloride interferes if its concentration exceeds 3,000 mg/L.

3.2 Oxidizing agents may interfere.

3.3 Glycine and urea at the 10-mg/L level do not interfere.

3.4 A concentration of 10 mg/L sulfide increases the apparent cyanide concentration by approx 0.02 mg/L. Concentrations of sulfide greater than 10 mg/L interfere considerably.

3.5 Thiocyanate is broken down to cyanide and sulfide by this procedure and, therefore, interferes on an equimolar basis.

3.6 Sulfate concentrations of 4,000 mg/L do not interfere. Higher concentrations were not tested.

4. Apparatus

4.1 *Distillation train* (fig. 21). An efficient gas washer is essential to the proper operation of the distillation assembly. The Fisher-Milligan unit has been found satisfactory. This apparatus is for use only with bottom materials.

4.2 *Heating element* for Claisen flask.

4.3 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold with ultraviolet digestor, proportioning pump, heating bath with distillation head, voltage stabilizer, recorder, and printer.

4.4 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 0.30 mg/L CN:

Absorption cell -----	15 mm
Wavelength --------	570 nm
Cam ---------------	20/h (6/1)
Heating-bath temperature ------------	155 °C

5. Reagents

5.1 *Chloramine-T solution*, 4.0 g/L: Dissolve 2.0 g chloramine-T in demineralized water and dilute to 500 mL.

5.2 *Cyanide standard solution I*, 1.00 mL = 0.100 mg CN: Dissolve 0.2500 g KCN (NOTE 1) in 0.1*M* NaOH and dilute to 1,000 mL with 0.1*M* NaOH. Discard after 3 months.

NOTE 1. **CAUTION—POISON: May be fatal if swallowed or inhaled. Contact with acid liberates poisonous gas. Contact with KCN may burn eyes and irritate skin.**

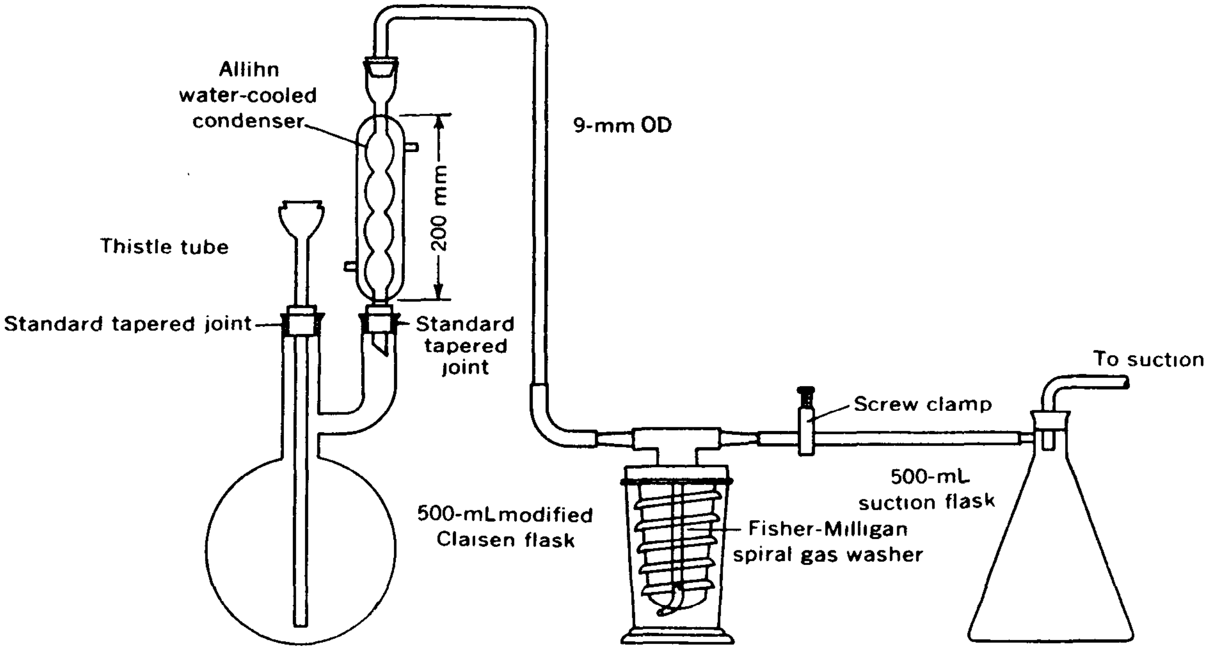

Figure 21.—Cyanide, distillation train

5.3 *Cyanide standard solution II*, 1.00 mL = 0.002 mg CN: Add 20 mL cyanide standard solution I to 800 mL 0.1*M* NaOH and dilute to 1,000 mL with 0.1*M* NaOH. Prepare fresh daily.

5.4 *Cyanide working standards*: Prepare fresh daily, a blank and 100 mL each of a series of cyanide working standards by appropriate quantitative dilution of cyanide standard solution II as follows:

Cyanide standard solution II (mL)	Cyanide concentration (mg/L)
1.0	0.020
2.0	.040
5.0	.100
10.0	.200
15.0	.300

5.5 *Magnesium chloride solution*, 24 g/100 mL: Dissolve 51 g $MgCl_2 \cdot 6H_2O$ in 100 mL demineralized water.

5.6 *Phosphate buffer solution*: Dissolve 13.6 g KH_2PO_4 and 0.28 g Na_2HPO_4 in demineralized water and dilute to 1 L. Add 0.5 mL Brij-35 solution and mix.

5.7 *Phosphoric acid-hypophosphorous acid distillation reagent*: Carefully add 250 mL concentrated H_3PO_4 (sp gr 1.69) and 50 mL hypophosphorous acid to approx 700 mL demineralized water. Dilute to 1 L with demineralized water.

5.8 *Pyridine-barbituric acid solution*: Place 15 g barbituric acid in a 1-L beaker and add enough demineralized water (about 100 mL) to wash the sides of the beaker and wet the barbituric acid. Add 75 mL pyridine and mix. Add 15 mL concentrated HCl (sp gr 1.19) and mix. Dilute to about 900 mL with demineralized water and mix until all the barbituric acid has dissolved. Transfer the solution to a 1,000-mL volumetric flask and dilute to volume with demineralized water.

5.9 *Sodium hydroxide*, 1*M*: Dissolve 4 g NaOH in 100 mL demineralized water.

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

6. Procedure

6.1 For water or water-suspended sediment proceed to paragraph 6.2. For bottom material proceed as follows:

6.1.1 Assemble the distillation train, consisting of Claisen flask, thistle tube, condenser, gas washer, screw clamp, suction flask, and aspirator (fig. 21).

6.1.2 Add a weighed portion (5 to 10 g) of bottom-material sample and 250 to 500 mL demineralized water to the boiling flask.

6.1.3 Add exactly 50 mL 1*M* NaOH and 100 mL demineralized water to the gas washer. Connect train and adjust suction so that 1 or 2 bubbles per second enter the boiling flask through the air inlet. Do not increase airflow beyond 2 bubbles per second.

6.1.4 Add 10 mL $MgCl_2$ solution through the thistle tube, and allow the airflow to mix for 3 min. Rinse air tube with demineralized water, then slowly add 20 mL concentrated H_2SO_4. Rinse the tube again.

6.1.5 Heat at a rate that provides rapid boiling, but not enough to flood the condenser inlet or permit the vapors to rise more than halfway into the condenser. Reflux for 1 h. Turn off heat, but permit airflow to continue for 15 min.

6.1.6 Transfer gas washer contents to a 200-mL volumetric flask. Wash the tube, from the condenser to the gas washer, and the gas washer with small amounts of demineralized water and add to contents of flask. Dilute contents of volumetric flask to 200 mL.

6.1.7 Refill the gas washer with NaOH and demineralized water, as in 6.1.3, and repeat reflux procedure. If only readily hydrolyzed cyanides are present, the absorber liquid from the first reflux period will contain all the available cyanide. If stable complex cyanides are present, a measurable yield will appear in the absorber liquid during the second and succeeding reflux periods, depending on the degree of stability of the compounds.

6.2 Set up manifold (fig. 22).

6.3 Allow the colorimeter, recorder, and heating bath to warm up for 30 min or until the heating-bath temperature has stabilized at 155 °C. Cold water must be flowing through the condensing jacket of the distillation head when heating bath is operating.

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

6.5 Place a complete set of standards and a blank in the first positions of the first sample tray, beginning with the most concentrated standard. Place individual standards of differing concentrations in approximately every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each tray with unknown samples. Each sample must be well mixed by vigorous shaking before transferring a portion to a sample cup.

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

7. Calculations

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

7.2 Compute the concentration of dissolved or total recoverable cyanide in milligrams per liter by comparing each sample peak height with 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 milligrams per kilogram of cyanide in bottom-material samples, first determine the milligrams per liter of cyanide in each sample as in paragraph 7.2; then:

$$\text{CN(mg/kg)} = \frac{\text{mL distillate}}{\text{wt of sample (g)}} \times \text{mg/L CN}$$

8. Report

8.1 Report cyanide, dissolved (00723) and total-recoverable (00720), concentrations as follows: less than 1.00 mg/L, nearest 0.01 mg/L; 1.00 mg/L and above, two significant figures.

8.2 Report cyanide, total-recoverable-in-bottom-material (00721), concentrations as follows: less than 10 mg/kg, nearest 0.1 mg/kg; 10 mg/kg and above, two significant figures.

9. Precision

9.1 Precision for dissolved cyanide expressed in terms of the percent relative standard deviation for replicate analysis by a single operator is as follows:

Mean (mg/L)	Relative standard deviation (percent)
0.041	2
.125	1
.224	1

9.2 It is estimated that the percent relative standard deviation for total recoverable cyanide

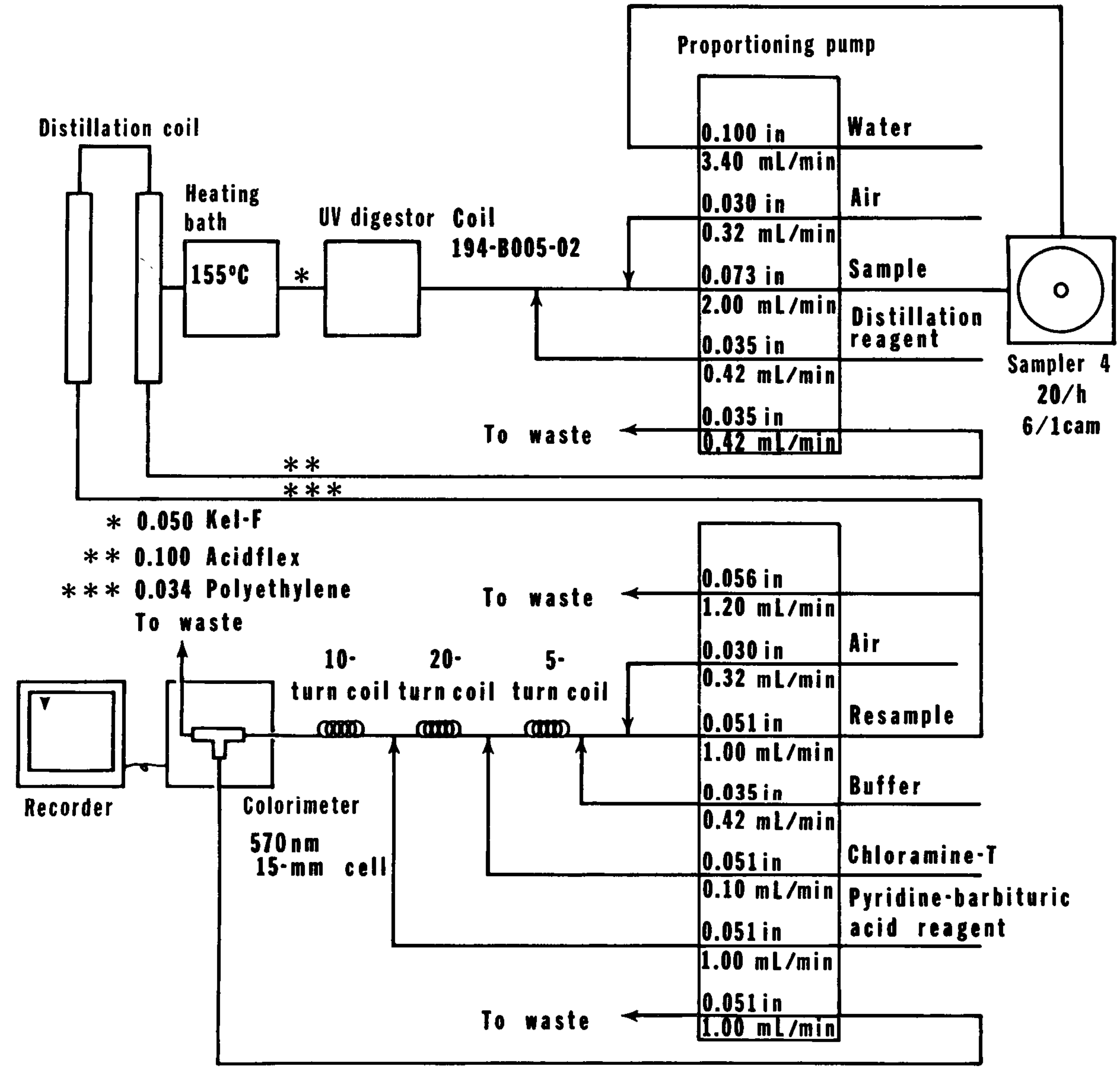

Figure 22.—Cyanide, barbituric acid manifold

and for recoverable cyanide in bottom material will be greater than that reported for dissolved cyanide.

References

Goulden, P. D., Afghan, B. K., and Brooksbank, Peter, 1972, Determination of nanogram quantities of simple and complex cyanides in water: Analytical Chemistry, v. 44, p. 1845–49.

U.S. Environmental Protection Agency, 1979, Methods for chemical analysis of water and wastes: Cincinnati, p. 353.3-1.

Cyanide, colorimetric, pyridine-pyrazolone

Parameters and Codes:

Cyanide, dissolved, I-1300-85 mg/L as CN): 00723
Cyanide, total, I-3300-85 (mg/L as CN): 00720
Cyanide, total-in-bottom-material, dry wt, I-5300-85 (mg/kg as CN): 00721

1. Application

1.1 The method may be used to determine cyanide in water and water-suspended sediment containing at least 0.01 mg/L of cyanide.

1.2 This method may be used to determine cyanide in bottom material containing at least 0.5 mg/kg.

1.3 Total cyanide in water-suspended sediment may be determined if each sample is shaken vigorously and a suitable aliquot of well-mixed sample withdrawn.

2. Summary of method

This method is based on the chlorination of cyanide and the subsequent reaction of the product with a mixed solution of pyridine-pyrazolone to form a stable complex dye. The method detects only simple cyanides; therefore, any complex cyanides present must be broken down. The decomposition of complex cyanides is accomplished by an acid reflux and distillation prior to the colorimetric procedure. The distillation also removes certain interferences from water samples.

3. Interferences

3.1 Common interferences include sulfide, heavy-metal ions, fatty acids, steam-distillable organic compounds, cyanate, thiocyanate, glycine, urea, oxidizing agents, and substances that may contribute color or turbidity to the sample.

3.2 These interferences may be removed or their effect minimized as follows:

3.2.1 Sulfide can be removed as lead sulfide by adding a slight excess of lead carbonate to 400 mL of the alkaline (pH 11.0 or above) sample. Filter the sample immediately, wash the precipitate with demineralized water, and add the washings to the filtrate.

3.2.2 Fatty acids can be removed by acidifying 400 mL of sample with acetic acid to a pH of between 6 and 7, and by extracting with 80 mL of either isooctane or hexane. A single extraction is usually sufficient.

3.2.3 Oxidizing agents can be removed by adding sodium sulfite solution to 400 mL of sample until a negative test with starch-iodide paper is obtained.

3.2.4 Most remaining interferences are removed by the distillation.

3.3 This method includes no provisions for removing these interferences or for minimizing their effects in water-suspended sediment and bottom material. The analyst must be aware that, when such interfering substances are present, the analytical result obtained may be in error, although distillation of the cyanide certainly separates it from some of the interfering substances.

4. Apparatus

4.1 *Distillation train* (fig. 23). An efficient gas washer is essential to the proper operation of the distillation assembly. The Fisher-Milligan unit has been found satisfactory.

4.2 *Heating element* for Claisen flask.

4.3 *Spectrometer* for use at 620 nm.

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

5. Reagents

5.1 *Acetic acid*, 3*M*: Mix 172 mL glacial $HC_2H_3O_2$ (sp gr 1.06) with demineralized water and dilute to 1 L.

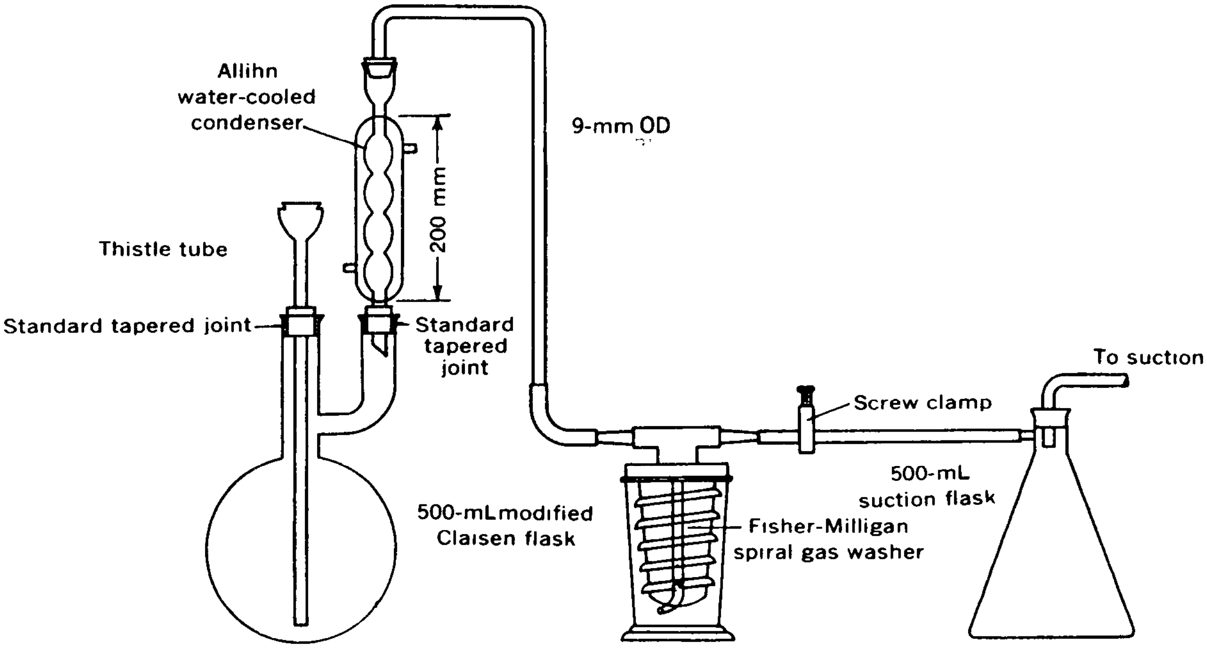

Figure 23.—Cyanide, distillation train

5.2 *Chloramine-T solution,* 1 g/100 mL: Dissolve 0.25 g chloramine-T in 25 mL demineralized water. This solution is unstable and must be prepared immediately before use. When a blank and standards are used, the chloramine-T solution may be used throughout a period of several hours, but each succeeding use results in lower absorbance readings for the same concentration of cyanide.

5.3 *Cyanide standard solution I,* 1.00 mL = 1.00 mg CN: Dissolve 2.50 g KCN (NOTE 1) in 1 L demineralized water. Standardize with silver nitrate standard solution, 1.00 mL = 1.00 mg CN, as follows: Adjust the pH of 5.0 mL cyanide standard solution I to 11.0 or above, and dilute to 250 mL with demineralized water. Add 0.5–1.0 mL 5-(p-dimethylaminobenzylidene)rhodamine indicator solution and titrate with standard silver nitrate solution to the first color change from canary yellow to salmon. Subtract the blank obtained by titrating an identical volume of water, alkali, and indicator. The cyanide solution is unstable and must be either restandardized weekly or prepared fresh when needed.

NOTE 1. **CAUTION—POISON: May be fatal if swallowed or inhaled. Contact with acid liberates poisonous gas. Contact with KCN may burn eyes and irritate skin.**

5.4 *Cyanide standard solution II,* 1.00 mL = 0.010 mg CN: Add 10.0 mL cyanide standard solution I to demineralized water and dilute to 1,000 mL. This solution must be prepared fresh before use.

5.5 *Cyanide standard solution III,* 1.00 mL = 0.001 mg CN: Add 10.0 mL cyanide standard solution II to demineralized water and dilute to 100 mL. This solution must be prepared fresh before use.

5.6 *Magnesium chloride solution,* 24 g/100 mL: Dissolve 51 g $MgCl_2 \cdot 6H_2O$ in 100 mL demineralized water.

5.7 *5-(p-Dimethylaminobenzylidene)rhodamine indicator solution,* 0.02 g/100 mL: Dissolve 0.02 g 5-(p-dimethylaminobenzylidene)rhodamine in 100 mL acetone. Eastman Kodak No. 2748 has been found satisfactory.

5.8 *Pyrazolone solution I*: Add 0.8 g 1-phenyl-3-methyl-5-pyrazolone to 150 mL demineralized water at 75 °C. Cool to room temperature, with stirring; filter. Eastman Kodak No. 1397 has been found satisfactory.

5.9 *Pyrazolone solution II*: Dissolve 0.025 g bis-pyrazolone in 25 mL pyridine and filter. Eastman Kodak No. 6969 has been found satisfactory. Several minutes of mixing are usually required to effect solution.

5.10 *Pyridine-pyrazolone reagent*: Mix 125 mL pyrazolone solution I with 25 mL pyrazolone solution II. After standing, the mixed reagent develops a pink color which does not affect color development. Prepare this reagent fresh daily or before each use.

5.11 *Pyridine*.

5.12 *Silver nitrate standard solution*, 1.00 mL 1.00 mg CN: Crush approx 5 g of $AgNO_3$ crystals and dry to constant mass at 40°C. Dissolve 3.2647 g $AgNO_3$ in demineralized water and dilute to 1 L. This solution is needed only to standardize the cyanide standard solution I.

5.13 *Sodium hydroxide, 1M*: Dissolve 4 g NaOH in 100 mL demineralized water.

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

6. Procedure

6.1 *Distillation*: Follow instructions in paragraph 6.1.1 for water or water-suspended sediment and paragraph 6.1.2 for bottom material, after assembling the distillation train, consisting of Claisen flask, thistle tube, condenser, gas washer, screw clamp, suction flask, and aspirator.

6.1.1 Add 400 mL water or water-suspended sediment (or smaller aliquot diluted to 400 mL) to the boiling flask.

6.1.2 Add a weighed portion (5–10 g) of bottom-material and 250–500 mL demineralized water to the boiling flask.

6.2 Add exactly 50 mL 1*M* NaOH and 100 mL demineralized water to the gas washer. Connect train and adjust suction so that 1 or 2 bubbles per second enter the boiling flask through the air inlet. Do not increase airflow beyond 2 bubbles per second.

6.3 Add 10 mL $MgCl_2$ solution through the thistle tube, and allow the airflow to mix for 3 min. Rinse air tube with demineralized water, then slowly add 20 mL concentrated H_2SO_4. Rinse the tube again.

6.4 Heat at a rate that produces rapid boiling, but not enough to flood the condenser inlet or permit the vapors to rise more than halfway into the condenser. Reflux for 1 h. Turn off heat, but permit airflow to continue for 15 min.

6.5 Transfer gas washer contents to a 200-mL volumetric flask. Wash the tube, from the condenser to the gas washer, and the gas washer with small amounts of demineralized water and add to contents of flask. Dilute contents of volumetric flask to 200 mL.

6.6 Refill the gas washer with NaOH and demineralized water, as in 6.2, and repeat reflux procedure. If only readily hydrolyzed cyanides are present, the absorber liquid from the first reflux period will contain all the available cyanide. If stable complex cyanides are present, a measurable yield will appear in the absorber liquid during the second and succeeding reflux periods, depending on the degree of stability of the compounds.

6.7 *Colorimetric procedure*: The standards and many of the reagents used in this procedure are unstable and must be prepared immediately before use if maximum color development is to be obtained. The color development is also dependent on the presence of approximately equal total-salt concentrations in both samples and standards. If the final distillate volume is 200 mL, it will be about 0.25*M* in NaOH. For this reason 0.25*M* NaOH must be used for dilutions and for the standards and blank. Any substantial deviation in the quantity of 3*M* $HC_2H_3O_2$ required to neutralize blank and standards will require additional manipulation to bring these volumes into approximate agreement. The variation should be less than 0.3 mL.

6.8 Prepare a blank by pipetting 15 mL of 0.25*M* NaOH into a 23-mm absorption cell fitted with a rubber stopper. Prepare standards containing 0.0005 mg and 0.001 mg CN, each diluted to 15 mL with 0.25*M* NaOH in similar containers.

6.9 Take 15-mL aliquots (or smaller volumes diluted to 15 mL with 0.25*M* NaOH) of the distillates from the purification procedure and place in 23-mm stoppered absorption cells.

6.10 Neutralize each sample, blank, and standard with 3*M* $HC_2H_3O_2$ using phenolphthalein indicator solution.

6.11 To each sample, blank, and standard add 4 drops chloramine-T solution, stopper, and shake. Allow 2 min for the reaction to proceed.

6.12 Add 5.0 mL pyridine-pyrazolone reagent and mix well. Allow 20 min for color development.

6.13 Read absorbances at 620 nm. The color is stable for 30 min. The absorbance decreases slowly over a period of 3 h and can probably be read during this period with some decrease in accuracy.

7. Calculations

7.1 Determine the concentration of dissolved or total cyanide in milligrams per liter as follows:

$$\text{CN(mg/L)} = \frac{1000}{\text{mL original sample}} \times \frac{\text{mL distillate}}{\text{mL aliquot}} \times \frac{A_{\text{sample}}}{A_{\text{std.}}} \times \text{mg standard}$$

where

A_{sample} = absorbance of sample,

and

$A_{\text{std.}}$ = absorbance of standard.

7.2 Determine the concentration of cyanide in bottom-material samples in milligrams per kilogram as follows:

$$\text{CN(mg/L)} = \frac{1000}{\text{wt of sample (g)}} \times \frac{\text{mL distillate}}{\text{mL aliquot}} \times \frac{A_{\text{sample}}}{A_{\text{std.}}} \times \text{mg standard}$$

where

A_{sample} = absorbance of sample,

and

$A_{\text{std.}}$ = absorbance of standard.

8. Report

8.1 Report cyanide, dissolved (00723) and total (00720), concentrations as follows: less than 1.0 mg/L, nearest 0.01 mg/L; 1.0 mg/L and above, two significant figures.

8.2 Report cyanide, total-in-bottom-material (00721), concentrations as follows: less than 10 mg/kg, nearest 0.1 mg/kg; 10 mg/kg and above, two significant figures.

9. Precision

Precision data are not available for this method.