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 Ca, 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	0.11	8.1
2.31	0.10	4.2
4.11	0.15	3.6
5.58	0.25	4.4
10.25	0.40	3.9

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

Number of replicates	Mean (ug/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	0.36	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	0.46	5.6	103
8.7	9.23	0.57	6.2	106
9.0	8.40	0.40	4.8	93
16	16.10	0.98	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	0.34	4.6	93
8.7	8.42	0.52	6.2	97
9.0	8.68	0.57	6.5	96
16	15	0.75	5.0	94
Tap water (NOTE 3)				
4.35	9.40	0.72	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.