

COPPER (dust and fume)

7029

Cu MW: 63.54 CAS: 7440-50-8 (Cu) RTECS: GL5325000

METHOD: 7029, Issue 2

EVALUATION: FULL

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OSHA : 0.1 mg/m³ (fume); 1 mg/m³ (dust)
NIOSH: 0.1 mg/m³ (fume); 1 mg/m³ (dust)
ACGIH: 0.2 mg/m³ (fume);
 1 mg/m³ (dust, mist)

PROPERTIES: soft metal; valence +1, +2 in salts
 MP 1083 °C

SYNONYMS: vary depending upon the compound; CAS #1317-39-1 (Cu₂O), CAS #1317-38-0 (CuO)

APPLICABILITY: The working range is 0.05 to 1.3 mg/m³ for a 100-L air sample. This is an elemental analysis, applicable to either dust or fume, with an additional separation step to quantitate soluble copper dust (e.g., CuSO₄) in the presence of copper fume. Aliquots of the samples can be analyzed separately for many additional metals.

INTERFERENCES: Background correction is not required. Interferences to the fume/soluble dust separation step include insoluble copper compounds and copper compounds such as copper acetate which form insoluble hydroxides when dissolved in water.

OTHER METHODS: This method combines and replaces P&CAM 173 [5], S354 [4], and S186 [6]. Method 7300, plasma emission (ICP-AES), is an alternate analytical method.

REAGENTS:

1. Nitric acid, conc.
2. Hydrochloric acid, conc.
3. Hydrochloric acid, 0.5 N. Add 41.5 mL conc. HCl to water, dilute to 1 L.
4. Calibration stock solution, 1000 µg/mL. Commercially available, or dissolve 1.000 g Cu metal in minimum volume of (1:1) HNO₃. Dilute to 1 L with 0.5 N HCl.
5. Distilled-deionized water.
6. Air, filtered.
7. Acetylene.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size, 37 mm-diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with an air-acetylene burner head and copper hollow cathode lamp and two-stage regulators for air and acetylene.
4. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.*
5. Volumetric flasks, 25-mL.*
6. Assorted volumetric pipets, as needed.*
7. Hotplate, surface temperature 140 °C and 400 °C.
8. Equipment for fume/dust separation step:
 - a. cellulose ester membrane filters, 47-mm, 0.3-µm pore size (Millipore PHWP or equivalent);
 - b. cellulose ester membrane filter, 47-mm, 5-µm pore size (Millipore SMWP or equivalent);
 - c. filtration apparatus (Gelman No. 1107 or equivalent).

* Clean all glassware with conc. nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a sample size of 50 to 1500 L. Do not exceed a total filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

NOTE: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD). Other quantitative ashing techniques (e.g., HNO₃-HClO₄ [Method 7300]) may be useful alternatives, especially if several metals are to be determined on a single filter.

3. Proceed to step 4 if fume/dust separation is not desired. For fume/dust separation:
 - a. Using forceps, prewet a 47-mm, 0.3-µm pore size cellulose ester membrane filter by placing it on the surface of distilled water. Remove the filter, tap off excess water, and mount it on the filtration unit.
 - b. Transfer the sample filter from the cassette filter holder to the filtration unit, placing it concentrically on top of the 47-mm filter with the fume deposit up.

- c. Apply and release the vacuum so that the 37-mm filter is gently wetted from the moisture retained on the 47-mm filter. This also insures the removal of any air bubbles between the filters.
 - d. When the fume sample is visually clear of air bubbles and wet throughout, apply a vacuum of 10 to 15 PSIG (69 to 103 kPa). Release the vacuum.
 - e. Place a 47-mm, 5- μ m cellulose ester membrane filter on the surface of water to wet it, remove excess water by blotting with tissue, and place it concentrically on top of the 37-mm filter. Press the surface of the top filter with a clean tissue to insure that no air bubbles remain between any of the filters.
 - f. Mount the upper part of the filtration unit, add 5 mL of distilled water, and allow vacuum to draw water through the filters. Repeat with 5 mL more water. Combine the filtrates which contain soluble copper compounds in a clean beaker. Start reagent blanks at this point.
 - g. Transfer all filters to a clean beaker. Proceed to step 5.
NOTE: Each sample blank is a combination of three filters.
4. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
 5. Add 6 mL conc. HNO_3 . Cover with a watchglass and heat on hotplate (140 °C) until the volume is reduced to approximately 0.5 mL. Repeat two more times using 2 mL conc. HNO_3 each time.
NOTE: Start reagent blanks at this point if step 3 was omitted.
 6. Add 2 mL conc. HCl, cover with a watchglass, heat on hotplate (400 °C) until the volume is reduced to approximately 0.5 mL. Repeat two more times using 2 mL conc. HCl. Do not allow the solution to go to dryness at any point.
 7. Cool solution and add 10 mL distilled water.
 8. Transfer the solution quantitatively to a 25-mL volumetric flask. Dilute to volume with distilled water.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards. Add known amounts, covering the range 0 to 125 μg Cu per sample, of calibration stock solution to 25-mL volumetric flasks and dilute to volume with 0.5 N HCl.
10. Analyze the working standards together with the blanks and samples (steps 15 and 16).
11. Prepare a calibration graph by plotting absorbance versus solution concentration ($\mu\text{g}/\text{mL}$).
12. Aspirate a standard for every 10 samples to check instrument drift.
13. Check analytical recoveries with at least one spiked media blank per 10 samples.
14. Use method of additions occasionally to check for interferences.

MEASUREMENT:

15. Set spectrophotometer as specified by the manufacturer and to conditions on page 7029-1.
16. Aspirate standards, samples, and blanks. Record absorbance readings.
NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute the sample solutions with 0.5 N HCl, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

17. Using the measured absorbances, calculate the corresponding concentrations ($\mu\text{g}/\text{mL}$) of copper in the sample, C_s , and average media blank, C_b , from the calibration graph.
18. Using the solution volumes (mL) of the sample, V_s , and media blanks, V_b , calculate the concentration of copper in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S186 was validated on August 29, 1975, with overall sampling and analytical precision, $\hat{S}_{rT} = 0.051$, over the range 0.47 to 1.8 mg/m³ for a 90-L sample of CuO dust [3,6] and Method S354 was validated on September 30, 1977, with overall sampling and analytical precision, $\hat{S}_{rT} = 0.058$, over the range 0.05 to 0.37 mg/m³ for a 480-L sample of Cu fume [1,4]. Copper fume atmospheres were generated by thermal decomposition and subsequent oxidation of cupric acetate aerosol. The size of the copper fume was 0.04 to 0.14 μm by electron microscopy and the collection efficiency of the sampler for this fume was 1.00 [1,4,9].

The dust-fume separation step was evaluated with samples laden with copper fume generated from copper welding; the samples were then placed into a dust generation system and overlaid with a known deposition of copper sulfate dust. With a dust loading of about 600 μg CuSO₄ and fume concentrations of 0.13 to 0.59 mg/m³, an average of 96.5% of the dust was removed. The analysis of the copper fume had a pooled \hat{S}_r of 4.4% with an average bias of 5.3% [2].

Efficiencies of removal of Cu dust and fume were determined from samples containing only dust or only fume. Measured efficiencies were: (1) from filters containing 213 to 265 μg CuSO₄, an average of 97.8% was removed using 10 to 50 mL water; (2) filters laden with ca. 200 μg Cu/filter lost 11.5% Cu after washing with 10 mL H₂O. Because the non-equilibrium nature of the washing process does not lend itself to accurate prediction of the amount of copper fume removed by the wash water, no correction factor for the amount of fume removed was determined or employed. The elemental analysis used in the evaluation did not distinguish between copper from the fume and from the dust [2].

REFERENCES:

- [1] Backup Data Report for Copper Fume, S354, prepared under NIOSH Contract No. 210-76-0123, available as "Ten NIOSH Analytical Methods, Set 5," Order No. PB 287-499 from NTIS, Springfield, VA 22101.
- [2] Carsey, T. Development of a Sampling and Analytical Method for Copper Fume, final report, NIOSH (DPSE) (unpublished, September, 1982).
- [3] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
- [4] Ibid, V. 4, Method S354, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
- [5] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
- [6] Ibid, V. 3, Method S186, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
- [7] Winefordner, J. D., Ed. Spectrochemical Methods of Analysis, John Wiley & Sons (1971).
- [8] Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer (1976).
- [9] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

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