METHOD SUMMARY

This method is an older reference method made available for labs without either flameless atomic absorption or inductively coupled plasma spectrophotometers. The sample is evaporated to remove the organic material and digested with concentrated acids to convert the copper to a water soluble sulfate. The solution is buffered and the pH adjusted to 9.1 ±0.1. Sodium diethyldithiocarbamate is reacted with the copper to form a yellow complex, which is measured by a spectrophotometer at about 448 nm. The absorbance is converted to concentration of copper by means of a calibration curve.

SAFETY

Acrylonitrile is hazardous to the health and dangerous to handle. Use acrylonitrile in a well ventilated hood. Review the MSDS for detailed information concerning toxicity, first aid procedures and safety precautions.

Perchloric acid is an acute irritant and highly toxic by inhalation or digestion. Perchloric acid can form explosive mixtures with organic materials. It can also violently decompose when shaken or heated. Use perchloric acid only in an acid fume hood. Store perchloric acid only in glass bottles, 250 ml or smaller, and away from organics. Wear rubber gloves when handling.

Refer to the appropriate safety section or site manual for the necessary protective equipment to use when handling any reagents or samples.

REFERENCES

ACEN-13, “Copper by Graphite Furnace Atomic Absorption”

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STM C 14-76, "Copper in Acrylonitrile and Acetonitrile," SOHIO Test Method, 1976.

INTERFERENCES

There are no known interferences to this method.

APPARATUS AND REAGENTS

1. **Spectrophotometer**, suitable for measurement in the visible range (CAL-1).
2. **Cells**, absorption**,** 1 cm matched, Pyrex.
3. **Filter funnel**
4. **Filter paper**, Whatman #42
5. **Beakers**, glass, 250 ml
6. **Beakers**, disposable polystyrene, 50 ml.
7. **Stir bar**, micro**.**
8. **Hot plate,** explosion proof, for evaporating flammable liquids.
9. **Flasks**, volumetric, 50, 100, 500 and 1000 ml, Class A
10. **Pipettes**, assorted sizes, Class A
11. **pH measurement apparatus**, capable of measuring 9.1 pH to an accuracy of 0.1.
12. **Water**, ASTM Type I, or equivalent. Minimum electrical resistivity 18.0 MΩ•cm at 298 K; maximum total organic carbon 50 µg/L; maximum sodium 1 µg/L; maximum chlorides 1 µg/L; maximum total silica 3 µg/L. Detailed specifications can be obtained from ASTM D1193-99e1: www.astm.org.
13. **Acid mixture**: Combine 500 ml of concentrated sulfuric acid with 200 ml of concentrated nitric acid.

14. **Ammonium citrate solution** (200 g/1): Dissolve 20g of ammonium citrate [CAS 3458-72-8] in ASTM water in a 100 ml volumetric flask. Dilute to the mark with water. Filter this solution if it has a cloudy appearance.

15. **Ammonium hydroxide**, [CAS1336-21-6] concentrated.

16. **Copper sulfate solution** (standard, 5 ug/ml). Polyethylene bottles should be used for the storage of copper sulfate solutions because the solutions become reduced in strength if stored in glass. The solutions should be prepared fresh monthly.

    i. Stock solution (500 mg/ul): Dissolve 0.1965g of copper sulfate [CAS 7758-98-7] (CuS04.5H20) in water in a 100 ml volumetric flask. Dilute to the mark with ASTM water. Alternately, use purchased 1000 ppm aqueous atomic absorption standards and dilute accordingly.

    ii. Standard solution (5 ug/ml): Pipet 10 ml of the stock copper sulfate solution into a one liter flask and dilute to the mark with ASTM water. A standard copper solution (1 mg/ml) can be purchased and the standard solution (5 ug/ml) prepared by diluting 5 ml to one liter with ASTM water in a volumetric flask. Fisher Scientific Co. Catalog No. SO-C-194, is satisfactory for this purpose.

17. **Nitric acid**, [CAS 7697-37-2] concentrated.

18. **Nitric acid (3:7)**: [CAS 7697-37-2] Cautiously add 250 ml of concentrated nitric acid ($HN0_3$) to 580 ml of ASTM water.

19. **Perchloric acid**, 70% [CAS 7601-90-3]. This reagent may be used in the optional step for the digestion of organic matter.

20. **Sodium diethyldithiocarbamate** (1 g/1): Dissolve O.lg of sodium diethyldithiocarbamate [CAS 20624-25-3] in ASTM water in a 100 ml volumetric flask. Dilute to the mark with water.

21. **Sulfuric acid**, [CAS 8014-95-7] concentrated (sp gr 1.84).

PROCEDURE

1. PREPARATION OF EQUIPMENT

Wash all glassware before using with hot (3:7) nitric acid and rinse with ASTM water to remove all traces of copper. The best results are obtained when the glassware is set aside and used only for this method.

2. PREPARATION OF SAMPLE

Filter the sample through Whatman #42 filter paper if it appears to be cloudy or if suspended matter is present. If the sample appears clear, no filtration is necessary.

3. CALIBRATION CURVE:

a) Standard samples: Prepare standards containing 5, 10, 15, 20 and 25 ug of copper as follows: Pipet 1, 2, 3, 4 and 5 ml aliquots of the standard copper solution (5 ug/ml) into separate 50 ml polystyrene beakers. Dilute to about 10 ml with ASTM water. Measure about 10 ml of ASTM water into an additional 50 ml beaker for the zero standard.

b) Color development: Complete the pH adjustment and color development steps for the standard samples and the zero standard as in steps 10 through 13.

c) Absorbance measurement: Establish the wavelength of maximum absorbance for each spectrophotometer by scanning the region 50 nm above and below 448 nm, using the 15 ug standard in the 1 cm sample cell and ASTM water in the reference cell. Use the wavelength which gives maximum absorbance if it falls within the specified limits. If it does not, recalibrate and readjust the wavelength. Zero the spectrophotometer with air in the sample and reference cell at the wavelength of maximum absorbance. Measure the absorbance of each standard sample against the reference cell containing the zero standard.

d) With graph paper, plot the absorbance vs. concentration (0-25 ug copper) and prepare a calibration curve by drawing the best straight line. Record the spectrophotometer settings on the graph paper.

4. Pour 125 ml of sample into an acid-washed beaker. 125 ml of sample weighs approximately 100 grams.

6. Evaporate the sample slowly to complete dryness. Allow the beaker to cool before proceeding to the next step.

7. Add 3 ml of acid mixture to the sample beaker and to an acid-washed beaker that will serve as the reagent blank. Place both on the hot plate and heat until the acid boils and the white fumes of sulfuric acid are observed. Remove the beaker from the hot plate to cool. If the residue is colored, repeat the digestion or perform the optional perchloric acid oxidation in Step 8. If colorless, proceed to Step 9 for dissolution of the residue.

8. Optional perchloric acid oxidation: If undigested organic matter is present, the following optional oxidation may be performed. After the beaker has cooled, cautiously add 0.2 ml of 70% perchloric acid. Add an equal amount to both sample and blank. CAUTION: Hazardous reagent - See SAFETY section. Carry out this oxidation step in a specially constructed oxidation fume hood. Return the beaker to the hot plate, apply heat, and fume until 2 to 3 ml of solution remains. Repeat digestion if the residue is colored. Proceed to Step 9 when the residue is colorless.

9. Add approximately 20 ml of ASTM water to dissolve the residue. Transfer the solution quantitatively to a 50 ml polystyrene beaker; keep the total volume to about 30 ml.

10. Add 5 ml of ammonium citrate solution and mix thoroughly.

11. Adjust the pH to 9.1 ±0.1 with concentrated ammonium hydroxide. Stir solutions with. a stir plate and a micro-sized stir bar.

12. Transfer the solution quantitatively to a 50 ml volumetric flask. Pipet 1 ml of sodium diethyldithiocarbamate solution into the flask and dilute to the mark with ASTM water. Mix thoroughly.

13. Allow 5 minutes for the maximum color development.

14. Set the spectrophotometer wavelength and zero with air in both sample and reference cells. Measure the sample absorbance with the reagent blank in the reference cell.

CALCULATIONS

Determine the copper content of the sample in micrograms from the net absorbance from the calibration curve. Calculate the copper contents in parts per million from the following equation:

$$\text{Copper, ppm} = \frac{a \div b}{c} = \frac{\mu g}{g}$$

where: a = net absorbance
b = slope from calibration curve
c = sample weight, g

REPORT

Report the copper concentration in parts per million to the nearest 0.01 ppm. Minnimum report value is 0.02 ppm. Report value less as <0.02 ppm.

Example: Copper, ppm = 0.02.

WORKSHEET FOR
CALCULATION OF CALIBRATION CURVE

C denotes Concentration A denotes Net Absorbance

Standard#	C	C^2	A	CA
1	_____	_____	_____	_____
2	_____	_____	_____	_____
3	_____	_____	_____	_____
4	_____	_____	_____	_____
5	_____	_____	_____	_____
6	_____	_____	_____	_____
Sum:	$\sum C$ =_____	$\sum C^2$= _____	$\sum A$ =_____	$\sum CA$ =
Average:	$\dot{C}$ =_____		$\bar{A}$ =_____	

Number of Points: n=_____

Step

(1) $\sum CA$ =_____

(2) $(\sum C)(\sum A) \div n$ =_____

(3) Step (1) - Step (2) = _____

(4) $\sum C^2$=_____

(5) $(\sum C)^2 \div n$ =_____

(6) Step (4) - Step (5) =_____

(7) Slope: b = Step (3) ÷ Step (6) = _____

(8) $\bar{A}$ = _____

(9) $b\dot{C}$ =_____

(10) Intercept: a = Step (8) - Step (9) =_____

(11) Net absorbance of sample: A_s =_____

(12) A_s - a = step (11) - step (10) =_____

(13) Concentration in Sample: C_s = Step (12) ÷ Step (7) =_____