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AMERICAN SOCIETY FOR TESTING AND MATERIALS  
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## Standard Test Method for Copper In Electrical Insulating Oil By Atomic Absorption Spectrophotometry<sup>1</sup>

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### 1. Scope

1.1 This test method covers the determination of copper in new or used electrical insulating oil by atomic absorption spectrophotometry.

1.2 The lowest limit of detectability is primarily dependent upon the method of atomization, but also upon the energy source, the fuel and oxidant, and the degree of electrical expansion of the output signal. The lowest detectable concentration is usually considered to be equal to twice the maximum variation of the background. For flame atomization, the lower limit of detectability is generally in the order of 0.1 ppm. For non-flame atomization, the lower limit of detectability is less than 0.01 ppm.

1.3 The values stated in acceptable metric units are to be regarded as the standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* See 5.3 for specific precautionary statements.

### 2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water<sup>2</sup>

D 2576 Method of Test for Metals in Water and Waste Water by Atomic Absorption Spectrophotometry<sup>3</sup>

### 3. Summary of Test Method

3.1 The sample of oil is diluted with an appropriate organic solvent and analyzed in an atomic absorption spectrophotometer. Alternate procedures are provided for instruments employing flame and non-flame atomization. Concentration is determined by means of calibration curves prepared from standard samples.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-27 on Electrical Insulating Liquids and Gases and is the direct responsibility of Subcommittee D27.03 on Analytical Tests.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol. 11.01.

<sup>3</sup> Discontinued; see *1980 Annual Book of ASTM Standards*, Part 31.

### 4. Significance and Use

4.1 Electrical insulating oil may contain small amounts of dissolved metals derived either directly from the base oil or from contact with metals during refining or service. When copper is present, it acts as a catalyst in promoting oxidation of the oil. This test method is useful for research and to assess the condition of service-aged oils.

### 5. Apparatus

5.1 *Volumetric flasks*, 100-mL capacity.

5.2 *Burets*, 5 and 50-mL capacity.

5.3 *Atomic Absorption Spectrophotometer* —The instrument shall have an atomizer, a spectral energy source, usually consisting of a copper hollow cathode lamp, a monochromator capable of isolating the desired line of radiation, an adjustable slit, a photomultiplier tube or other photosensitive device as a light measuring and amplifying device, and a read-out mechanism for indicating the amount of absorbed radiation. **Caution:** Proper ventilation must be provided to remove toxic metal vapors.

5.3.1 Instruments employing flame atomization require a nebulizer assembly, burner head, and suitable pressure and flow regulating devices to maintain constant oxidant and fuel flow for the duration of the tests.

5.3.1.1 *Oxidant-Air*, cleaned and dried through a suitable filter to remove oil, water, and other foreign substances.

5.3.1.2 *Acetylene*, purified grade.

NOTE 1—Acetylene cylinders should be replaced when the pressure reaches 100 psi to prevent acetone, always present, from entering and damaging the burner head.

5.3.1.3 *Glass Syringe*,<sup>4</sup> 10-mL capacity.

5.3.1.4 *Platinum Dish*, 200-mL capacity minimum.

5.3.2 Instruments employing non-flame atomization require a suitable pressure regulating device to maintain an inert atmosphere.

5.3.2.1 *Argon*, commercial grade.

<sup>4</sup> B-D Multitip syringes with glass Luer tips, available from Becton, Dickinson and Co., Rutherford, NJ have been found satisfactory for this method.

- 5.3.2.2 *Carbon Rod Analyzer and Carbon Tube Atomizer*.<sup>5</sup>  
 5.3.2.3 *Strip Chart Recorder*<sup>6</sup> (if permanent record is required).  
 5.3.2.4 *Pipets*,<sup>7</sup> 1 and 5- $\mu$ L.

## 6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>8</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to the requirements in Specification D 1193 for Reagent Water, Type 1.

6.3 *Nitric Acid (1 + 2)*—Add one volume of nitric acid ( $\text{HNO}_3$  sp gr 1.42) to two volumes of water.

6.4 *New Oil*—Unused oil of the same type as that being tested.

6.5 *Methyl Isobutyl Ketone (MIBK)*.

6.6 *Bis (1-Phenyl-1, 3-Butanediono) Copper (II)*—National Institute of Standards and Technology Metallo-Organic Compound No. 1080.<sup>9</sup>

## 7. Preparation of Glassware

7.1 All glassware should be washed thoroughly, rinsed with  $\text{HNO}_3$  (1 + 2), and then with distilled water. Dry thoroughly.

## 8. Procedure A—Flame Atomization

8.1 *Preparation of Standard Copper Solution* (500 ppm Cu):

8.1.1 Dissolve 0.3030 g of NIST Standard No. 1080, bis(1-phenyl-1, 3-butanediono) copper (II), according to instructions received with the standard, and dilute to  $100.0 \pm 0.1$  g with new oil to make a 500 ppm standard copper solution. Shake well.

8.2 *Preparation of Working Standards*:

8.2.1 Dilute 2.00 g of the standard copper solution to 100 mL with new oil to give an intermediate standard containing approximately  $10\mu$  g/mL Cu. This working standard contains the  $10\mu$  g/mL Cu added plus any copper present in the new oil used to make the standard. If the copper content of the new oil is not known, it must be determined. A method for making this determination is contained in Appendix X1.

<sup>5</sup> Equipment from Varian Techtron, 670 E. Arquez Ave., Sunnyvale, CA 94086, has been found satisfactory for this method.

<sup>6</sup> Strip chart recorder from Leeds and Northrup, Sumneytown Pike, North Wales, PA 19454, has been found satisfactory for this method.

<sup>7</sup> Pipets from Oxford Laboratories, 1149 Chess Dr., Foster City, CA 94404, have been found satisfactory for this method.

<sup>8</sup> "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

<sup>9</sup> Available from the Office of Standard Reference Materials, U.S. Department of Commerce, National Institute of Standards and Technology, Washington, DC 20234.

8.2.2 Dilute the  $10\mu$  g/mL Cu solution with new oil so as to obtain four standards containing additions of 0.0, 0.5, 1.0, and  $3.0\mu$  g/mL Cu; dilute each with MIBK to obtain an oil to ketone ratio of 10% (V/V) as follows (Note 2):

Working Standard	10 $\mu$ g/mL Cu standard, mL	New Oil, mL	MIBK, mL
No. 1	0.0	10.0	90
No. 2	0.5	9.5	90
No. 3	1.0	9.0	90
No. 4	3.0	7.0	90

NOTE 2—The new oil used to make these dilutions must be the same new oil used to make the  $10\mu$  g/mL standard. Good transfers can be affected if a 50-mL buret is used for the new oil and a 5-mL buret is used for the  $10\mu$  g/mL Cu standard. Do not transfer the solutions too rapidly.<sup>10</sup>

8.2.3 Shake well after dilution with MIBK.

8.3 *Preparation of Sample*:

8.3.1 Using a 10-mL glass syringe, transfer 10 mL of the sample to be tested to a 100-mL volumetric flask. Dilute to volume with MIBK and shake well.

8.4 *Spectrophotometric Measurement*:

8.4.1 Operate the atomic absorption spectrophotometer according to the manufacturer's instructions for the determination of copper with the following exceptions and additions:

8.4.1.1 Set the auxiliary air at twice the aspirating air.

8.4.1.2 For narrow slit burners, reduce flow as low as possible while maintaining the flame on the burner head. For three slit burners, reduce fuel flow as low as possible while aspirating straight MIBK so that orange streaks rising from the rivet heads are still visible in the flame.

8.4.1.3 Adjust the aspiration rate for maximum absorbance while burning No. 4 working standard.

8.4.1.4 Set the instrument at zero absorbance while burning No. 1 working standard.

8.4.2 Run the standards and sample in the following order: Standards, sample, standards, sample, and standards.

NOTE 3—If a sample has a copper concentration greater than the range of the working standards, a more accurate result can be obtained by diluting a small aliquot of the sample with appropriate addition of new oil and MIBK to keep the 10% oil to ketone ratio and re-running against the working standards.

## 9. Calculation and Report

9.1 Average the readings, and if the scale was expanded, divide the averages by the scale expansion factor and convert to absorbances. Subtract the absorbance of the No. 1 working standard as a blank from the absorbances of the other standards and samples and plot versus copper added.

9.2 Calculate the copper concentration, in parts per million, as follows:

$$\text{Copper, ppm} = \frac{A + B}{d}$$

where:

A = copper concentration of the sample solution determined from the concentration plot,  $\mu$ g/mL, (Note 4),

<sup>10</sup> Dilutors from Labindustries, 1802 2nd St., Berkeley, CA 94710, have been found satisfactory for this method.