Designation: D 3635 – 90 (Reapproved 1998)

AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428
Reprinted from the Annual Book of ASTM Standards. Copyright ASTM

Standard Test Method for Copper In Electrical Insulating Oil By Atomic Absorption Spectrophotometry [1]

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[2]

D 2576 Method of Test for Metals in Water and Waste Water by Atomic Absorption Spectrophotometry[3]

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.

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*, [4] 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.

---

[1] This test method is under the jurisdiction of ASTM Committee D-27 on Electrical Insulating Liquids and Gasesand is the direct responsibility of Subcommittee D27.03on Analytical Tests.

Current edition approved Jan. 26, 1990. Published March 1990. Originally published as D 3635 – 77. Last previous edition D 3635 – 84.

[2] *Annual Book of ASTM Standards,* Vol. 11.01.

[3] Discontinued; see *1980 Annual Book of ASTM Standards,* Part 31.

[4] B-D Multifit syringes with glass Luer tips, available from Becton, Dickenson and Co., Rutherford, NJ have been found satisfactory for this method.

5.3.2.2 *Carbon Rod Analyzer and Carbon Tube Atomizer*. [5]

5.3.2.3 *Strip Chart Recorder*[6] (if permanent record is required).

5.3.2.4 *Pipets*, [7] 1 and 5-µL.

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.[8] 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 (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.[9]

7. Preparation of Glassware

7.1 All glassware should be washed thoroughly, rinsed with 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 ± 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 10µ g/mL Cu. This working standard contains the 10 µg/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.

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

Working Standard	10 µg/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 µg/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 10µ g/mL Cu standard. Do not transfer the solutions too rapidly.[10]

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, µg/mL, (Note 4),

---

[5] Equipment from Varian Techtron, 670 E. Arquez Ave., Sunnyvale, CA 94086, has been found satisfactory for this method.

[6] Strip chart recorder from Leeds and Northrup, Sumneytown Pike, North Wales, PA 19454, has been found satisfactory for this method.

[7] Pipets from Oxford Laboratories, 1149 Chess Dr., Foster City, CA 94404, have been found satisfactory for this method.

[8] "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."

[9] Available from the Office of Standard Reference Materials, U.S. Department of Commerce, National Institute of Standards and Technology, Washington, DC 20234.

[10] Dilutors from Labindustries, 1802 2nd St., Berkeley, CA 94710, have been found satisfactory for this method.

B = copper concentration of the new oil used to prepare the working standards, µg/mL and
d = density of the oil sample, g/mL.

NOTE 4—This value will be negative if the copper in the new oil used to make the working standards is greater than the copper in the samples tested. When this occurs, the negative sign should be retained in the above formula.

9.3 Report the results to the nearest 0.1 ppm.

10. Procedure B—Non-Flame Atomization

10.1 Follow 8.1 to 8.2.1, inclusive, in Procedure A.

NOTE 5—The copper concentration of the new oil used to make the 10 µg/mL standard in 8.2.1 does not need to be determined by Appendix X1 for Procedure B.

10.2 Dilute the 10 µg/mL Cu solution with new oil so as to obtain five intermediate standards containing additions of 0.00, 0.05, 0.10, 0.50, and 1.00 µg/mL copper, respectively. Dilute each with MIBK to obtain an oil to ketone ratio of 10 % (V/V) as follows (Note 2):

Working Standard	10 mg/mL Cu Standard, mL	New Oil, mL	MIBK, mL
No. 1	0.00	10.0	90
No. 2	0.05	9.95	90
No. 3	0.10	9.90	90
No. 4	0.50	9.50	90
No. 5	1.00	9.00	90

10.2.1 Shake the standard solutions well after dilution with MIBK.

10.3 Prepare samples as indicated in 8.3.1 (Note 3).

10.4 Set up the carbon rod parameters for oil samples. A 5-µL sample size can be used for the above standard solutions. Operate the carbon rod analyzer according to the manufacturer's instructions with the following exceptions and additions.

10.4.1 The following decontamination and sample run parameters have been found satisfactory.

NOTE 6—The temperatures achieved by control settings are only approximate and may vary with individual instruments.

Decontamination Run

Cycle	Control Setting
Dry cycle	= 5 s, 150°C
Ash cycle	= 10 s, 550°C
Atomize cycle	= 4 s, 2500°C

Sample Run

Cycle	Control Setting
Dry cycle	= 5 s, 150°C
Ash cycle	= 10 s, 550°C
Atomize cycle	= 4 s, 2500°C

10.4.1.1 A decontamination run is recorded. If no signal is recorded above the noise level, make a sample run of the blank oil. If a signal is obtained on the decontamination run, repeat it. If a signal still persists, increase the atomize cycle temperature to 2700°C and repeat the run. If a signal still persists, refer to the instrument manual.

10.4.2 Once a decontamination run has been obtained with no spurious signals, obtain triplicate absorbance values for each standard used.

10.4.3 When an unknown sample signal is brought on scale according to the manufacturer's recommendation, obtain triplicate absorbance values for each sample.

11. Calculation and Report

11.1 Plot the absorbance versus the copper added (microgram per millilitre) to the standards in 10.2. The negative value of the concentration intercept represents the copper concentration in the new oil used to prepare these standards and in the MIBK used to dilute them.

11.2 Calculate the copper concentration in the samples as indicated in 9.2.

11.3 Report the results to the nearest 0.01 ppm.

12. Precision and Bias

12.1 It is not practicable to specify the precision and bias of this test method due to the difficulties involved in circulating samples for round robin testing.

APPENDIX

(Nonmandatory Information)

X1. METHOD FOR DETERMINING COPPER IN INSULATING OIL BY ASHING AND ATOMIC ABSORPTION SPECTROPHOTOMETRY

X1.1 Transfer to a clean platinum dish approximately 100 g of new oil weighed to the nearest 0.1 g. Heat the dish with a Bunsen burner until the contents ignite and burn readily. Continue heating with the burner in such a manner that the sample burns at a moderate and uniform rate until only ash and carbon remain after burning ceases. If an additional sample is required to obtain sufficient copper for accurate analysis, cool the dish, transfer additional weighed sample and burn as above. Wet the residue with 2 mL of sulfuric acid (H_2SO_4, 1 + 1) and heat carefully with the burner until no more sulfur trioxide (SO_3) is evolved. Place in a muffle furnace and ignite at 600 ± 25°C until oxidation of carbon is complete. Cool to room temperature.

X1.2 Treat the residue (X1.1) with 20 mL of 6 *N* HNO_3 and evaporate to moist dryness. Add 10 mL of 1% HNO_3 and transfer the contents of the dish to a 100-mL beaker with 10 mL 1 % HNO_3. Filter through an ashless close-texture paper into a 50-mL volumetric flask, wash thoroughly with 1 % HNO_3, and dilute to 50 mL with 1 % HNO_3.

X1.3 Determine the copper in the solution (X1.2) by atomic absorption spectrophotometry in accordance with Test Method D 2576.

X1.4 If the copper value of the solution (X1.3) is below the working range of the instrument, place a 40-mL aliquot of the solution in a 100-mL beaker and evaporate to about 5 mL. Cool and transfer quantitatively to a 10-mL volumetric flask and dilute to 10 mL. Determine the copper in accordance with X1.3.

X1.5 *Calculation*—Calculate the copper content of the original oil as follows:

$$\text{copper, ppm} = A \times 0.05/W$$

or

$$\text{copper, ppm} = B \times 0.0125/W$$

where:

A = copper concentration determined in 8.3,
B = copper concentration determined in 8.4,
W = weight of sample, g.