



# Standard Test Method for Dissolved Copper In Electrical Insulating Oil By Atomic Absorption Spectrophotometry <sup>1</sup>

This standard is issued under the fixed designation D 3635; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers the determination of copper in new or used electrical insulating oil of petroleum origin 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 or 0.1 mg/kg. For non-flame atomization, the lower limit of detectability is less than 0.01 ppm.

1.3 The values stated in SI 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 5.4 for specific precautionary statements.

## 2. Referenced Documents

2.1 *ASTM Standards:*

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

D 3487 Specification for Mineral Insulating Oil Used in Electric Apparatus<sup>3</sup>

D 5222 Guide for High Fire-Point Mineral Electrical Insulating Oils<sup>3</sup>

## 3. Summary of Test Method

3.1 The test specimen of oil is filtered and 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 for new oils and to assess the condition of service-aged oils. Consideration should be given to the limits of detection outlined in the scope.

## 5. Apparatus

5.1 *Volumetric flasks*, 100-mL capacity.

5.2 *Membrane filter*, 0.45  $\mu\text{m}$ .

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

5.4 *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.

5.4.1 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.

5.4.1.1 *Glass Syringe*, 10-mL capacity.

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

5.4.2.1 *Graphite Furnace* with background correction.

5.4.2.2 *Output Device, Printer or Strip Chart Recorder* (if permanent record is required).

5.4.2.3 *Pipets*, 1 and 5- $\mu\text{L}$ .

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

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 10.03.

## 6. Reagents

6.1 *Purity of Reagents*—Use reagent grade chemicals in all tests.

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<sub>3</sub> sp gr 1.42) to two volumes of water.

6.4 *New Oil*—Unused oil of the same type as that being tested, such as oil meeting the requirements of Specification D 3487 or as described in Guide D 5222.

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>4</sup>

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

6.8 *Acetylene*, atomic absorption grade (Note 1).

6.9 *Argon*, commercial grade.

NOTE 1—Acetylene cylinders should be replaced when the pressure reaches 700 kPa (~100 psi) to prevent acetone, always present, from entering and damaging the burner head.

## 7. Preparation of Glassware

7.1 Wash all glassware thoroughly, rinse with HNO<sub>3</sub> (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 10 μg/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. When detectable levels of copper are suspected in the new oil or the copper content is simply unknown, refer to 8.4.1.5.

8.2.2 Add to new oil aliquots of 10 μg/mL Cu solution 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 (blank)	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 effected if a 50-mL buret is used for the new oil and a 5-mL buret is used for the 10 μg/mL Cu standard. Do not transfer the solutions too rapidly.<sup>5</sup>

8.2.3 Shake well after dilution with MIBK.

8.3 *Preparation of Test Specimen*:

8.3.1 Filter the test specimen using a 0.45 μm filter.

8.3.2 Using a 10-mL glass syringe, transfer 10 mL of the filtered test specimen to a 100-mL volumetric flask. Dilute to volume with MIBK and shake well (Note 3).

NOTE 3—If a test specimen 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 test specimen with appropriate addition of new oil and MIBK to keep the 10 % oil to ketone ratio and rerunning against the working standards.

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 if this is within the range of instrument parameters.

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 neat 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.

8.4.1.5 Set the instrument at zero absorbance while burning methyl isobutyl ketone (MIBK). Plot a standard curve of absorbance versus copper concentration for standards no. 1-4. Extrapolate this curve to zero absorbance. The absolute value of the copper concentration at zero absorbance (a negative number) provides an estimate of the copper contained in the standard oil.

8.4.2 Run the standards and test specimen in the following order: Standards, test specimen, standards, test specimen, and 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 test specimens and plot versus copper added.

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

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

where:

<sup>4</sup> Available from the Office of Standard Reference Materials, U.S. Department of Commerce, National Institute of Standards and Technology, Washington, DC 20234.

<sup>5</sup> Dilutors from Labindustries, 1802 2nd St., Berkeley, CA 94710, have been found satisfactory for this method.

$A$  = copper concentration of the test specimen solution determined from the concentration plot,  $\mu\text{g/mL}$  and

$d$  = density of the test specimen,  $\text{g/mL}$ .

9.3 Report the results to the nearest 0.1 ppm.

## 10. Precision and Bias

10.1 It is not possible to specify the precision of procedure A in Test Method D 3635 for measuring dissolved copper in electrical insulating oil because of the difficulty in arranging a round-robin test with a large-enough sample of participating laboratories. Attempts continue to be made to locate a laboratory capable of providing data from which the repeatability of this procedure can be estimated.

10.2 No information can be presented on the bias of Test Method D 3635, procedure A, because no material having an accepted reference value of copper in electrical insulating oil has been made available from a standards organization. Furthermore, the responsible subcommittee has been unable as of yet to attract volunteers for an interlaboratory study.

## 11. Procedure B—Non-Flame Atomization

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

11.1.1 Follow 8.1 in Procedure A.

11.2 *Preparation of Working Standards:*

11.2.1 Follow 8.2.1 in Procedure A.

11.2.2 Add to new oil aliquots of the 10  $\mu\text{g/mL}$  Cu solution so as to obtain five intermediate standards containing additions of 0.00, 0.05, 0.10, 0.50, and 1.00  $\mu\text{g/mL}$  copper, respectively. Dilute each with MIBK to obtain an oil to ketone ratio of 10 % (V/V) as follows (Note 2):

Working Standard	10 $\mu\text{g/mL}$ Cu Standard, mL	New Oil, mL	MIBK, mL
No. 1 (blank)	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

11.2.3 Shake the standard solutions well after dilution with MIBK.

11.3 *Preparation of Test Specimens:*

11.3.1 Prepare samples as indicated in 8.3 (Note 3).

11.4 Set up the graphite furnace atomic absorption spectrophotometer for oil test specimens. A 5- $\mu\text{L}$  sample size can be used for the above standard solutions. Operate the spectrophotometer according to the manufacturer's instructions with the following exceptions and additions.

11.4.1 The following decontamination (instrument blank) and test specimen run parameters have been found satisfactory.

NOTE 4—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

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

11.4.1.1 Record a decontamination run. If no signal is recorded above the noise level, make a run of the blank oil test specimen. 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.

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

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

## 12. Calculation and Report

12.1 Plot the absorbance versus the copper added ( $\mu\text{g/mL}$ ) to the standards in 11.2. 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.

12.2 Calculate the copper concentration in the test specimens as indicated in 9.2.

12.3 Report the results to the nearest 0.01 ppm.

## 13. Precision and Bias

13.1 It is not possible to specify the precision of procedure B in Test Method D 3635 for measuring dissolved copper in electrical insulating oil because of the difficulty in arranging a round robin-test with a large enough sample of participating laboratories. An estimate of the repeatability has been developed based on data supplied by a single laboratory. These data are presented in Appendix X1. These results suggest that the 95 % repeatability limit for copper content is 8.5 % of the test result or approximately 1 ppb, when the mean copper level is 10 ppb.

13.2 No information can be presented on the bias of Test Method D 3635, procedure B, because no material having an accepted reference value of copper in electrical insulating oil has been made available from a standards organization. Furthermore, the responsible subcommittee has been unable to attract enough volunteers for a valid interlaboratory study.

## 14. Keywords

14.1 atomic absorption; copper; electrical insulating oil; spectroscopy

**APPENDIX**
**(Nonmandatory Information)**
**X1. REPEATABILITY DATA ESTIMATE FOR A SINGLE LABORATORY TEST SERIES OF ANALYSES**

X1.1 Data are given from a single laboratory for the measurement of the copper content of two oil samples used as quality control standards which contained copper at known levels. The test results are from two series of test results on two standards on separate dates and are presented in Table X1.1.

These determinations were made using Procedure B of Test Method D 3635.

**TABLE X1.1 Results of Separate Copper-in-oil Determinations**

Sample	Tested on Jan. 13, 1997	Tested on Mar. 28, 1997
Known standard conc.	ppb 11.56	ppb 9
1	10.3	10
2	10.7	10
3	10.8	10
4	10.1	10
5	10.8	10
6	10.7	10
7	10.6	9
8	10.8	10
9	10.4	10
10	11.2	10
11	10.6	
12	10.8	
13	10.8	
14	10.5	
15	10.8	
16	10.8	
Average	10.7	9.9
Standard Deviation (SD)	0.25	0.30
RSD, %	2.3	3.0
Repeatability, %	6.5	8.5

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