Designation: D ~~3635 – 90 (Reapproved 1998)~~ 3635 – 01

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

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 (ϵ) 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 ~~acceptable metric~~ 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 ~~5.3~~ 5.4 for specific precautionary statements.

2. Referenced Documents

2.1 *ASTM Standards:*

---

[1] 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.

Current edition approved ~~Jan. 26, 1990.~~ April 10, 2001. Published ~~March 1990.~~ June 2001. Originally published as D 3635 – 77. Last previous edition D 3635 – 90 (Reapproved 1998~~4~~).

D 1193 Specification for Reagent Water[2]
D ~~2576 Method of Test~~ 3487 Specification for Mine~~t~~ral Insulating Oil Used in ~~Water and Waste Water by Atomic Absorption Spectrophotometry~~ Electric Apparatus[3]
D 5222 Guide for High Fire-Point Mineral Electrical Insulating Oils[3]

3. Summary of Test Method

3.1 The ~~sample~~ 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 µm.

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

5.~~3~~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.~~3~~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.

~~5.3.1.1 *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~~

5.4.1.1 *Glass Syringe*~~, [4]~~, 10-mL capacity.

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

~~5.3.2 Instruments~~

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

~~5.3.2.1 *Argon*, commercial grade.~~

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

~~5.3.2.3 *Strip*~~

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).

---

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

~~[3] Discontinued; see *1980 Annual*~~

[3] *Annual Book of ASTM ~~Standards~~*~~, Part 31.~~ Standards, Vol 10.03.

~~[4] B-D Multifit syringes with glass Luer tips, available~~

[4] Available from ~~B~~ the Offic~~t~~e of Standard Reference Materials, U.S. D~~i~~epartment of Commerc~~k~~e, National Institute of Standards and ~~Co., Rutherford, NJ have been found satisfactory for this method.~~ Technology, Washington, DC 20234.

~~[5] Equipment~~

[5] Dilutors from ~~Varian Techtron, 670 E. Arquez Ave., Sunnyvale,~~ Labindustries, 1802 2nd St., Berkeley, CA ~~94086, has~~ 94710, have been found satisfactory for this method.

5.~~3~~4.2.~~4~~3 *Pipets*~~,[6]~~, 1 and 5-µL.

6. Reagents

6.1 *Purity of Reagents*—~~R~~Use 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.[6] 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.~~ 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)~~ (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, 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-~~P~~phenyl-1, 3-~~B~~butanediono)~~—C~~ *copper* (II)—National Institute of Standards and Technology Metallo-Organic Compound No. 1080.[6]

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 ~~A~~Wash all glassware~~ should be washed~~ thoroughly, rinse~~d~~ with HNO_3 ~~(1 + 2),~~ (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~~ When detectable levels of copper are suspected in~~ Appendix X1.~~

~~8.2.2 Dilute~~ 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~~ 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. 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~~ a~~ effected 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.[5]

8.2.3 Shake well after dilution with MIBK.

8.3 *Preparation of~~ Sample~~ Test Specimen* :

8.3.1 ~~U~~Filter the test specimen using a 0.45 µm filter.

8.3.2 Using a 10-mL glass syringe, transfer 10 mL of the~~ sample~~ filtered test specimen to~~ be tested 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~~ straight~~ 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.

~~8.4.2 Run~~

8.4.1.5 Set the~~ standards and sample in the following order: Standards, sample, standards, sample, and standards.~~

~~Note 3—If~~ instrument at zero absorbance while burning methyl isobutyl ketone (MIBK). Plot a~~ sample has a~~ standard curve of absorbance versus copper concentration~~ greater than the range~~ for standards no. 1-4. Extrapolate this curve to zero absorbance. The absolute value of the~~ working standards, a more accurate result can be obtained by diluting a small aliquot~~ copper concentration at zero absorbance (a negative number) provides an estimate of the~~ sample with appropriate addition of new oil and MIBK to keep~~ copper contained in the~~ 10 % oil to ketone ratio~~ standard oil.

8.4.2 Run the standards and~~ re-running against~~ test specimen in the~~ working~~ 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 ~~samples~~ test specimens and plot versus copper added.

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

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

$$C\text{ opper, ppm} = \frac{A}{d}$$

where:

A = copper concentration of the~~ sample~~ test specimen solution determined from the concentration plot,~~ µg/mL, (Note 4),~~ µg/mL and

~~B = copper concentration of the new oil used to prepare the working standards, µg/mL and~~

d = density of the~~ oil sample, g/mL.~~ test specimen, 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. 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~~ to 8.2.1, inclusive,~~ in Procedure A. ~~Note 5—The copper concentration~~

11.2 *Preparation of~~ the~~ Working Standards* :

11.2.1 Follow 8.2.1 in Procedure A.

11.2.2 Add to new oil~~ used to make~~ aliquots of 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~~ Working Standard	~~10 mg/mL Cu Standard, mL~~ 10 µg/mL Cu Standard, mL	~~New Oil, mL~~ New Oil, mL	~~MIBK, mL~~ MIBK, mL
~~No. 1~~	~~0.00~~	~~10.0~~	~~90~~
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

1~~0~~1.2.~~1~~3 Shake the standard solutions well after dilution with MIBK.

1~~0~~1.3 *Preparation of Test Specimens* :

11.3.1 Prepare samples as indicated in ~~8.3.1~~ 8.3 (Note 3).

1~~0~~1.4 Set up the ~~carbon rod parameters~~ graphite furnace atomic absorption spectrophotometer for oil ~~samples.~~ test specimens. A 5-μL sample size can be used for the above standard solutions. Operate the ~~carbon rod analyzer~~ spectrophotometer according to the manufacturer's instructions with the following exceptions and additions.

1~~0~~1.4.1 The following decontamination (instrument blank) and ~~sample~~ test specimen run parameters have been found satisfactory.

NOTE ~~6~~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

~~Sample Run~~

Test Specimen Run

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

1~~0~~1.4.1.1 ~~A~~Record a decontamination ~~run is recorded.~~ run. If no signal is recorded above the noise level, make a ~~sample~~ 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.

1~~0~~1.4.2 Once a decontamination run has been obtained with no spurious signals, obtain triplicate absorbance values for each standard used.

1~~0~~1.4.3 When an unknown ~~sample~~ test specimen 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.~~ test specimen.

12. Calculation and Report

12.1 Plot the absorbance versus the copper added (μg/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

1~~2~~3.1 It is not ~~practicable~~ possible to specify the precision ~~and bias~~ 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 ~~method due to~~ result or approximately 1 ppb, when the ~~difficulties involved~~ 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 elec~~i~~trical 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 stu~~n~~dy.

14. Keywords

14.1 atomic absorption~~ t~~; copper; electrical insulating~~.~~ oil; spectroscopy

APPENDIX

(Nonmandatory Information)

~~X1. METHOD~~

X1. REPEATABILITY DATA ESTIMATE FOR ~~DETERMINING COPPER IN INSULATING OIL BY ASHING AND ATOMIC ABSORPTION SPECTROPHOTOMETRY~~ A SINGLE LABORATORY TEST SERIES OF ANALYSES

X1.1 ~~Transfer to~~ Data are given from a ~~clean platinum dish approximately 100 g~~ single laboratory for the measurement 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~~ content of two oil samples used 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~~ quality control standards which contained copper at ~~600 ± 25°C until oxidation~~ known levels. The test results are from two series of ~~carbon is complete. Cool to room temperature.~~

~~X1.2 Treat the residue (X1.1) with 20 mL of 6 *N* HNO_3~~ test results on two standards on separate dates 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~~ are presented in ~~the solution (X1.2) by atomic absorption spectrophotometry in accordance with~~ Table X1.1. These determinations were made using Procedure B of Test Method ~~D 2576.~~

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

Sample	Tested on Jan. 13, 1997	Tested on Mar. 28, 1997
	ppb	ppb
Known standard conc.	11.56	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

~~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*~~ *D 3635.* ~~—Calculate the copper content of the original oil as follows:~~

~~copper, ppm = $A \times 0.05/W$~~

~~or~~

~~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.~~

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org).