Designation: D3635 – 13 (Reapproved 2021)

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

This standard is issued under the fixed designation D3635; 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 SI units are to be regarded as standard. No other units of measurement are included in this 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D3487 Specification for Mineral Insulating Oil Used in Electrical Apparatus

D5222 Specification for High Fire-Point Mineral Electrical Insulating Oils

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 µm.

5.3 *Burets,* 5-mL 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. **Warning—**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.

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

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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-µL and 5-µL.

5.5 *Analytical Balance,* capable of weighing to 0.0001 g.

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 D1193 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, such as oil meeting the requirements of Specification D3487 or as described in Specification D5222.

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.[3]

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_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 g ± 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. 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 µg/mL, 0.5 µg/mL, 1.0 µg/mL, 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 10µ g/mL Cu standard. Do not transfer the solutions too rapidly.[4]

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 Nos. 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.

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

[4] The sole source of supply of dilutors known to the committee at this time is Labindustries, 1802 2nd St., Berkeley, CA 94710. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.