



Designation: D1533 – 20

Standard Test Method for Water in Insulating Liquids by Coulometric Karl Fischer Titration¹

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1. Scope

1.1 This test method covers the measurement of water present in insulating liquids by coulometric Karl Fischer titration. This test method is used commonly for test specimens below 100 % relative saturation of water in oil. The coulometric test method is known for its high degree of sensitivity (typically 10 $\mu\text{g H}_2\text{O}$). This test method requires the use of equipment specifically designed for coulometric titration.

1.2 This test method recommends the use of commercially available coulometric Karl Fischer titrators and reagents.

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. For specific precautionary statements see 8.1 and A2.1.*

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

D923 Practices for Sampling Electrical Insulating Liquids

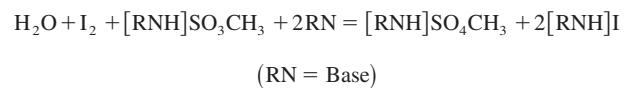
¹ This test method is under the jurisdiction of ASTM Committee D27 on Electrical Insulating Liquids and Gases and is the direct responsibility of Subcommittee D27.06 on Chemical Test.

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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.

3. Summary of Test Method

3.1 This test method is based on the reduction of iodine containing reagent according to the traditional Karl Fischer reaction. The proposed reaction mechanism is as follows:³



The endpoint is determined amperometrically with a platinum electrode that senses a sharp change in cell resistance when the iodine has reacted with all of the water in the test specimen.

3.2 The coulometric Karl Fischer test method requires the use of an automatic titrator with commercially available reagents. Karl Fischer instruments regenerate iodine coulometrically from the iodide in the Karl Fischer reagent. The test specimen is injected into a titration cell where the iodine consumed by the reaction with water is electrolytically regenerated by anodic oxidation of iodide. The completion of the reaction is detected with a platinum sensing electrode. The coulombs of electricity required to generate the necessary amount of iodine then is converted into the amount of water present in the test specimen by use of the Faraday equation.

3.3 *Titration Cell*—The coulometric titration cell consists of either a sealed vessel containing both an anode and cathode which are separated by a diaphragm or a sealed vessel containing an anode and cathode which are not separated by a diaphragm. In both cells the anode compartment contains a solution consisting of sulfur dioxide, iodide, and an amine in a solvent containing methanol/chloroform or methanol/longer chain alcohol. In the cell with a diaphragm the cathode compartment contains similar reagents optimized for cathodic reduction.

4. Significance and Use

4.1 Electrical characteristics of an insulating liquid may be affected deleteriously by excessive water content. A high water

³ Scholz, E., "Karl-Fischer Titration," Springer-Verlag, Berlin, Heidelberg, New York, Tokyo, 1984, 140 pp.

content may make a dielectric liquid unsuitable for some electrical applications due to deterioration of properties such as the dielectric breakdown voltage.

4.2 This test is suitable for use in acceptance specifications, in control of processing, and in evaluating the condition of dielectric liquids in service.

5. Interferences

5.1 Compounds such as aldehydes, ketones, free halogens, most acids, and oxidizing or reducing agents may interfere with coulometric Karl Fischer titrators. If a drifting end point is noted, an alternative solvent system or another titration method is warranted. If this drifting end point cannot be corrected, the water values should be regarded as suspect. A detailed discussion of interfering substances can be found in the treatise on aquametry.⁴

5.2 Studies have shown that the water content of an insulating liquid sample may be influenced significantly by the sample container.⁵ A sample may either gain or lose water on storage in a glass container depending upon the initial water content of the sample, the manner in which the container is cleaned and dried, and the length of storage time before analysis. In addition, sample bottles should not be dried at temperature in excess of 110°C and should be rinsed with the liquid being tested prior to taking the test specimen. Plastic containers should not be used. Glass syringes or metal cans that can be filled to the very top and capped are the most suitable containers for this test.

5.3 Erroneous low readings may be obtained if previous spent oil test specimens are not removed from the solvent system on a routine basis. Excess oil may not mix thoroughly with the solvent system thus preventing the total water content of that test specimen from being measured properly. Stirring should be at such a rate that an oil layer will not form on top of the reagent. If such an oil layer does form while at the instruments maximum stirrer speed, stop testing and remove the oil layer. If accurate results can not be obtained, the solution should be discarded.

5.4 Upon setting up of the titration vessel and solvent system, the walls of the titration vessel should be wetted by swirling the solvent system solution around in the vessel.

5.5 Some solvent systems may not perform well with natural esters. Alternate solvent systems should be explored to provide the best analysis.

6. Apparatus

6.1 *Coulometric Titrator*, consisting of a detector electrode, generator electrode, titration vessel, magnetic stirrer, and control unit.

6.1.1 *Detector Electrodes*—This electrode pair amperometrically determines the end point of titration by measuring a sharp change in cell resistance.

6.1.2 *Generator Electrodes*—This electrode pair performs the cathodic reduction of iodide, which allows the Karl Fischer reaction to take place. It may consist of two platinum meshes or wires separated by a diaphragm within a glass assembly or two platinum meshes or wires not separated by a diaphragm.

6.2 *Titration Flask*—The titration flask will be of suitable capacity and will be protected against atmospheric moisture. A bottom drain cock is desirable but not necessary for removing reagents.

6.3 *Stirrers*—Means for agitation during titration will consist of a magnetic stirrer with a glass or TFE-fluorocarbon-covered stirring bar about 2 to 5 cm long or appropriate to the titration vessel. The bar should be cleaned thoroughly, rinsed with methanol, dried in an oven for 1 h at 100°C, and stored in a desiccator until used. In a sealed system, recleaning and redrying are not necessary for routine use.

6.4 *Transfer Syringes*—Syringes shall be used of a suitable size to accommodate instrument manufacturers' recommendation of sample size. Syringes may be glass or plastic. Glass syringes shall be cleaned and dried for 1 h at 100°C prior to use. Plastic syringes shall be disposed of following each sample use.

6.5 *Needles*—Needles that are to be fitted to the transfer syringes shall be long enough to inject samples directly below the surface of the Karl Fischer reagent. They should be of a large enough gauge to allow for easy transfer of the sample.

6.6 *Septums*, used to seal sample port, allowing the introduction of test specimens with a minimum amount of contamination from atmospheric moisture.

6.7 *Sealing Grease*—If the apparatus does not have a gasket seal, use a sealing grease to seal the titration chamber against atmospheric moisture.

6.8 *Drying Oven*, vacuum or air circulating.

6.9 *Desiccator*, standard laboratory type with color change indicator.

6.10 *Analytical Balance*, capable of weighing to ± 0.001 g.

7. Reagents

7.1 *Purity of Reagents*—Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁶

7.2 *Coulometric Karl Fischer Reagent*, can be obtained commercially. Refer to *Annex A1* for information on alternative solvent systems.

⁴ Mitchell, J., Jr. and Smith, D. M., "Aquametry—A Treatise on Methods for the Determination of Water, Part III—the Karl Fischer Reagent," 2nd ed., J. Wiley and Sons, Inc., New York, NY 1977.

⁵ Gedemer, T., "Determination of Water in Oil by Karl Fischer Method, Part II, Changes in Moisture Content During Storage," *American Laboratory*, 7 (10), pp. 43-50, 1975.

⁶ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analal Standard for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

7.2.1 *Anode Reagent*, frequently referred to as vessel solution.

7.2.2 *Cathode Reagent*, frequently referred to as generator solution.

7.3 Verification Solutions—Verification solutions are available commercially.⁷ Verification solutions may be formulated in-house from long chain alcohols.

7.3.1 The moisture content of water-saturated octanol is:

Water-saturated 1-Octanol 39.2 ± 0.85 mg/mL of solution⁸

7.3.2 The water-saturated alcohol can be prepared by adding deionized water to the alcohol (ACS reagent grade) at 25°C such that the final mixture consists of a two-phase system in which the lower water phase is at least 2 cm high. Initially, this solution should be mixed thoroughly and allowed to stand at room temperature for at least three days to achieve complete equilibration.

NOTE 1—For the best accuracy the solution should not be mixed or shaken after standing. Remove the sample aliquot from the top phase and inject it immediately into the titration cell. The degree of saturation of the water-saturated 1-Octanol varies <1 % between 10 and 30°C.

7.3.3 The response of the instrument shall be verified with 1 to 2 µL of water; this can give a response value of 1000 to 2000 µg within the specified precision of the instrument.

8. Safety Precautions

8.1 Pyridine was the organic amine that was traditionally used in Karl Fischer reagents; however, pyridine-free formulations are now available commercially. Pyridine-free reagents titrate faster and are less toxic, less odorous, and more stable than pyridine types. The reagents may contain potentially hazardous chemicals, such as iodine, pyridine, sulfur dioxide, methanol, chloroform, chlorinated hydrocarbons, or other organic materials. Wear chemical resistant gloves when mixing the reagents and removing solution from the titration chamber. Care must be exercised to avoid unnecessary inhalation of reagent vapors or direct contact of the reagents with the skin or eyes. Following accidental spillage, flush the affected area with copious amounts of water.

NOTE 2—Carefully read and follow manufacturers' instructions and Safety Data Sheet when using commercially available reagent systems.

9. Sampling

9.1 The preferred method for sampling insulating liquids is Practices D923. If the sample is cloudy or contains free water, it may be difficult to obtain a representative test specimen.

10. Preparation of Apparatus

10.1 Thoroughly clean and dry the titration vessel and then reassemble according to the manufacturer's recommendations.

⁷ The sole source of supply of verification solutions, RM 8506 and RM 8507, known to the committee at this time is the National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899. 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.

⁸ SRM 2890 Water Saturated 1-Octanol Certificate of Analysis, NIST, Gaithersburg, MD, 25 August 1998.

Follow the instructions provided in Annex A2 for detailed instructions on cleaning.

10.2 Fill reagent reservoirs with appropriate reagents according to the manufacturer's instructions.

10.3 Turn the instrument on and allow to stabilize.

11. Verification of System Operation

11.1 The accuracy of titration of the instrument and reagents shall be verified prior to beginning of testing by use of a suitable verification solution (see 7.3) containing a known quantity of water. It is desirable to verify the system operation using a solution that approximates the same range of water expected to be in the samples. Verification solutions shall be run with new reagents prior to testing. If verification solution results lie outside parameters established by the manufacturer for acceptable water content of the solution, reagents shall be changed and reverified.

12. Procedure

12.1 After verifying the system is operating properly, allow the instrument to restabilize prior to use.

12.2 Follow the manufacturer's instructions for suggested specimen size for an expected range of water content.

12.3 Using an appropriate syringe and needle (see 6.4 and 6.5) sample the insulating fluid to be tested. Prior to sampling, rinse the syringe and needle with the liquid to be tested one time.

12.4 Determine the sample mass by difference to three significant figures by weighing the test specimen before and after injection. Alternately, inject a known volume of a sample whose density is known at the test temperature to determine sample size.

12.5 Reagent solutions can be used until verification solutions no longer test accurately. See Section 11 for instructions on the use of verification solutions.

13. Calculation

13.1 Most commercially available coulometric Karl Fischer instruments automatically calculate the water content in ppm or percent. If not, calculate the amount of water in the sample as follows:

$$\text{Water Content, mg/kg (ppm)} = A/B \quad (2)$$

where:

A = mass of water, (µg) (instrument readout), and
B = mass of test specimen, g.

14. Report

14.1 Report the following information:

14.1.1 Water content of the test specimen in mg/kg (ppm) rounded to the nearest integer.

14.1.2 Sample identification.

14.1.3 Sample temperature when collected, if available.

15. Precision and Bias

15.1 *Precision*:

15.1.1 The following criteria may be used for judging precision of test results on new and used oils at the 95 % probability level. The precision statements for this test method were based on 9 samples and 37 laboratories.⁹

15.1.1.1 *Repeatability*—The difference between results obtained by the same operator with the same apparatus under constant operating conditions on identical test material, in the long run, would exceed 7 ppm, only 1 case in 20, in the 0 to 50 mg/kg (ppm) range.

15.1.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material, in the long run, would exceed 14 ppm, only 1 case in 20, in the 0 to 50 mg/kg (ppm) range.

15.2 *Bias*—The bias of the procedure in this test method for measuring water content of electrical insulating fluids has not been determined from the collaborative interlaboratory round-robin study, since there is no suitable standard for which the exact water content is known.

15.3 The typical method detection limit (MDL) at the 95 % confidence level has been found to be 8 ppm water for the mineral oil samples.

⁹ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D27-1012.

NOTE 3—The MDL is defined here as the minimum concentration of a substance that can be measured and reported with 95 % confidence using a 7-mL oil sample. The value of 8 ppm has been determined from the reproducibility of the results in interlaboratory test of two new and one used oil sample containing about 11 mg/kg (ppm) water.

NOTE 4—A value of the MDL for an individual laboratory may be calculated from the results of n replications of complete analysis of a sample using the following equation:¹⁰

$$\text{MDL}_{0.95} = t_{(n-1, 0.95)} \times S \quad (3)$$

where:

$t_{(n-1, 0.95)}$ = student's t value for $n - 1$ df and a confidence level of 95 %, and

S = standard deviation of n replicate analyses.

The MDL for an individual laboratory may differ from the MDL of 8 mg/kg (ppm) calculated for this collaborative study.

16. Keywords

16.1 coulometric Karl Fischer titration; free water; Karl Fisher method; Karl Fischer reagent; solvent verification solutions; water content

¹⁰ Glaser, J. A., Foerst, D. L., McKee, G. D., Quave, S. A., and Budde, W. L., "Trace Analysis for Wastewaters," *Environmental Science and Technology*, Vol 15, pp. 1426-1435 (1981).

ANNEXES

(Mandatory Information)

A1. ALTERNATIVE SOLVENT SYSTEMS

A1.1 Some high viscosity oils, as well as silicones, may give erroneous water values when titrated in accordance with this test method. Many of these problems, however, may be overcome by the use of alternative solvent systems.

A1.2 If a problem with erroneous answers is known to exist, or is suspected, check the instrument calibration before and after the introduction of a suspected test specimen. If calibration discrepancies are noted, the solvent system or the applicability of the method is suspect and changing of the solvent system from a methanol-chloroform system to a more appropriate solvent system probably is indicated.

A1.3 For certain high viscosity oils, the addition of a low molecular weight hydrocarbon solvent, such as heptane or toluene, to the titration vessel has been found to be suitable.

A1.4 For dimethylsilicones, a 1:1 mix of Karl Fischer reagent and formamide for the titration solvent has been found to be suitable.

A1.5 If an alternative solvent system is used, instrument or titrant calibration checks must be made before and after the addition of the test specimen. If significant calibration discrepancies are noted, the results should be regarded as suspect.

A1.6 To determine the accuracy of a method when using an alternative solvent system, test specimens of known water content should be analyzed. If such samples are not available, commercial standards⁷ or water-saturated octanol⁸ should be used to assess the response of the instrument.

A1.7 Because of the wide variety of insulating liquids and solvent systems possible, no precision and bias statement is possible for these modifications.

A2. CLEANING OF THE TITRATION VESSEL AND ELECTRODES

A2.1 The system must be kept clean to obtain reliable results. (**Warning**—Procedures listed herein involve the use of nitric acid, either hot, concentrated acid or 75 % aqueous solutions. Nitric acid and its vapors can cause severe burns. Handle concentrated nitric acid with extreme care. This procedure must be used by persons knowledgeable in the safe handling and disposal of this material.)

A2.2 Cleaning is best done with an appropriate solvent for the samples analyzed. Since the commercial generators are made of glass, platinum and TFE-fluorocarbon, they will withstand most solvents and strong acids. If a solvent is known that adequately will clean the frit, it may be used. Otherwise, the following method may be used.

A2.3 If the frit is clogged, it generally can be cleaned by the use of methanol followed by a water rinse, and then nitric acid. The use of a water aspirator or vacuum pump to pull the fluid through the frit helps to ensure that the pores in the frit will be cleaned.

A2.4 First disassemble the generator and rinse in water. Fill a small beaker with enough nitric acid to cover the frit as the generator is slowly lowered into it. Attach the aspirator to the generator, and pull enough acid through the frit to at least cover the cathode. The acid initially will be dark brown. Discard this acid and pull additional acid through the frit until the acid is colorless.

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A2.5 Most deposits can be removed with the use of 75 % nitric acid. Some deposits may require the use of hot, concentrate nitric acid. An aqueous 75 % nitric acid solution should be tried first, and only if that does not remove the deposits, should concentrated nitric acid be used.

A2.6 After cleaning the deposits from the frit or generator, or both, (with nitric acid, as described in A2.3 – A2.5) make sure that all the nitric acid is rinsed from the equipment with water to be followed by methanol.

A2.7 Dry the entire assembly in an oven for at least 30 min at 65°C before assembling and refilling the unit.

A2.8 The entire system will require occasional cleaning while the generator will require periodic cleaning. Inspect the sensing electrode for any cracks in the glass or vapor in the glass tube. If there are vent holes in the cover or generator tubes, these should be kept open and inspected occasionally. Consult the manufacturer's manuals for general cleaning procedures.