Designation: D6304 – 20

Standard Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration[1]

This standard is issued under the fixed designation D6304; 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope*

1.1 This test method covers the direct determination of entrained water in petroleum products and hydrocarbons using automated instrumentation. This test method also covers the indirect analysis of water thermally removed from samples and swept with dry inert gas into the Karl Fischer titration cell. Mercaptan, sulfide (S^- or H_2S), sulfur, and other compounds are known to interfere with this test method (see Section 6). The precision statement of this method covers the nominal range of 20 mg⁄kg to 25 000 mg/kg for Procedure A, 30 mg⁄kg to 2100 mg⁄kg for Procedure B, and 20 mg⁄kg to 360 mg⁄kg for Procedure C.

1.2 This test method is intended for use with commercially available coulometric Karl Fischer reagents and for the determination of water in additives, lube oils, base oils, automatic transmission fluids, hydrocarbon solvents, and other petroleum products. By proper choice of the sample size, this test method may be used for the determination of water from mg/kg to percent level concentrations.

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

D1298 Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method

D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products, Liquid Fuels, and Lubricants

E203 Test Method for Water Using Volumetric Karl Fischer Titration

E1064 Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration

3. Terminology

3.1 For general terminology, refer to Terminology D4175.

4. Summary of Test Method

4.1 This method uses Karl Fischer titration to determine the amount of water in a sample. A coulometric apparatus is used to generate iodine for the Karl Fischer reaction at the anode. When all the water has been titrated, excess iodine is detected by an electrometric end point detector and the titration is

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.06 on Analysis of Liquid Fuels and Lubricants.

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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.

***A Summary of Changes section appears at the end of this standard**

terminated. Based on the stoichiometry of the reaction, 1 mole of iodine reacts with 1 mole of water; thus, the quantity of water is proportional to the total integrated current according to Faraday's Law.

4.2 In Procedure A, a representative portion of the test specimen is injected directly into the titration cell. This procedure is recommended only for low viscosity samples without expected interferences (Section 5).

4.3 Procedures B and C can be used to analyze samples appropriate for Procedure A, those that do not readily dissolve in Karl Fischer reagent, viscous samples, or samples with components that are expected to interfere with the Karl Fischer reaction. These procedures use either a water oven accessory or water evaporator accessory.

4.3.1 In Procedure B, a representative portion of the sample is placed into a sealed glass vial and heated in an oven to extract any water present into the headspace of the vial. The vaporized water in the headspace is carried into the Karl Fischer titration cell by a dry non-reactive carrier gas where the water is titrated. Co-solvents may be used to enhance water extraction from the sample.

4.3.2 In Procedure C, a representative portion of the test specimen is injected into a heated solvent or mineral oil in the water vaporizer accessory and the vaporized water is carried to the Karl Fischer cell by a dry non-reactive carrier gas where the water is titrated.

4.4 For samples that can be analyzed by all procedures, the referee procedure is A.

5. Significance and Use

5.1 A knowledge of the water content is important in the manufacturing, purchase, sale, or transfer of petroleum products to help in predicting their quality and performance characteristics.

5.2 The presence of moisture could lead to premature corrosion and wear, an increase in the debris load resulting in diminished lubrication and premature plugging of filters, an impedance in the effect of additives, and undesirable support of deleterious bacterial growth.

6. Interferences

6.1 A number of substances and classes of compounds associated with condensation or oxidation-reduction reactions interferes in the determination of water by Karl Fischer titration.

6.1.1 The following types of chemicals are known to interfere in Karl Fischer type analyses: mercaptans, sulfides, amines, ketones, aldehydes, oxidizing and reducing agents, and some organometallic compounds.

6.1.2 For more information on substances that interfere in the determination of water by the Karl Fischer titration method, see Test Method E203. Some interferences, such as ketones, may be overcome if the appropriate reagents are used.

6.2 In petroleum products, the most common interferences are mercaptans and sulfides. At levels of less than 500 mg⁄kg as sulfur, the interference from these compounds is insignificant for water concentrations greater than 0.02 % by mass. The significance of the mercaptan and sulfide interference on the Karl Fischer titration for water in the 10 mg⁄kg to 200 mg⁄kg range has not been determined experimentally. At these low water concentrations, however, the interference may be expected to be significant for mercaptan and sulfide concentrations of greater than 500 mg⁄kg as sulfur.

6.3 The indirect analysis using a water vaporizer accessory (Procedure B and C) may minimize interferences.

6.3.1 A higher than appropriate extraction temperature may cause sample decomposition resulting in chemical interferences. These interferences may cause erroneously high results.

6.4 Helpful hints in obtaining reliable results are given in Appendix X1.

7. Apparatus

7.1 *Coulometric Automatic Titrator,* consisting of a control unit, titration vessel, dual platinum sensing electrode, generator electrode assembly, and magnetic stirrer. The instrument is designed to coulometrically generate iodine that reacts stoichiometrically with the water present in the sample solution. The coulombs of electricity required to generate the reagent are converted to micrograms of water, which is obtained as a direct digital readout. Measuring cells with and without diaphragms may be used.

7.2 *Water Oven Accessory*—A standalone or automated device where samples are weighed into vial, sealed with a septa cap, and inserted into an oven where the sample is heated. The volatilized water is transferred using a dry carrier gas via a transfer line to a coulometric titration cell where it is titrated for water content. See Appendix X2, Fig. X2.1.

7.3 *Water Evaporator Accessory*—An apparatus where a measured sample aliquot is transferred to a heated vessel of mineral oil or other suitable solvent where the volatilized water is transferred using a dry carrier gas via a transfer line to a coulometric titration cell where it is titrated for water content. See Appendix X2, Fig. X2.2.

7.4 *Gas-tight Syringe,* fitted with a cannula needle of appropriate length and gauge for introducing sample into the titration chamber or removing excess solution from titration chamber (see Note 1). The volume of the syringe will depend on the sample size and is recommended the sample to occupy at least 25 % of the syringe volume. If using plastic syringes the material must be compatible with the sample matrix.

NOTE 1—If using glass syringes it is suggested that all parts of the glass syringes and needles be rinsed with dry methanol or ethanol after cleaning, then dried in an oven and stored in a desiccator

7.5 *Oven,* suitable for drying glassware.

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

7.7 *Analytical Balance,* capable of weighing to ±0.0001 g.

7.8 *Glass Vials,* for use with oven accessory in Procedure B.

7.9 *Septa Caps (Crimp or Screw Caps with Septa),* for use with oven accessory in Procedure B.

8. Reagents and Materials

8.1 *Purity of Reagents*—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.[3] 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.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II or Type III reagent water, conforming to Specification D1193, or better.

8.3 *Karl Fischer Reagents*—Commercial coulometric Karl Fischer (KF) reagents and reagent systems of various types are available for use with autotitrators for water determination. Traditionally, pyridine was the organic base used in KF reagents. Pyridine-free formulations are available and are preferred by most KF instrument manufacturers for use with their equipment. The pyridine-free reagents are less toxic, less odorous, and more stable than those containing pyridine. The use of pyridine-free reagents is recommended whenever possible. Coulometric titrations normally require two reagent solutions: an anolyte and a catholyte or generator solution. However, with the use of an integrated or diaphragm-less cell, a single solution that contains all of the reagents needed for a KF titration may be used.

8.3.1 *Catholyte Solution*—Contains ammonium salts and methanol.

8.3.2 *Anolyte Solution*—Contains iodide, sulfur dioxide and a buffer in a suitable solvent.

8.3.3 *One Component Solution*—Contains iodide, sulfur dioxide, a buffer, and bases in a suitable solvent. This solution may be used as the only solution in a coulometric system with a diaphragm-less generator cell or as the anolyte solution in a diaphragm cell if specified by the manufacturer

8.3.4 If the sample to be analyzed contains ketone, use commercially available reagents that have been specially modified for use with ketones.

NOTE 2—Some laboratories add the ketone suppressing reagent as part of their standard analytical procedure since often the laboratory does not know whether the sample contains ketone.

8.4 *Water Standards,* 0.1 % by mass and 1 % by mass, commercially prepared in organic solvent are recommended. Other concentrations of prepared standards may be used. Oven accessory standards containing up to 5 % water are acceptable for use. Consult with oven accessory manufacturer in the selection of standards.

8.5 *Xylene, Reagent Grade,* less than 200 mg⁄kg water, dried over a molecular sieve (**Warning—**Flammable. Vapor harmful).

8.6 *White Mineral Oil*—Also called paraffin oil or mineral oil.

8.7 *Molecular Sieve* or other suitable drying agent.

8.8 *Toluene—Reagent Grade,* less than 200 mg⁄kg water (**Warning—**Flammable. Vapor harmful).

8.9 *Nitrogen*—Used as a carrier for transferring moisture into the Karl Fischer titration vessel in Procedure B and C. Other dry gasses may be used.

9. Safety Precautions

9.1 The reagents contain one or more of the following: iodine, organic base, sulfur dioxide, and methanol or other alcohol. Wear chemically resistant gloves when mixing the reagents and removing solution from the titration chamber. Exercise care to avoid inhalation of reagent vapors or direct contact of the reagent with the skin.

10. Sampling

10.1 Sampling is defined as all the steps required to obtain an aliquot representative of the contents of any pipe, tank, or other system and to place the sample into a container for analysis by a laboratory or test facility.

10.2 *Laboratory Sample*—The sample of petroleum product presented to the laboratory or test facility for analysis by this test method. Only representative samples obtained as specified in Practices D4057 and D4177 and handled and mixed in accordance with Practice D5854 shall be used to obtain the laboratory sample.

NOTE 3—Examples of laboratory samples include bottles from a manual sampling, receptacles from automatic samplers, and storage containers holding a product from a previous analysis.

10.3 *Test Specimen*—A representative aliquot obtained from the laboratory sample for analysis by this test method. Irrespective of the type of sample a homogenization step is recommended.

NOTE 4—Homogenization may be necessary to measure a representative analytical sample.

10.3.1 Exercise care at all times to avoid contaminating the sample with moisture from the sample container, the atmosphere, or transfer equipment.

10.3.2 Verify that samples are single phase before taking an aliquot to test. Water can separate from hydrocarbon if the solubility limit is exceeded. The solubility limit depends on the makeup of the sample, concentration levels, and the temperature. If phase separation occurs after mixing, sample is not suitable for testing.

NOTE 5—Once the sample is drawn from the original container, either use the entire portion of the test specimen for the analysis or dispose of the excess. It should not be reintroduced back into the original sample container for future use.

11. Preparation of Apparatus

11.1 Follow the manufacturer's directions for preparation and operation of the coulometric automatic titrator and accessories.

[3] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards 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.

11.2 Seal all joints and connections to the vessel following manufacturer's recommendations to prevent atmospheric moisture from entering the apparatus.

11.3 Add the Karl Fischer anode solution to the anode (outer) compartment. Add the solution to the level recommended by the manufacturer.

11.4 Add the Karl Fischer cathode solution to the cathode (inner) compartment when using generator electrodes with diaphragm. Add the solution to a level 2 mm to 3 mm below the level of the solution in the anode compartment.

NOTE 6—There is no need of cathode solution when using diaphragmless generator electrodes.

11.5 *Conditioning of the Coulometric Titration Apparatus:*

11.5.1 Turn on the apparatus and start the magnetic stirrer of the titration cell for a smooth stirring action. Condition the titration vessel by pre-titrating any moisture in the vessel until a baseline is achieved that is less than the maximum recommended by the manufacturer of the instrument.

11.6 *Conditioning of the Water Vapor Accessory*—Additionally to 11.5, the water vaporizer accessory is conditioned as follows:

11.6.1 Adjust temperature and gas flow according to the manufacturer's recommendations and sample requirements.

11.6.2 Allow the residual water from the vaporizer accessory in the titration cell to be titrated until the end-point is reached and the baseline is less than the manufacturer's recommended value.

12. Verification of System Performance

12.1 Coulometric automatic titrators may vary in verification procedures by manufacturer. Consult the operating manual for the coulometer and oven accessory or water vaporizer if used. Stable, prepackaged water standards are commercially available and suitable for use. It is desirable to verify system performance with a standard solution that approximates the same level of water expected to be in the samples.

12.2 Because reagent performance deteriorates with use, it should be regularly monitored by commercially available water standards as recommended by the equipment manufacturer. In the absence of this, the recommended intervals are initially with fresh reagent, each day test samples are analyzed and after every ten determinations. If the measured value exceeds ±5 % of the known amount, take appropriate corrective action to return the value of the verification sample into the acceptable range before proceeding with sample analysis (see Note 7).

NOTE 7—Follow manufacturer's instructions for possible causes of poor recovery of standards. This may require replacing the reagent solutions or identifying and correcting issues with the oven accessory (Procedure B) or water vaporizer accessory (Procedure C) if used.

12.2.1 It is recommended that a control chart be established and maintained according to generally accepted guidelines. Practice D6299 may be used for this purpose.

13. Procedure A (Direct Injection)

13.1 Prepare the coulometric automatic titrator as described in Section 11 and verify system performance as described in Section 12.

TABLE 1 Recommended Test Sample Size Based on Expected Water Content

NOTE 1—This table includes expected water concentrations that exceed the scope of Procedure B and Procedure C.

Expected Water Concentration, %	Sample Size g or mL	Water Titrated µg
0.001 to <0.01	5	50 to 500
0.01 to <0.03	3	300 to 900
0.03 to <0.07	1	300 to 700
0.07 to <0.1	0.5	350 to 500
0.1 to <0.5	0.25	250 to 1250
0.5 to 2.5	0.1	500 to 2500

13.2 Add the test specimen to the coulometric titration vessel as follows:

13.2.1 Using a clean, dry syringe of suitable capacity (see Table 1 and Note 5), withdraw and discard to waste a portion of the test specimen. Immediately withdraw a further portion of the test specimen, wipe the needle to remove excess sample, and weigh the syringe and either record the weight of the sample and syringe to the nearest 0.1 mg or tare the balance to zero.

13.3 Start the titration, insert the needle through the inlet port septum, taking care that the test specimen is transferred to the titration reagent and not to parts of the titration vessel outside of contact with the liquid. Withdraw the syringe and record the weight to the nearest 0.1 mg. If the syringe and sample were tared to zero before sample introduction, the negative weight displayed on the balance is the sample weight. If the syringe and sample weight before injection were recorded, subtract the weight of the sample and syringe after sample introduction as the sample weight.

13.4 After the endpoint is reached, record the micrograms of water titrated or the mg/kg (or %) water calculated by the titrator

NOTE 8—If the concentration of water in the sample is completely unknown, it is advisable to start with a small trial portion of sample to avoid excessive titration time and depletion of the reagents. Further adjustment of the aliquot size may then be made as necessary.

13.4.1 When the titration is complete and a stable baseline is achieved additional test specimens may be added as per 13.2.1.

13.5 When problems with sample analysis or verification occur, or the titration cell becomes fouled, clean the coulometric titration vessel and generator electrode, replace the reagents as suggested in X1.2.7, prepare the apparatus as described in Section 11, and verify system performance as described in Section 12.

14. Procedure B (Oven Accessory)

14.1 Prepare the coulometric automatic titrator as described in Section 11 and adjust the nitrogen or other dry, non-reactive carrier gas flow according to the manufacturer's instructions. Heat evaporation chamber to the temperature appropriate for a particular product type. The minimum recommended oven temperature is 90 °C. Co-solvents such as toluene may be used to assist in the recovery of water. Follow manufacturer's instructions and take appropriate safety precautions. Ensure

that the oven temperature chosen is high enough to remove the water without degrading the sample. Refer to X1.5.3 for more information on selecting an appropriate extraction temperature.

NOTE 9—The 2019 ILS used to determine the precision for Procedure B used an extraction temperature of 150 °C for the following sample types: Lubricant Additives, Automatic Transmission Fluids, Base Oil, Biodiesel, Compressor Lubricant, Ultra-Low Sulfur Diesel, Gear Oil, Hydraulic Oil and Turbine Oil.

14.2 A vial blank determination is necessary to account for any moisture in the sample vial and co-solvent if used.

14.2.1 A vial blank value is determined by running a series of sealed vials without sample. If a co-solvent is used, the blank is to be determined using the same volume of co-solvent as the sample.

NOTE 10—The vial blank is directly related to the amount of water absorbed on the interior of the vial and cap as well as the humidity of the air in the vial. Because of this, vials should not be reused for vial blank determinations unless the cap is removed, and the interior of the vial allowed to equilibrate to the humidity conditions present in the laboratory.

14.2.2 The temperature and gas flow used for the analysis of the blank must be the same for the sample analysis.

14.2.3 The vial blank shall be determined daily or prior to the sample analysis.

14.2.4 Analyze the vial blank following the manufacturer's operating instructions.

14.2.5 Record the mass of water (micrograms) for each blank determination. The blank value will be used to calculate the mass of water in the samples.

NOTE 11—For best precision, the quantity of water titrated for the vial blank in micrograms, should be less than half the quantity of water titrated in the sample.

14.3 Weigh the sample test specimen into an unused vial using Table 1 and record the weight to the 0.0001 g. Seal the vials according to manufacturer's direction.

NOTE 12—If the concentration of water in the sample is completely unknown, it is advisable to start with a small trial portion of sample to avoid excessive titration time and depletion of the reagents. Further adjustment of the aliquot size may then be made as necessary.

NOTE 13—Sample sizes >0.5 g may require the use of a co-solvent or subsurface gas purge to successfully remove the water in test samples.

14.4 Weigh the sample test specimen into an unused vial using Table 1 and record the weight to the 0.0001 g. Seal the vials according to manufacturer's direction.

NOTE 14—Sample sizes >0.5 g may require the use of a co-solvent or subsurface gas purge to successfully remove the water in test samples.

14.5 Analyze the test specimen at the appropriate temperature to release the moisture without degrading the sample. A temperature gradient can be used to determine the appropriate temperature for analysis. Refer to Fig. X1.1.

14.6 Record the micrograms of water titrated.

14.7 Condition the KF titration vessel and oven apparatus in preparation for the next sample according to manufacturer's direction to ensure the system is dry. (**Warning—**Sample vials will be hot when leaving the oven assembly. Use the appropriate PPE to handle hot vials.)

14.8 When problems with sample analysis or verification occur, or the titration cell becomes fouled, clean the coulometric titration vessel and generator electrode, replace the reagents as suggested in X1.2.7, prepare the apparatus as described in Section 11 and verify system performance as described in Section 12.

15. Procedure C (Water Evaporator or Oil Vaporizer Accessory)

15.1 Prepare the coulometric automatic titrator as described in Section 11. Add the amount of white mineral oil, toluene, or suitable solvent recommended by the manufacturer to the evaporator accessory. Adjust the non-reactive carrier gas flow through the evaporation chamber according to the manufacturer's instructions. Heat evaporation chamber to the temperature suggested by the instrument manufacturer for a particular product type.

NOTE 15—Follow manufacturer's instructions and take appropriate safety considerations when using toluene or other solvents. Ensure that the temperature chosen is high enough to evaporate the azeotrope without degrading the sample.

NOTE 16—The added white mineral oil, xylene, toluene, or other solvent is dried during the conditioning phase of the device before starting the measurement. The evaporator without blank value (with direct dosing of sample into the evaporator vessel after preconditioning) should be used for very small concentrations of water.

15.2 Add the test specimen to the evaporator vessel as follows:

15.2.1 Using a clean, dry syringe of suitable capacity (see Table 1 and Note 5), withdraw and discard to waste a portion of the test specimen. Immediately withdraw a further portion of the test specimen, wipe the needle to remove excess sample, and weigh the syringe and either record the weight of the sample and syringe to the nearest 0.1 mg or tare the balance to zero.

15.3 Start the titration, insert the needle through the inlet port septum or plugged hole in the evaporator chamber, taking care that the test specimen is transferred to the evaporation chamber and not to parts of the chamber outside of contact with the liquid. Withdraw the syringe and record the weight to the nearest 0.1 mg. If the syringe and sample were tared to zero before sample introduction, the negative weight displayed on the balance is the sample weight. If the syringe and sample weight before injection were recorded, subtract the weight of the sample and syringe after sample introduction to calculate the sample weight.

NOTE 17—If the concentration of water is completely unknown, it is advisable to start with a small trial portion test specimen to avoid excessive titration time and depletion of the reagents. Further adjustment of the aliquot size may then be made as necessary.

15.4 After the end point is reached, record the micrograms of water titrated.

15.5 When the titration is complete and a stable baseline is achieved additional specimens may be added as per 15.2.1. Condition the KF titration vessel and azeotrope water evaporator apparatus in preparation for the next sample according to manufacturer's directions to ensure the system is dry.

15.6 Evacuate and replenish the azeotrope evaporator chamber as needed according to the manufacturer's directions.

15.7 When problems with sample analysis or verification occur, or the titration cell becomes fouled, clean the coulometric titration vessel and generator electrode, replace the reagents as suggested in X1.2.7, prepare the apparatus as described in Section 11 and verify system performance as described in Section 12.

16. Quality Control Checks

16.1 Confirm the performance of the instrument or the procedure each day it is in use by analyzing a QC sample that is representative of samples typically analyzed. Quality control frequency should be increased if a large number of samples are routinely analyzed. If the analysis is shown to be in statistical control, QC frequency may be reduced. Analysis of result(s) from these QC samples may be performed using control chart techniques[4] or other statistical techniques. If the QC sample result determined causes the laboratory to be in an out-of-control situation, such as exceeding the laboratory's control limits, investigate and take corrective action to bring the test back into control before proceeding. An ample supply of QC sample material shall be available for the intended period of use and shall be homogeneous and stable under the anticipated storage conditions. Prior to monitoring the measurement process, the user of the method needs to determine the average value and control limits of the QC sample. The QC sample precision shall be checked against the ASTM method precision to ensure data quality.

17. Calculation

17.1 Calculate the water concentration in the sample as follows:

$$\text{water content, mg/kg} = \frac{(\mu\text{g water} - B)}{(W1 - W2)} = \frac{(\mu\text{g water} - B)}{W} \quad (1)$$

$$\text{water content, mass percent} = \quad (2)$$

$$\frac{(\mu\text{g water} - B)}{(W1 - W2) \times 10000} = \frac{(\mu\text{g water} - B)}{W \times 10000}$$

$$\text{water content, volume percent} = \quad (3)$$

$$\text{water content, mass percent} \times \frac{\text{density of sample at } t}{\text{density of water at } t}$$

where:

t = test temperature,
W_1 = mass of sample and syringe before injection in grams,
W_2 = mass of sample and syringe after injection in grams,
W = net sample mass, and
B = µg water for blank determination (Procedures B).

17.1.1 Density may be measured using test methods such as Test Method D1298 and Test Method D4052. If the density is measured in units of g/mL and the density of water at test temperature is assumed to be 1 g/mL, Eq 2.

18. Report

18.1 Report water concentration values less than 1000 mg/kg or 0.1 % by mass or volume to two significant figures; and values equal or greater than 1000 mg/kg or 0.1 % by mass or volume to three significant figures.

18.2 Report the water concentration as obtained by Test Method D6304, Procedure A, Procedure B, or Procedure C.

19. Precision and Bias[5]

19.1 The precision of this test method, which was determined by statistical examination of interlaboratory results submitted by as many as 16 laboratories, testing 12 materials in duplicate, using Practice D6300, is as follows.[6]

19.1.1 *Repeatability*—The difference between two independent results obtained by the same operator in a given laboratory applying the same test method with the same apparatus under constant operating conditions on identical test material within short intervals of time would exceed the following value with an approximate probability of 5 % (one case in 20 in the long run) in the normal and correct operation of the test method:

Procedure A Repeatability = 0.9810 * X ^ 0.7055 mg/kg
Procedure B Repeatability = 5.0429 (X + 2.5001) ^ 0.4229 mg/kg
Procedure C Repeatability = 0.6041 * X ^ 0.8055 mg/kg

where X is the average of the two results.

19.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators applying the same test method in different laboratories using different apparatus on identical test material would exceed the following value with an approximate probability of 5 % (one case in 20 in the long run) in the normal and correct operation of the test method:

Procedure A Reproducibility = 2.3362 * X ^ 0.7055 mg/kg
Procedure B Reproducibility = 21.727 (X + 2.5001) ^ 0.4229 mg/kg
Procedure C Reproducibility = 1.0938 * X ^ 0.8055 mg/kg

where X is the average of the two results.

19.1.3 The precision for Procedure B was determined using an extraction temperature of 150 °C for the following sample types: Lubricant Additives, Automatic Transmission Fluids, Base Oil, Biodiesel, Compressor Lubricant, UltraLow Sulfur Diesel, Gear Oil, Hydraulic Oil and Turbine Oil.

19.2 The range of valid test results for applying the precision functions (r and R) and reporting purpose are:

Procedure A:

lowest retained ILS sample mean =	20 mg/kg
highest retained ILS sample mean =	24 000 mg/kg
lowest test result =	1 mg/kg
highest test result =	26 876 mg/kg

Procedure B:

lowest retained ILS sample mean =	33 mg/kg
highest retained ILS sample mean =	2094 mg/kg
lowest test result =	4 mg/kg
highest test result =	2646 mg/kg

[4] ASTM MNL7, *Manual on Presentation of Data Control Chart Analysis*, 6th Edition, Section 3: Control Charts for Individuals, ASTM International, W. Conshohocken, PA.

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1436. Contact ASTM Customer Service at service@astm.org.

[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-2013. Contact ASTM Customer Service at service@astm.org.

Procedure C:

lowest retained ILS sample mean =	20 mg/kg
highest retained ILS sample mean =	359 mg/kg
lowest test result =	8 mg/kg
highest test result =	484 mg/kg

20. Keywords

20.1 coulometric titration; Karl Fischer oven; Karl Fischer titration; water vaporizer

APPENDIXES

(Nonmandatory Information)

X1. HELPFUL HINTS FOR COULOMETRIC KARL FISCHER WATER ANALYSIS

X1.1 Following precautions are suggested to obtain accurate and precise results by this test method. Some of these suggestions are also described in the text of the test method, but are compiled here for easy reference.

X1.2 *Suggestions for Procedures A, B, and C:*

X1.2.1 The following types of chemicals are known to interfere in Karl Fischer type analyses: mercaptans, sulfides, amines, ketones, aldehydes, oxidizing and reducing agents, and some organometallic compounds. Some of the interferences can be eliminated by addition of suitable reagents, for example, addition of benzoic or succinic acid for aldehyde and ketone interference.

X1.2.1.1 At low water concentrations (<0.02 % by mass), the interference by mercaptan and sulfide (>500 mg/kg as sulfur) may be significant (see Test Method E203).

X1.2.2 All equipment should be scrupulously clean of moisture. Rinse all syringes, needles, and weighing bottles with anhydrous methanol or 2-propanol after cleaning. Then dry in an oven and store in a desiccator.

X1.2.3 During initial conditioning of the Karl Fischer cell, high background current for a prolonged period may be due to moisture on the inside walls of the titration vessel. Wash the inside with the electrolyte by gently shaking the vessel or by more vigorously stirring.

X1.2.4 Although standardization is not necessary in coulometric titrations, reagent performance deteriorates with use and should be regularly monitored by commercially available water standards as suggested by the equipment manufacturer. In the absence of this the recommended intervals are initially with fresh reagent, each day test samples are analyzed and then after every ten determinations.

X1.2.5 If the concentration of water in the sample is unknown, it is advisable to start with a small trial portion of sample to avoid excessive titration time and depletion of the reagents. Further adjustment of the aliquot size may then be made as necessary

X1.2.6 Water recovery of <50.0 µg may reduce precision. When highest precision is required re-run test samples with a larger sample size unless the maximum sample size has been taken or matrix issues interfere.

X1.2.7 Any time one of the following situations occurs, clean the coulometric titration vessel and generator electrode, replace the anode solution (and cathode solution if used) and then prepare the apparatus as described in Section 11 and verify system performance as described in Section 12:

X1.2.7.1 Persistently high and unstable background current or drift.

(1) If problems persist use a different batch of KF reagent if available.

(2) Check generator and sensing electrode contacts. Defective contacts may lead to errors.

X1.2.7.2 Phase separation in the anode compartment or the sample coating the electrodes.

(1) If the titration vessel becomes contaminated with the sample, thoroughly clean the anode and cathode compartments with xylene. Never use acetone or similar ketones.

(2) When using Karl Fischer titration cells with a diaphragm, the frit separating the vessel compartments may get clogged with sample residues (no titration current registrable). Disassemble the apparatus in such cases and clean the frit according to the manufacturer's directions.

X1.2.7.3 The total amount of sample added to the titration vessel exceeds one fourth of the volume of solution in the anode compartment.

X1.2.7.4 The solutions in the titration vessel are over one week old.

KF reagent contaminated/exhausted: change the solution, possibly use a different batch.

Check electrical contacts; defective contacts can lead to an unstable measuring signal.

X1.3 *Suggestions for Procedure A*:

X1.3.1 Fill the dry cooled sample bottle as rapidly as possible with the sample within 15 mm of the top and immediately seal.

X1.3.2 After removing a sample aliquot from the bottle with a dry syringe, inject dry gas into the sample bottle with the syringe to displace the removed sample void.

X1.3.3 Rinse the clean dry syringe at least three times with the sample and discard the aliquots before taking an aliquot for injecting into the titration vessel.

X1.4 *Suggestions for Procedures B and C*:

X1.4.1 The amount and precision of the water recovered from test samples in Procedure B and Procedure C may be impacted by the water extraction temperature and the use of co-solvents or extraction agents in Procedure B and different oils or solvents in Procedure C.

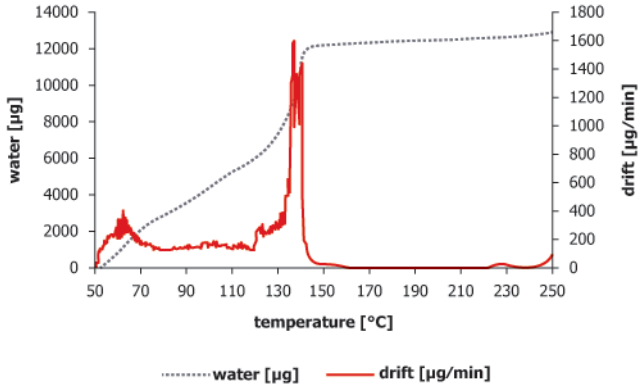

FIG. X1.1 Temperature Gradient (2 °C/min) of Sodium Tartrate Dihydrate Showing the Amount of Released Water and the Associated Drift Value as a Function of the Temperature

X1.4.2 A higher than appropriate extraction temperature may cause sample decomposition resulting in chemical interferences as described in X1.2.1. These interferences may cause erroneously high results.

X1.5 *Suggestions for Procedure B*:

X1.5.1 *Relative Blank*—Values for the Relative Blank are established by analysis of a series of empty sample vials using the same settings and extraction temperature used for sample analysis. If a co-solvent is used to aid in water extraction, a representative portion of the solvent is included in the blank vial. This value is used to correct for atmospheric water absorbed on the surface of the sample vial/cap and humidity in the air that is captured in the vial.

X1.5.1.1 For the sample determination, if at least half of the vial is filled with sample (and co-solvent), the blank value determined from an empty vial will be greater than what should be subtracted from the sample due to the full volume of air and its associated humidity. To obtain correct results, the moisture content of the air displaced by the sample should be calculated and subtracted from the mass of water measured during the titration.

X1.5.2 *Needle Positioning*—The inlet needle used for introducing dry carrier gas may be positioned in the headspace above or below the level of liquid sample in the sample vial.

X1.5.2.1 Positioning the needle in the vial headspace (above the level of liquid sample) may help prevent needle clogging and provides adequate water recovery for many samples.

X1.5.2.2 Positioning the needle below the level of liquid sample facilitates mixing of the sample and can assist in the transfer of water to the carrier gas.

X1.5.2.3 The outlet needle used for transferring the water to the Karl Fischer cell must be positioned above the level of the liquid to prevent blockage of the transfer line or sample contamination of the Karl Fischer cell.

X1.5.3 *Extraction Temperature*—The extraction temperature should be high enough to effectively extract the water from the test sample while at the same time not so high that sample decomposition occurs.

X1.5.3.1 An extraction temperature of 150 °C was used in the 2019 ILS used to develop the precision statement for Procedure B and is suitable for many samples.

X1.5.3.2 When co-solvents are used, an extraction temperature at or slightly above the co-solvent boiling point is suggested.

X1.5.3.3 Sample types that contain components that are thermally unstable at 150 °C may need to be run at lower temperatures due to potential chemical interferences.

X1.5.3.4 Temperatures higher than 150 °C may be used for sample types that do not decompose at higher temperatures.

X1.5.3.5 A temperature profile may be helpful to determine the appropriate extraction temperature to be used with oven accessories (Procedure B). Fig. X1.1 below shows a plot of temperature, water content, and drift.

(1) The temperature curve in Fig. X1.1 can be used to determine the appropriate extraction temperature for this sample type. At a temperature of approximately 150 °C the temperature is high enough for the water to be extracted without decomposition of the sample. At a temperature of approximately 220 °C the background signal begins to rise as the sample starts to decompose. Generally the extraction temperature should be at least 20 °C below the start of decomposition. For this sample an appropriate extraction temperature would be 150 °C to 200 °C.

X1.5.4 Investigate the following when poor precision (reproducibility) is observed:

X1.5.4.1 Ensure that correct titration and control parameters are used. Update parameters as required.

X1.5.4.2 Check whether the sample vials are correctly sealed. Caps that are crimped too tight or too loose can leak.

X1.5.4.3 Drift too high: Switch off the gas flow.

(1) If drift value decreases: check that the carrier gas is used and that the molecular sieve is not exhausted. Check for contamination of needle system and/or transfer tube, clean with water, and rinse with methanol. Dry the components before use.

(2) If drift value does not change: check titration cell, septum and/or seals for leaks, that the generator electrode molecular sieve is not exhausted, poorly conditioned reagent, and inefficient mixing in the coulometric titration cell.

X1.5.4.4 Contamination of generator or sensing electrodes: clean according to the manufacturer's instructions.

X1.6 *Suggestions for Procedure C*:

X1.6.1 The white mineral oil used in Procedure C is a suitable solvent for many types of petroleum products.

X1.6.2 When using a solvent such as toluene, hexane, or xylene, the "distillation" during the evaporation process may allow some sample matrix to be transferred together with the solvent.

X1.6.2.1 The volume of liquid in the titration vessel may increase due to the distillation. Replace the anode solution when the total volume of sample/solvent transferred to the titration vessel exceeds one fourth of the volume of solution in the anode compartment.

X2. OPERATING PRINCIPLE ILLUSTRATIONS

X2.1 See Figs. X2.1 and X2.2.

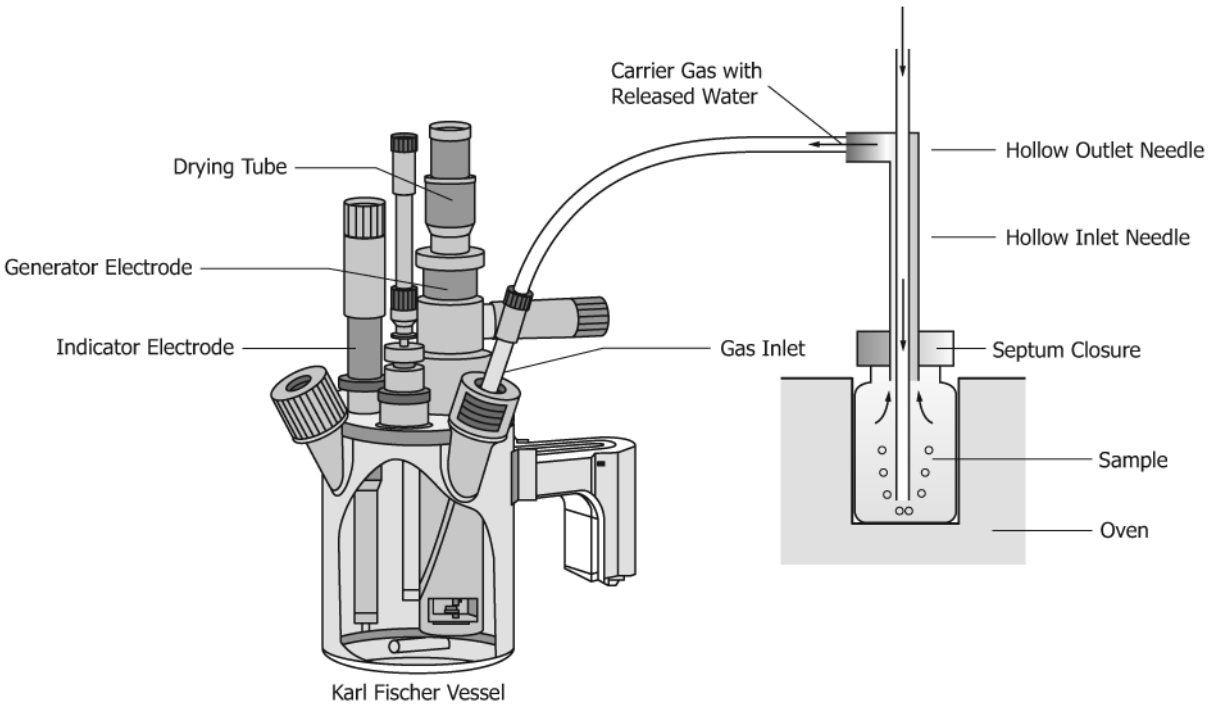

FIG. X2.1 Example of Water Oven Accessory Operating Principle

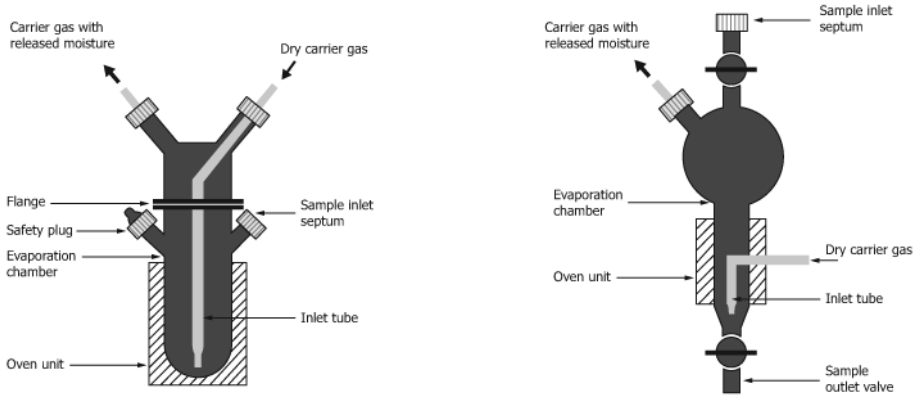

FIG. X2.2 Example of Water Evaporator Accessories

SUMMARY OF CHANGES

Subcommittee D02.06 has identified the location of selected changes to this standard since the last issue (Dec. 1, 2020) that may impact the use of this standard. (Approved D6304 – 16$^{\varepsilon 1}$.)

(1) Revisions throughout to update method to current products on the market being used by laboratories.

(2) New Research Report added to provide provision statement for the test method.