



Designation: ~~D6304 – 16~~<sup>ε1</sup> D6304 – 20

## Standard Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration<sup>1</sup>

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 reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

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

~~<sup>ε1</sup> NOTE—Reference to a Summary of Changes was removed editorially in September 2016.~~

### 1. ~~Scope~~ Scope\*

1.1 This test method covers the direct determination of ~~water in the range of 10 mg/kg to 25 000 mg/kg~~ 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 ( $S^{2-}$  or  $H_2S$ ), sulfur, and other compounds are known to interfere with this test method (see Section 56). 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~~ safety, health, and health 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:<sup>2</sup>

[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](#)

<sup>1</sup> 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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<sup>2</sup> 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

[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 ~~An aliquot is injected into the titration vessel of a coulometric Karl Fischer apparatus in which~~ 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 ~~is generated coulometrically~~ Fischer reaction at the anode. When all of the water has been titrated, excess iodine is detected by an electrometric end point detector and the titration is terminated. Based on the stoichiometry of the reaction, ~~1 mol~~ 1 mole of iodine reacts with 1 mol 1 mole of water; thus, the quantity of water is proportional to the total integrated current according to Faraday's ~~Faraday's~~ Law.

4.2 ~~The sample injection can be done either by mass or volume.~~ 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 ~~The viscous samples can be analyzed by using a water vaporizer accessory that heats the sample in the evaporation chamber, and the vaporized water is carried into the Karl Fischer titration cell by a dry inert carrier gas.~~ 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 of lubricating oils, additives, and similar products is important in the manufacturing, purchase, sale, or transfer of such petroleum products to help in predicting their quality and performance characteristics.

5.2 ~~For lubricating oils, the~~ 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. 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. 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.

6.1.1 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 Karl Fischer Apparatus (using electrometric end point)*—Automatic Titrator, A number of automatic coulometric Karl Fischer titration assemblies consisting of titration cell, platinum electrodes, magnetic stirrer, and a control unit are available on the market. Instructions for operation of these devices are provided by the manufacturers and are not described herein. 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.

6.1.1 *Water Vaporizer Accessory*—A number of automatic water vaporizer accessories are available on the market. Instructions for the operation of these devices are provided by the manufacturers and are not described herein.

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 *Syringes*—*Gas-tight Syringe*, Samples are most easily added to the titration vessel by means of accurate glass or disposable plastic syringes with luer fittings and hypodermic needles of suitable length to dip below the surface of the anode solution in the cell when 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](#) inserted through the inlet port septum. The bores of the needles used shall be kept as small as possible, but large enough to avoid problems arising from back pressure or blocking while sampling. Suggested syringe sizes are as follows:-). 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.

6.2.1 Ten microlitres, with a needle long enough to dip below the surface of the anode solution in the cell when inserted through

**TABLE 1 Test Sample Size Based on Expected Water Content**

Expected Water Concentration	Sample Size g or mL	µg Water Titrated
10 mg/kg to 100 mg/kg or µg/mL	3.0	30 to 300
10 mg/kg to 500 mg/kg or µg/mL	2.0	200 to 1000
0.02 % to 0.1 %	1.0	200 to 1000
0.1 % to 0.5 %	0.5	500 to 2500
0.5 % to 2.5 %	0.25	1250 to 6250

**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

the inlet port septum and graduated for readings to the nearest 0.1 µL or better. This syringe can be used to accurately inject a small quantity of water to check reagent performance as described in Section 10.

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

6.2.2 As identified in Table 1, syringes of the following capacities: 250 µL accurate to the nearest 10 µL; 500 µL accurate to the nearest 10 µL; 1 mL accurate to the nearest 0.01 mL; 2 mL accurate to the nearest 0.01 mL; and 3 mL accurate to the nearest 0.01 mL. A quality gas-tight glass syringe with a TFE-fluorocarbon plunger and luer fitting is recommended.

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  $\pm 0.0001$  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*—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.<sup>3</sup> 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 reagent water as defined by Type II or Type III reagent water, conforming to Specification D1193, or better.

<sup>3</sup> *Reagent Chemicals, American Chemical Society Specifications*; *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 *Annual Analytical 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.

~~7.3 Xylene, Reagent Grade, less than 100 mg/kg to 200 mg/kg water, dried over a molecular sieve (Warning—Flammable. Vapor harmful).~~

~~8.3 Karl Fischer Reagent, Reagents—standard commercially available reagents for Commercial coulometric Karl Fischer titrations. (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 Anode-One Component Solution—Mix six parts of commercial Karl Fischer anode solution with four parts of reagent grade xylene on a volume basis. Newly made Karl Fischer anode solution shall be used. Other proportions of anode solution and xylene Contains iodide, sulfur dioxide, a buffer, and bases in a suitable solvent. This solution may be used and determined for a particular reagent, apparatus, and sample tested. Some samples may not require any xylene, whereas others will require the solvent effect of the xylene (as the only solution in a coulometric system with a diaphragm-less generator cell or as the anolyte solution in a diaphragm cell) Warning—Flammable, toxic if inhaled, swallowed, or absorbed through skin). if specified by the manufacturer~~

~~NOTE 1—Toluene may be used in place of xylene. However, the precision data in Section 17 were obtained using xylene.~~

~~7.4.2 Cathode Solution—Use standard commercially available cathode Karl Fischer solution. Newly made solution shall be used (Warning—Flammable, may be fatal if inhaled, swallowed, or absorbed through skin. Possible cancer hazard.).~~

~~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.~~

<https://standards.iteh.ai/catalog/standards/sist/5f2e4206-3597-45a6-92fb-2f2e8063275e/astm-d6304-20>

~~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 Hexane, Xylene, Reagent Grade, less than 100 mg/kg to 200 mg/kg water—water, dried over a molecular sieve (Warning—Flammable. Vapor harmful). Dried over molecular sieve.~~

~~8.6 White Mineral Oil—Also called paraffin oil or mineral oil. Reagent grade.~~

~~8.7 Molecular Sieve 5Å—8 to 12 mesh 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*—~~The A representative aliquot obtained from the laboratory sample for analysis by this test method. Once drawn, use the entire portion of the test specimen in the analysis.~~ 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.

8.4 Select the test specimen size as indicated in **Table 1** based on the expected water concentration.

## 11. Preparation of Apparatus

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

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~~ 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 diaphragm-less generator electrodes.

11.5 ~~Turn on the apparatus and start the magnetic stirrer for a smooth stirring action. Allow the residual moisture in the titration vessel to be titrated until the end point is reached. Do not proceed beyond this stage until the background current (or background titration rate) is constant and less than the maximum recommended by the manufacturer of the instrument.~~ Conditioning of the Coulometric Titration Apparatus:

NOTE 4—High background current for a prolonged period may be due to moisture on the inside walls of the titration vessel. Gentle shaking of the vessel (or more rigorous stirring action) will wash the inside with electrolyte. Keep the titrator on to allow stabilization to a low background current.

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.

## **10. Calibration and Standardization**

~~10.1 In principle, standardization is not necessary since the water titrated is a direct function of the coulombs of electricity consumed. However, reagent performance deteriorates with use and shall be regularly monitored by accurately injecting a known quantity of water (see 7.2) that is representative of the typical range of water concentrations being determined in samples. As an example, one may accurately inject 10 000 µg or 10 µL of water to check reagent performance. Suggested intervals are initially with fresh reagent and then after every ten determinations (see 11.3).~~

## **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  $\pm 5\%$  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 (by Mass)(Direct Injection)**

~~13.1 Add newly made solvents to the anode and cathode compartments of the titration vessel. Prepare the coulometric automatic titrator as described in Section 11 and bring the solvent to end-point conditions as verify system performance as described in Section 12 described in Section 9.~~

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.