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AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428

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

This standard is issued under the fixed designation D 6304; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the direct determination of water in the range of 10 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 Fisher titration cell. Mercaptan, sulfide ($S=$ or H_2S), sulfur, and other compounds are known to interfere with this test method (see Section 5).

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 Values stated in SI units are to be regarded as the standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]
D 1298 Practice for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method[3]
D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter[4]
D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[4]
D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products[4]
D 5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products[5]
E 203 Test Method for Water Using Volumetric Karl Fisher Titration[6]

3. Summary of Test Method

3.1 An aliquot is injected into the titration vessel of a coulometric Karl Fisher apparatus in which iodine for the Karl Fisher reaction is generated coulometrically 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 of iodine reacts with 1 mol of water; thus, the quantity of water is proportional to the total integrated current according to Faraday's Law.

3.2 The sample injection can be done either by mass or volume.

3.3 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.

4. Significance and Use

4.1 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.

4.2 For lubricating oils, 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.

5. Interferences

5.1 A number of substances and classes of compounds associated with condensation or oxidation-reduction reactions interferes in the determination of water by Karl Fisher 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 mass %. For more

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[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D2.02 on Static Petroleum Measurement.

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

[3] *Annual Book of ASTM Standards*, Vol 5.01.

[4] *Annual Book of ASTM Standards*, Vol 5.02.

[5] *Annual Book of ASTM Standards*, Vol 5.03.

[6] *Annual Book of ASTM Standards*, Vol 15.05.

information on substances that interfere in the determination of water by the Karl Fischer titration method, see Test Method E 203. Some interferences, such as ketones, may be overcome if the appropriate reagents are used.

5.2 The significance of the mercaptan and sulfide interference on the Karl Fischer titration for water in the 10 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.

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

6. Apparatus

6.1 *Coulometric Karl Fischer Apparatus (using electrometric end point)*—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.

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.

6.2 *Syringes*—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 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:

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 the inlet port septum and graduated for readings to the nearest 0.01 µL or better. This syringe is used in the standardization step (see Section 10).

6.2.2 Two hundred fifty microlitres, 500 µL, and 1 mL capacities and accurate to the nearest 1 µL, 1 µL, and 0.01 mL, respectively. A quality gas-tight glass syringe with a TFE-fluorocarbon plunger and luer fitting is recommended.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society[7], where such specifications are available. Use other grades, provided the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D 1193.

7.3 *Xylene, Reagent Grade*, less than 100 to 200 mg/kg water, dried over a molecular sieve (see Note 1 - **Warning**).

NOTE 1—**Warning:** Flammable. Vapor harmful.

7.4 *Karl Fischer Reagent*, standard commercially available reagents for coulometric Karl Fischer titrations.

7.4.1 *Anode 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 may be used and determined for a particular reagent, apparatus, and sample tested. Some samples may not require and xylene, whereas others will require the solvent effect of the xylene (see Note 2 - **Warning**).

NOTE 2—**Warning:** Flammable, toxic if inhaled, swallowed, or absorbed through skin.

NOTE 3—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 (see Note 4 - **Warning**).

NOTE 4—**Warning:** Flammable, may be fatal if inhaled, swallowed, or absorbed through skin. Possible cancer hazard.

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

NOTE 5—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.

7.5 *Hexane, Reagent Grade*, less than 100 to 200 mg/kg water (see Note 6 - **Warning**). Dried over molecular sieve.

NOTE 6—**Warning:** Flammable. Vapor harmful.

7.6 *White Mineral Oil*—Also called paraffin oil or mineral oil. Reagent grade.

7.7 *Molecular Sieve 5Å*—8 to 12 mesh.

8. Sampling

8.1 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.

8.2 *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 D 4057 and D 4177 and handled and mixed in accordance with Practice D 5854 shall be used to obtain the laboratory sample.

NOTE 7—Examples of laboratory samples include bottles from a manual sampling, receptacles from automatic samplers, and storage containers holding a product from a previous analysis.

8.3 *Test Specimen*—The 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.

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

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[7] *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 *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.

TABLE 1 Test Sample Size Based on Expected Water Content

Expected Water Concentration	Sample Size g or mL	µg Water Titrated
10 to 100 mg/kg or µg/mL	3.0	30 to 300
10 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

9. Preparation of Apparatus

9.1 Follow the manufacturer's directions for preparation and operation of the titration apparatus.

9.2 Seal all joints and connections to the vessel to prevent atmospheric moisture from entering the apparatus.

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

9.4 Add the Karl Fischer cathode solution to the cathode (inner) compartment. Add the solution to a level 2 to 3 mm below the level of the solution in the anode compartment.

9.5 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.

NOTE 8—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.

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 100 000 µg or 100 µL of water (see 7.2). Suggested intervals are initially with fresh reagent and then after every ten determinations (see 11.3).

11. Procedure A (By Mass):

11.1 Add newly made solvents to the anode and cathode compartments of the titration vessel and bring the solvent to end-point conditions as described in Section 9.

11.2 Add the petroleum product test specimen to the titration vessel using the following method:

11.2.1 Starting with a clean, dry syringe of suitable capacity (see Table 1 and Note 9), withdraw and discard to waste at least three portions of the sample. Immediately withdraw a further portion of sample, clean the needle with a paper tissue, and weigh the syringe and contents to the nearest 0.1 mg. Insert the needle through the inlet port septum, start the titration, and with the tip of the needle just below the liquid surface, inject the test specimen. Withdraw the syringe, wipe clean with a paper tissue, and reweigh the syringe to the nearest 0.1 mg. After the end point is reached, record the micrograms of water titrated.

NOTE 9—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.

11.2.2 When the background current or titration rate returns to a stable reading at the end of the titration as discussed in 9.5, additional specimens may be added as per 11.2.1.

11.3 Replace the solutions when one of the following occurs and then repeat the preparation of the apparatus as in Section 9.

11.3.1 Persistently high and unstable background current.

11.3.2 Phase separation in the anode compartment or oil coating the electrodes.

11.3.3 The total oil content added to the titration vessel exceeds one quarter of the volume of solution in the anode compartment.

11.3.4 The solutions in the titration vessel are greater than one week old.

11.3.5 The instrument displays error messages that directly or indirectly suggest replacement of the electrolytes—see instrument operating manual.

11.3.6 The result of a 0.01 mL injection of water is outside 100 000 ± 1000 µg.

11.4 Thoroughly clean the anode and cathode compartment with xylene if the vessel becomes contaminated with product. Never use acetone or similar ketones. Clogging of the frit separating the vessel compartments will cause instrument malfunction.

11.5 For products too viscous to draw into a syringe, add the sample to a clean, dry bottle and weigh the bottle and product. Quickly transfer the required amount of sample to the titration vessel by suitable means, such as with a dropper. Reweigh the bottle. Titrate the sample as in 11.2.

12. Procedure B (By Volume):

12.1 Follow steps 11.2.1 through 11.5 from Procedure A, taking sample by volume instead of mass.

NOTE 10—A volume aliquot of the product is titrated to an electrometric end point using a coulometric Karl Fischer apparatus. The steps described in Procedure A are followed except as noted. The volume injection method is applicable only when the vapor pressure and viscosity of the sample permit an accurate determination of the volume of the sample.

NOTE 11—The referee procedure for determination of water in liquid petroleum products by coulometric Karl Fischer titration is Procedure A, which uses a mass measurement of the product test specimen.

NOTE 12—The presence of gas bubbles in the syringe can be a source of uncertainly. The tendency of product to form gas bubbles is a function of product type and corresponding vapor pressure. Viscous products can prove to be difficult to measure volumetrically with a precision syringe.

NOTE 13—Helpful hints in obtaining reliable results are given in Appendix X1.

13. Procedure C (Water Evaporator Accessory):

13.1 If using the water evaporator accessory for samples difficult to analyze by Procedure A or B due to sample viscosity, matrix interference, or extremely small concentrations of water (for example, <100 mg/kg), add 10 mL of white oil to the evaporator accessory. Bubble dry nitrogen gas at about 300 mL/min through the oil. Heat the oil to the temperature suggested by the instrument manufacturer for a particular product type.

13.2 Dissolve 5 ±0.01 g of accurately weighed viscous sample in a 10 mL volumetric flask. Make up to volume with dried hexane. Shake the sample until it is completely dissolved in the solvent.

NOTE 14—All parts of the glass assembly must be thoroughly dry before use. The smallest amount of contamination by moisture will cause erroneous results. Perform several preliminary runs with known content standards to determine that the system is operating correctly. Water-in-alcohol standards must be capped with rubber septa rather than rubber stoppers.

13.3 Inject 1 mL of dissolved sample into the evaporator assembly. Start the operating sequence. Follow steps 11.1 through 11.5 in Procedure A. After the end point is reached, record the micrograms of water titrated from the digital readout on the instrument.

14. Quality Control Checks

14.1 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[8] 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.

15. Calculation

15.1 Calculate the water concentration in mg/kg or µl/mL of the sample as follows:

$$\text{water, mg/kg or µL/min} = \frac{W_1}{W_2} \text{ or } \frac{V_1}{V_2} \quad (1)$$

where:

W_1 = mass of water titrated, µg,
W_2 = mass of sample used, kg,
V_1 = volume of water titrated, µL, and
V_2 = volume of sample used, mL.

15.2 Calculate the water concentration, in mass or volume %, of the sample as follows:

$$\text{water, mass \%} = \frac{W_1}{10\,000 \times W_2} \text{ or volume, \%} = \frac{V_1}{10 \times V_2} \quad (2)$$

where W_1, W_2, V_1, and V_2 are same as in 15.1.

15.3 Use the following equation for calculating the water content of the sample in units of volume % from mass %, or of mass % from volume %.

water, volume % = water, mass % / density of product at room temperature (density may be measured using Practice D 1298 or Test Method D 4052.)

16. Report

16.1 Report the water concentration to the nearest whole (mg/kg), nearest 0.01 mass %, nearest whole µL/mL, or nearest 0.01 volume %.

16.2 Report the water concentration as obtained by Test Method D 6304, Procedure A, Procedure B, or Procedure C.

17. Precision and Bias [9]

17.1 The precision of this test method as determined by the statistical examination of interlaboratory test results is as follows:

17.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in 1 case in 20.

17.1.2 *Reproducibility*—The difference between 2 single and independent results obtained by different operators working in different laboratories on identical test materials would, in the long run, exceed the following values in only 1 case in 20.

	Volumetric Injection	Mass Injection
Repeatability	0.08852 $x^{0.7}$ volume %	0.03813 $x^{0.6}$ mass %
Reproducibility	0.5248 $x^{0.7}$ volume %	0.4243 $x^{0.6}$ mass %

where x is the mean of duplicate measurements.

17.2 *Bias*—This test method has no bias since the coulometric determination can be defined only in terms of this test method.

18. Keywords

18.1 coulometric titration; Karl Fischer titration; water

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[8] ASTM MNL7, Manual on Presentation of Data Control Chart Analysis, 6th Edition, Section 3: Control Charts for Individuals.

[9] Supporting data are available from ASTM Headquarters, Request RR:D02-1436.

APPENDIX

(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.

X1.1.1 A number of chemicals interfere in this titration: mercaptans, sulfides, amines, ketones, aldehydes, oxidizing and reducing agents, and so forth. 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.

X1.1.2 At low water concentrations (<0.02 mass %), the interference by mercaptan and sulfide (>500 mg/kg as sulfur) may be significant (see Test Method E 203).

X1.1.3 All equipment should be scrupulously clean of moisture. Rinse all syringes, needles, and weighing bottles with anhydrous acetone after cleaning. Then dry in an oven at 100°C for at least an hour and store immediately in a desiccator.

X1.1.4 Fill the dry cooled sample bottle as rapidly as possible with the sample within 15 mm of the top and immediately seal.

X1.1.5 After removing a sample aliquot from the bottle with a dry hypodermic syringe, inject dry nitrogen into the sample bottle with the syringe to displace the removed sample void.

X1.1.6 The presence of gas bubbles in the syringe may be a source of uncertainty. Viscous samples may be difficult to measure with a precision syringe. In such cases, taking the sample aliquot by mass is preferred to volume measurement.

X1.1.7 Although standardization is not necessary in coulometric titrations, reagent performance deteriorates with use and must be regularly monitored by accurately injecting 100 000 µg or 100 µL of pure water. Suggested intervals are initially with fresh reagent, and then after every ten determinations.

X1.1.8 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.

X1.1.9 During the blank measurement instrument preparation, 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.

X1.1.10 The frit separating the vessel compartments may get clogged with sample residues; Disassemble the apparatus in such cases and acid clean the frit.

X1.1.11 Any time one of the following situations occurs, replace the anode and the cathode solutions and then repeat the preparation of the apparatus as in Section 9.

X1.1.11.1 Persistently high and unstable background current.

X1.1.11.2 Phase separation in the anode compartment or the sample coating the electrodes.

X1.1.11.3 The total amount of sample added to the titration vessel exceeds one fourth of the volume of solution in the anode compartment.

X1.1.11.4 The solutions in the titration vessel are over one week old.

X1.1.11.5 The instrument displays error messages that suggest replacement of the electrodes.

X1.1.11.6 The results of a 0.01 mL injection of water is outside 100 000 ± 1000 µg.

X1.1.12 If the titration vessel gets contaminated with the sample, thoroughly clean the anode and cathode compartments with xylene. Never use acetone or similar ketones.