Designation: D7375 – 08

Standard Test Method for Trace Quantities of Water in Aromatic Hydrocarbons and Their Mixtures by Coulometric Karl Fischer Titration[1]

This standard is issued under the fixed designation D7375; 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 describes the use of the Coulometric Karl Fischer (KF) titration for the determination of water in aromatic hydrocarbons and their mixtures, derivatives and related chemicals.

1.2 This test method is applicable to samples with water concentrations from 10 to 400 mg/kg.

1.3 In determining the conformance of the test results using this method to applicable specifications, results shall be rounded off in accordance with the rounding-off method of Practice E29.

1.4 Values stated in SI units are to be regarded as the standard. The preferred units are milligrams per kilogram (mg/kg).

1.5 *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.* For a specific hazard statement see Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D3437 Practice for Sampling and Handling Liquid Cyclic Products

D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E203 Test Method for Water Using Volumetric Karl Fischer Titration

2.2 *Other Standard:*

OSHA Regulations, 29 CFR paragraphs 1910 and 1910.1200[3]

3. Summary of Test Method

3.1 In the Karl Fischer reaction, water will react with iodine in the presence of sulfur dioxide, alcohol and an organic base according to the following equation:

$$H_2O+I_2+SO_2+CH_3OH+3RN\rightarrow(RNH)SO_4CH_3+2(RNH)I \qquad (1)$$

where:

RN = organic base.

3.2 In the coulometric titration test method, the sample is injected into an electrolytic cell where the iodine required for the reaction with water is produced by an anodic oxidation of iodide. With this technique, no standardization of reagents is required.

4. Significance and Use

4.1 High water concentrations can have a detrimental effect on many uses of aromatic hydrocarbons, their mixtures and related compounds.

4.2 Water can inhibit desired reactions when aromatic hydrocarbons, their mixtures and related compounds are used in formulations and chemical processes.

4.3 Water can cause corrosion problems and detrimental effects during the manufacture and processing of aromatic hydrocarbons, their mixtures and related compounds.

5. Interferences

5.1 Certain compounds or classes of compounds interfere with the accurate determination of water by the Karl Fischer test method. They include aldehydes, ketones, free halogens, ferric salts and strong oxidizing and reducing agents.

5.2 Free halogens can oxidize the iodate in the KF reagents to form iodine: this causes erroneously low water values.

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[1] This test method is under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and is the direct responsibility of Subcommittee D16.04 on Instrumental Analysis.

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

[3] Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, http://www.access.gpo.gov.

5.3 A more detailed discussion of KF interferences can be found in Test Method E203 and other sources.[4]

6. Apparatus

6.1 *Coulometric Titrator*—Consisting of a single or dual bath electrolytic cell, dual platinum electrode, magnetic stirrer and control unit.

6.1.1 *Dual Bath Electrolytic Cell*—The dual bath coulometic titration cell consists of a sealed vessel containing both an anode and cathode compartment (a Fritted Cathode Cell). The anodic compartment usually contains a solution consisting of sulfur dioxide, iodide and an amine in an alcoholic based solvent. The cathodic compartment contains similar reagents optimized for the cathodic reduction. When a sample containing water is injected into the anode compartment, the electrolytic cell generates its own supply of iodine from the iodide present. The iodine reacts stoichiometrically with the water and the completion of the reaction is detected with a dual platinum-sensing electrode. The coulombs of electricity required to generate the necessary amount of iodine is then translated by the microprocessor in the control unit into the amount of water that was present in the sample.

6.1.2 *Single Bath Electrolytic Cell*— The single bath electrolytic cell consist of a sealed vessel with an anode and cathode electrode (a Frittless Cathode Cell), a dual platinum sensing electrode and is filled with a single bath reagent. When a sample containing water is injected into the vessel, the electrolytic cell generates its own supply of iodine from the iodide present. The iodine reacts stoichiometrically with the water and the completion of the reaction is detected with a dual platinum-sensing electrode. The coulombs of electricity required to generate the necessary amount of iodine is then translated by the microprocessor in the control unit into the amount of water that was present in the sample.

6.2 *Sampling Syringes*—5 and 10-mL gastight syringes.

6.3 *Standard Gastight Syringe*—10-µL size.

6.4 *Silicone Rubber Blocks Silicone Rubber Septa,* or equivalent.

6.5 *Drying Oven*—Air circulating capable of maintaining a drying temperature of 110°C.

6.6 *Desiccator* with desiccant.

6.7 *Analytical Balance*—Capable of weighing to the nearest 0.0001 g accurately.

7. Reagents and Materials

7.1 *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 American Chemical Society where such specifications are available.[5] Other grades may be used, providing it is first ascertained that 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 conforming to Type II of Specification D1193.

7.3 *Anode Reagent*—For dual bath titration use reagent recommended by manufacturer of titrator.

7.4 *Cathode Reagent*—For dual bath titration use reagent recommended by manufacturer of titrator.

7.5 *Single Bath Reagent*—For single bath titration use reagent recommended by manufacturer of titrator.

7.6 *Toluene*—Reagent grade.

7.7 *Dry Molecular Sieve Type 4A*—4-8 mesh.

7.8 *Dried Toluene Solution*—Fill a narrow top 1 L glass bottle with approximately 2 in. of Molecular Sieve Type 4A, 4-8 Mesh and fill the bottle with reagent grade toluene taking care to minimize or eliminate the headspace. Agitate/mix the toluene and molecular sieve in the bottle and let the solution stand for 2 days in a flammable storage cabinet or fume hood before using.

7.9 *Quality Assurance (QA) Samples*— Samples that are aromatic hydrocarbons or standards of known water content. These (QA) samples are to be used to check the validity of the testing process as described in Section 11. An ample supply of QA sample material should be available for the intended period of use and must also be homogenous and stable under the anticipated storage time and conditions.

8. Hazards

8.1 Consult current OSHA regulations and suppliers Material Safety Data Sheets (MSDS) for materials used in this test method.

9. Sampling

9.1 Obtain a test sample in accordance with Practice D3437. Since aromatic hydrocarbons normally contain low concentrations of water, care must be taken to eliminate the introduction of water from sampling equipment and atmospheric moisture.

9.2 Without taking the proper sampling precautions, more error is typically introduced into the determination of water through sampling techniques than in the titration process itself.

9.3 Dry sample bottles and closures in an oven at 110°C for 1 to 2 h. Place caps on the bottles immediately after removing from the oven.

9.4 Transfer the sample to the bottles as quickly as possible. Adjust the liquid level to achieve as close to zero headspace as

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

[5] *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.

possible, taking into account the type of sample. Immediately place the cap on the bottle and tighten.

9.5 When removing a portion of sample from the bottle for KF analysis use syringes that have been thoroughly dried as outlined in 12.5. Replace the cap on the bottle immediately.

9.6 If more that one portion of sample is to be taken from the bottle or if the sample is to be retained for further water analysis, it is a good practice to blanket the top of the bottle with dry nitrogen when removing the sample. If septum cap closures are being used, dry nitrogen can be introduced with a syringe at the same time a portion of the sample is being removed with a second syringe.

10. Verification of Instrument Accuracy

10.1 Coulometric titrators do not have a titrant that needs to be standardized since the iodine is being generated on demand by the titration cell. However, occasional checks of the instrument accuracy are recommended. This can be done by analyzing either:

(a) A standard solution available from reagent supplier for accuracy verification containing a known amount of water dissolved in an appropriate solvent or

(b) A known amount of distilled reagent water.

10.2 *Standard Solution*—A known volume or weight of a standard solution is analyzed and amount of water determined is compared with the certified (theoretical) amount of water stated by the manufacturer. The deviation from the certified (theoretical) value should not be larger than ±5 %.

10.3 *Distilled Reagent Water*—Use a 10-µL syringe to accurately inject 3.0 µL of water into the titration cell. Once the titration is complete, the analyzer should report a value of 3000 µg (3.0 mg) H_2O. The deviation from the theoretical value should not be larger than ±5 %.

11. Preparation of Apparatus

11.1 Amounts of coulometric reagents recommended for addition to the electrolytic titration cell usually have the capacity to react with approximately 200 to 500 mg of water. These reagents must be replaced when they are depleted.

11.2 Coulometric reagents are hygroscopic and must be stored in tightly capped containers to reduce the absorption of atmospheric moisture.

11.3 Since the titrator automatically generates iodine to keep the reaction vessel in a dehydrated state, it is important to keep the cell sealed to prevent introduction of excess atmospheric moisture that will decrease reagent life.

11.4 The total amount of solution plus sample in the anode section of the electrolytic titration cell can affect the KF reaction. Typically, the total liquid volume of sample added to the anode section of the electrolytic titration cell should not exceed 50 % of the original reagent volume. If the reagents become too dilute, the stochiometry and rate of the Karl Fischer reaction can be adversely affected. This fact should be considered and taken into account when using large sample sizes.

11.5 Follow the recommended maintenance procedures of the instrument manufacturer.

12. Procedure

12.1 Set up the coulometric titrator according to the manufacturer's instructions and add the proper amount of reagents.

12.2 The cell solutions must be anhydrous prior to introduction of sample. Follow the manufacturer's instructions for drying down the titration cell.

12.3 The amount of aromatic sample that is injected into the titration cell is dependent upon the quantity of water in the sample. Table 1 lists recommended sample size for the anticipated water concentration. Other samples sizes may be used as long as the analysis meets the performance criteria of the method.

12.4 When more than one replicate of a sample will be analyzed, determine the syringe size that will contain the desired sample injection volume multiplied by the number of replicates desired plus 0.5 mL. Follow the same calculation for other replicates and sample sizes. Table 2 is an example of syringe size determination for different injection volumes when the number of replicates equals three.

12.5 Prepare the syringe for injection by one of the following methods as outlined in section 12.5.1, 12.5.2, or 12.5.3.

12.5.1 Rinse the gastight syringe with the Dried Toluene Solution (see 7.8) a minimum of 5 times.

12.5.2 Thoroughly clean and dry the sampling syringe. Drying the syringe in an oven at 110°C and storing in a desiccator before use has proven to be an effective method.

12.5.3 Other approaches may be used as long as the they meet the performance criteria of the method.

12.6 Fill the syringe to the desired volume for the total number of replicates to be analyzed as determined in 12.4 and Table 2. Take care when filling the syringe to slowly withdraw the plunger thereby not agitating or mixing inside the syringe body the sample with air. Displace enough sample from the syringe to eliminate any air bubble that remains inside the needle of the syringe.

12.7 Cover the syringe needle with a silicone rubber block or piece of silicone rubber septa to prevent evaporation or spillage during the weighing process.

12.8 Transfer the filled syringe to an analytical balance and weigh the syringe and contents to the nearest 0.0010 g.

12.9 Follow the manufacturer's directions to prepare the analyzer for sample analysis and injection.

12.10 Remove the syringe from the balance. Remove the silicone block and insert the needle into the titration cell through the septum taking care the tip of the needle is

TABLE 1 Recommended Injection Volume vs. Expected Moisture Concentration

Sample Volume mL	Expected Concentration mg/kg
1.50 mL	0 – 20 mg/kg
1.00 mL	24 – 400 mg/kg

approximately ⅛ in. (3 mm) from surface of anode solution of the titration cell. Slowly inject the volume of the sample determined in 12.3, taking care not to touch the needle to the surface of the anodic solution. While the syringe is still inside the cell, withdraw the plunger very slightly to remove/withdraw any sample droplet remaining on the tip of the needle back into the needle and remove the needle from the cell.

TABLE 2 Determination of Syringe Size

Injection Volume mL	Number of Replicates	Total Volume + 0.5 mL	Syringe Size mL
1.0	3	3.5	5
1.5	3	5.0	5
2.0	3	6.5	10
5.0	3	15.5	20

12.11 Place the silicone block back onto the tip of the needle and reweigh the empty syringe. The weight difference between the first and second weighing will be the amount of sample injected into the titration cell.

12.12 Enter the sample weight into the moisture analyzer.

12.13 Repeat the steps outlined in 12.8-12.12 for the number of replicates determined in 12.4.

NOTE 1—The make and model of the titrator being used will determine the actual steps performed to carry out the analytical process. In most cases, all that is required is to press the start titration or run key on the instrument either immediately prior to or after the sample is injected.

12.14 Once the titration is complete, the amount of water (µg or mg of H_2O) that was measured in the sample will appear on the instrument's display. Most instruments will also calculate concentration, usually in weight ppm or %, if the sample weight is entered into the instrument's control panel or software.

13. Calculation

13.1 Calculate the water content of the sample as follows:

$$mg/kg\ H_2O = (W/M) \times K \qquad (2)$$

where:

W = µg H_2O found,
M = grams of sample injected weighed to the nearest 0.001 g, and
K = (1000 g/kg) / (1000 µg/mg).

14. Precision and Bias

14.1 *Precision*—A ruggedness study was performed by analyzing on two samples 10 times each over the shortest practical time. The calculated repeatability is shown in Table 3.

TABLE 3 Demonstration of Repeatability mg/kg

Average Conc. mg/kg	Repeatability mg/kg
9.9	1.1
383	36

14.2 *Repeatability*—See Table 3.

14.3 *Reproducibility*—To be determined.

15. Quality Guidelines

15.1 Refer to Guide D6809 for suggested QA/QC activities that can be used as a part of this method. It is recommended that the operator of this method select and perform relevant QA/QC activities like the ones in Guide D6809 to help insure the quality of data generated by this method.

16. Keywords

16.1 aromatics; Karl Fischer; microcoulometry; water

APPENDIX

(Nonmandatory Information)

X1. QUALITY CONTROL

X1.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample.

X1.2 Prior to monitoring the measurement process, the user of the test method needs to determine the average value and control limits of the QC sample (See Guide D6809 and MNL 7).[6]

X1.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process (see Guide D6809 and MNL 7). Any out-of-control data should trigger investigation for root causes. The results of this investigation may, but not necessarily, result in instrument recalibration.

X1.4 In the absence of explicit requirements given in the test method, the frequency of QC testing is dependent of the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample is analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample precision should be checked against the ASTM test method precision to ensure data quality.

X1.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the material routinely analyzed. An ample supply of QC sample material

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[6] ASTM MNL7, Manual on Presentation of Data Control Chart Analysis, 6 th ed., available from ASTM International Headquarters.

should be available for the intended period of use, and must be homogeneous and stable under the anticipated storage conditions. See Guide D6809 and MNL 7 for further guidance on QC and control charting techniques.

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