Designation: D7995 – 19

Standard Test Method for Total Water in Liquid Butane by Liquefied Gas Sampler and Coulometric Karl Fischer Titration[1]

This standard is issued under the fixed designation D7995; 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 a specialized liquefied gas sampler coupled to a coulometric Karl Fischer (KF) titrator for the determination of water in liquid butane with water concentrations from 1 mg⁄kg to 100 mg⁄kg.

NOTE 1—Other liquefied petroleum gases described in Specification D1835 including propane, propene (propylene), butylenes and mixtures of these materials and other light hydrocarbons, and dimethyl ether described in Specification D7901, can be analyzed by this method but the precision has not been studied and therefore the stated precision has not been validated for these materials.

1.2 The values stated in SI units are to be regarded as standard. The values given in parentheses after SI units are provided for information only and are not considered standard.

1.3 *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.* See Section 10 for specific warning statements.

1.4 *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]

D1265 Practice for Sampling Liquefied Petroleum (LP) Gases, Manual Method

D1835 Specification for Liquefied Petroleum (LP) Gases

D2713 Test Method for Dryness of Propane (Valve Freeze Method)

D3700 Practice for Obtaining LPG Samples Using a Floating Piston Cylinder

D5623 Test Method for Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection

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 and Lubricants

D6304 Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration

D7901 Specification for Dimethyl Ether for Fuel Purposes

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E203 Test Method for Water Using Volumetric Karl Fischer Titration

2.2 *Occupational Safety and Health Administration Document:*

OSHA Regulations—29 CFR paragraphs 1910.1000 and 1910.1200[3]

2.3 *Other Standards:*

UOP 163 Hydrogen Sulfide and Mercaptan Sulfur in Liquid Hydrocarbons by Potentiometric Titration[4]

3. Terminology

3.1 *Definitions:*

3.1.1 *liquefied petroleum gas, (LP Gas, LPG), n*—a narrow boiling range mixture of hydrocarbons consisting of propane, propylene, butanes and butylenes, individually or in specified combinations, with limited amounts of other hydrocarbons and naturally occurring non-hydrocarbons.

3.1.2 *dimethyl ether (DME), n*—the chemical compound CH_3OCH_3.

3.2 *Definitions of Terms Specific to This Standard:*

[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.H0 on Liquefied Petroleum Gas.

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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, Washington, DC 20401-0001, http://www.access.gpo.gov.

[4] Available from https://www.astm.org/

3.2.1 *coulometric Karl Fischer titration (coulometric titration), n*—in reference to Karl Fischer titration methods, a process of measuring the water content of a sample using an electrolytic process to generate iodine in situ.

3.2.2 *mass flow meter, n*—a device used to measure the flow of gases.

3.3 *Abbreviations:*

3.3.1 *DME*—dimethyl ether

3.3.2 H_2S—hydrogen sulfide

3.3.3 *KF*—Karl Fischer (titration)

3.3.4 *LPG*—liquefied petroleum gas

3.3.5 *MFM*—mass flow meter

3.3.6 *QA*—quality assurance

3.3.7 *QC*—quality control

4. Summary of Test Method

4.1 An aliquot of pressurized liquid butane sample is introduced into the liquefied gas sampler, where the sample is totally volatilized and passes through a heated chamber (typically 60 °C to 80 °C) to ensure the sample is in a gaseous state. The gas then flows through a calibrated mass flow meter (MFM) or a fixed volume sample loop and bubbles into the electrolytic cell of a coulometric Karl Fischer (KF) titrator. The MFM is calibrated to the sample composition analyzed and a calibration factor is used to calculate the mass of pressurized sample. Alternatively, when a fixed volume sample loop is used, the temperature and the pressure are measured to calculate the volume of the volatized sample gas. The gas flow is stopped when a suitable amount of sample is introduced to the coulometric KF titrator. The water in the gas is absorbed by the anode reagent and titrated automatically by the coulometric KF titrator. The concentration of water in the original pressurized sample is calculated by the amount of water measured (µg) and the sample size (g) introduced by the MFM or sample loop.

4.1.1 *General Descriptions of Volumetric Liquefied Gas Sampler*—There are two types of liquefied gas sampler. The first utilizes a mass flow meter to accurately measure the mass or volume of liquefied gas is introduced into a KF titration cell, see Fig. 1. Once the specified mass or volume of sample is delivered, the sampler automatically stops the flow into the titration cell. The second type of sampler uses a fixed volume sample loop to accurately deliver an aliquot of liquefied gas into the titration cell, see Fig. 2. The fixed volume is carefully delivered into the KF titration cell by means of a restrictor valve.

4.2 In the coulometric KF titration technique, the sample is introduced into an electrolytic cell where the iodine required for the reaction with water is produced by an anodic oxidation of iodide. With the coulometric KF titration technique, no standardization of reagents is required.

5. Significance and Use

5.1 High water concentrations can have a detrimental effect on the many uses of liquefied petroleum gas (LPG). Wet butane, propane, and other low molecular weight hydrocarbon products can cause operational issues in customer equipment and downstream processes. Water can cause corrosion problems and create safety hazards during the storage, distribution and use of liquefied petroleum gas (LPG) and pressurized low molecular weight hydrocarbon samples.

5.2 While the dryness of propane may be monitored with a "functional" test such as the valve freeze Test Method D2713, this test method provides an analytical method to directly measure water content in LPG and pressurized low molecular weight hydrocarbons and their mixtures.

6. Interferences

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

6.2 In LPG, the most common interferences are mercaptan sulfur and hydrogen sulfide by means of the reactions in Eq 1 and 2. In commercial butane, propane, and LPG, ethyl mercaptan is commonly used as an odorant. For propane, the

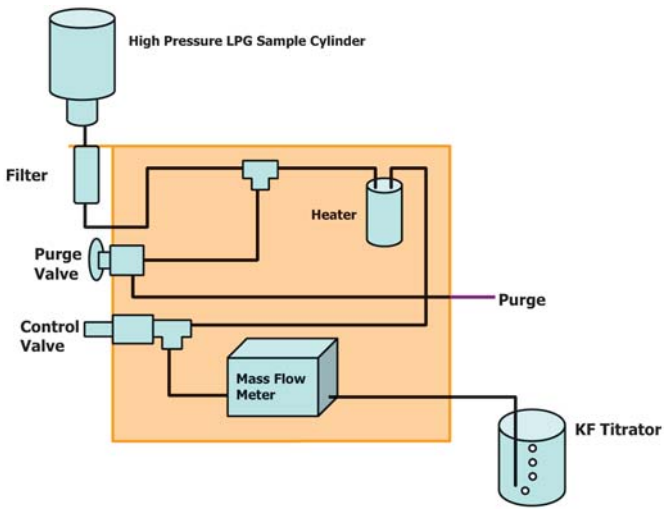

FIG. 1 Typical Block Flow Diagram of Liquefied Gas Sampler Using Mass Flow Meter

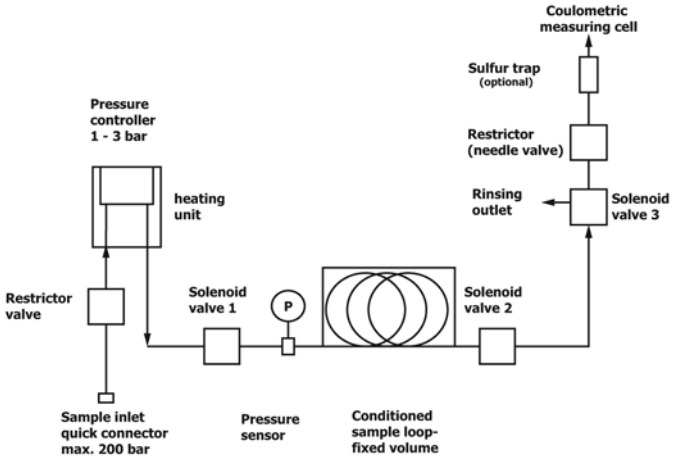

FIG. 2 Typical Block Diagram of Liquefied Gas Sampler With Fixed Volume Sample Loop

standard practice is to add 1.5 lb of ethyl mercaptan to 10 000 gal of propane which equates to 25 ppm by volume or 35 mg⁄kg ethyl mercaptan.

$$2R\text{-}SH + I_2 \rightarrow RS\text{-}SR + 2HI \quad (1)$$

where:

R-SH = mercaptan, and
RS-SR = organic disulfide.

$$H_2S + I_2 \rightarrow S + 2HI \quad (2)$$

6.2.1 If the concentration of mercaptans in the samples is expected to be above 35 mg⁄kg or the interference from mercaptan concentrations in the sample will result in significant interference relative to the expected amount of water in the samples being analyzed, refer to Appendix X2 for handling of mercaptan interference.

6.3 Free halogens can oxidize the iodide in the KF reagent to form iodine and cause erroneously low water values.

6.4 A more detailed discussion of KF interferences can be found in Test Method E203 and other sources.[5]

7. Apparatus

7.1 *Liquefied Gas Sampler*—An apparatus that automatically controls the introduction of liquefied sample (3.1.1) from a sample cylinder into the electrolytic titration cell of a coulometric Karl Fischer (KF) titrator as specified in 7.3. The amount of the volatilized sample introduced into the titration cell is based on the type of liquefied gas sampler being used. A typical block flow diagram of the types two of liquefied gas samplers are shown in Fig. 1 and Fig. 2.

7.1.1 *Liquefied Gas Sample Utilizing a Mass Flow Meter*—The pressurized sample is introduced into the sampler and vaporized at 60 °C to 80 °C. Sample flow is controlled with a needle valve and monitored with a built-in MFM calibrated to the sample matrix being analyzed (see Section 14). The flow of sample into the titration vessel is stopped when the set amount of sample has been introduced into the titration vessel and is then analyzed.

7.1.2 *Liquefied Gas Sample Utilizing a Fixed Sample Loop*—The pressurized sample is introduced into the sample and vaporized at 60 °C to 80 °C and flows into the fixed sample loop. The sample loop is filled and is introduced into the titration vessel. The amount of sample introduced into the titration vessel is automatically calculated based on the volume of the built-in sample loop, temperature, and pressure at the time of analysis.

7.1.3 The liquefied gas sampler may be programmed to automatically sample and analyze multiple replicates from the same pressurized sample cylinder with no operator intervention (see 7.3).

7.2 *Balance*—A balance is required to determine the calibration factor of each type of gas passing through the mass flow meter. To achieve a sufficient level of accuracy, the sample weight difference should have at least three significant figures for calibration. It is recommended the balance have accuracy to one hundredth of a gram.

7.3 *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 iodine are converted to micrograms of water, which is obtained as a direct digital readout.

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,

[5] 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.

where such specifications are available.[6] Other grades may be used, provided it is pure enough to be used without lessening the accuracy of the determination.

8.2 *Certified Water Standard*—A certified standard solution that contains 0.1% water dissolved in an appropriate solvent. Commercial certified water standards are acceptable for use.

8.3 *Certified Gas Standard*—A certified standard gas that contains a definite water concentration (<100 mg⁄kg). Commercial certified water in gas standards based on nitrogen, methane, or LPG are acceptable for use.

8.4 *Anode Reagent,* for dual chamber (Fritted or Diaphragm) titration use reagent recommended by manufacturer of titrator.

8.5 *Cathode Reagent,* for dual chamber (Fritted or Diaphragm) titration use reagent recommended by manufacturer of titrator.

8.6 *Single Chamber Reagent*—Use single chamber (Fritless or Diaphragm Free) reagent recommended by manufacturer of titrator.

NOTE 2—Pyridine was the organic amine that was traditionally used in Karl Fischer reagents; however, pyridine-free formulations from various manufacturers are now available and preferred by most KF instrument manufacturers. Pyridine-free reagents are less toxic, less odorous, and more stable than pyridine-based reagents.

8.7 *Methanol,* dry, water content <150 mg⁄kg, may be used to maintain constant volume of titration cell due to reagent volume loss by evaporation.

8.8 *Inert Gas (Nitrogen, Helium or Argon),* minimum 99.999 % purity, used to pressurize the sample cylinders prior, to and after analysis.

8.9 *Gas-tight Luer-Lock Syringe,* fitted with a cannula needle of appropriate length and gauge for introducing water standard into the titration chamber or removing excess solution from titration chamber. The volume of the syringe will depend on the sample size. Sample should occupy at least 25 % of the syringe volume.

8.9.1 It is recommended to rinse all glass syringes and needles with dry methanol or ethanol after cleaning, and then dry in an oven at 100 °C for at least 1 h and store in a desiccator.

9. Quality Guidelines

9.1 Autotitrators vary in calibration procedures by manufacturer. Consult the operating manual for the autotitrator in use. Stable, prepackaged Quality Control (QC) water standards are commercially available with 0.1 % by mass water content for this purpose. It is desirable to verify calibration with a standard solution that approximates the same range of water expected to be in the samples.

9.1.1 Certified water in gas standards are commercially available and may be used to verify system functionality.

9.2 It is recommended that a control chart measuring a QC standard sample be established and maintained according to generally accepted guidelines. Practice D6299 may be used for this purpose. Measure the titration control sample each day samples are tested. If the measured value exceeds ±10 % of the known amount, take appropriate action before proceeding with the sample test.

10. Hazards

10.1 Consult suppliers' Safety Data Sheets (SDS) for materials used in this test method as well as any appropriate OSHA or equivalent USA or international safety rules and regulations.

10.2 Liquid butane, LPGs, and low molecular weight hydrocarbons gases under high pressures occur in the test method. Use cylinders and materials that are rated for containing these pressurized gases in all sample containers, tubing, and sample transfer apparatus that are exposed to these high pressures.

10.3 LPG and pressurized low molecular weight hydrocarbons and their volatilized gases are extremely flammable. The gas vapors generated during the sampling and purging process of the liquefied gas sampler shall be safely vented to avoid potential fire and explosion conditions to occur.

11. Sampling, Test Specimens, and Test Units

11.1 Obtain a pressurized test sample in accordance with Practice D1265 or D3700. Since LPG normally contains a low concentration of water, ensure that sampling equipment is dry and is not exposed to atmospheric moisture. Sampling equipment may be dried with a dry inert gas.

11.2 When running replicate analyses from the same cylinder, ensure there is enough sample to support the number of replicates to be analyzed. See Table 1 for estimated sample amounts required based on expected water content.

11.3 It is recommended to pressurize all sample cylinders to the same pressure, nominally 1300 kPa to 2750 kPa (200 psi to 400 psi), with an inert gas (8.6) and maintain sufficient pressure in the sample cylinder during the analytical process to ensure representative and consistent samples for the number of replicate analyses being performed.

12. Preparation of Apparatus

12.1 The recommended amount of coulometric reagents added to the electrolytic titration cell of a coulometric KF titrator usually has the capacity to react with up to 1000 mg of water. Replace these reagents when they are depleted by following manufacturer's instructions.

TABLE 1 Recommended Sample Size versus Expected Water Concentration

Expected Water Concentration (mg/kg)	Sample Size (g)
0 to 50	1.5 to 10.0
50 to 150	0.5 to 5.0

[6] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *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.