

Designation: D8094 - 21

# Standard Test Method for Determination of Water Content of Liquefied Petroleum Gases (LPG) Using an Online Electronic Moisture Analyzer<sup>1</sup>

This standard is issued under the fixed designation D8094; 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 ( $\varepsilon$ ) indicates an editorial change since the last revision or reapproval.

# 1. Scope\*

1.1 This test method covers the quantitative determination of water in liquefied petroleum gases (LPG) from 1 mg/kg to 250 mg/kg using an online electronic moisture analyzer, also known as an electronic hygrometer or dew point analyzer, in the absence of methanol or other anti-freeze agent.

1.1.1 These analyzers commonly use sensing cells based on aluminum oxide,  $Al_2O_3$ , silicone, phosphorus pentoxide,  $P_2O_5$ , piezoelectric-type cells, or laser-based technologies to measure the dew point temperature of LPG.

1.1.2 Knowledge of the hydrocarbon composition of the LPG is required to calculate the water content on a mass basis from the dew point temperature of an LPG sample.

1.1.3 The LPG shall be free of alcohol (sometimes added as an anti-freeze agent) as it can interfere with the electronic moisture analyzer. Thus the method will be most useful in a process facility where it is known that no methanol has been added to the LPG product.

1.2 The values stated in SI units are to be regarded as standard.

1.2.1 There is an exception in Appendix X1, where the unit "mbar" is used in data provided by an external source, and parts per million by weight (ppm by weight) is widely used in industry.

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.

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:<sup>2</sup>
- D1142 Test Method for Water Vapor Content of Gaseous Fuels by Measurement of Dew-Point Temperature
- D1145 Test Method for Sampling Natural Gas (Withdrawn 1986)<sup>3</sup>
- D1835 Specification for Liquefied Petroleum (LP) Gases
- D2163 Test Method for Determination of Hydrocarbons in Liquefied Petroleum (LP) Gases and Propane/Propene Mixtures by Gas Chromatography
- D2421 Practice for Interconversion of Analysis of  $C_5$  and Lighter Hydrocarbons to Gas-Volume, Liquid-Volume, or Mass Basis
- D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
- D6624 Practice for Determining a Flow-Proportioned Average Property Value (FPAPV) for a Collected Batch of Process Stream Material Using Stream Analyzer Data
- D6849 Practice for Storage and Use of Liquefied Petroleum Gases (LPG) in Sample Cylinders for LPG Test Methods
- D7453 Practice for Sampling of Petroleum Products for Analysis by Process Stream Analyzers and for Process Stream Analyzer System Validation
- D7808 Practice for Determining the Site Precision of a Process Stream Analyzer on Process Stream Material

## 3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 *capacitance-type cell*, n—a sensor that can store electric charge which changes with the partial pressure of water vapor in the system.

3.1.1.1 *Discussion*—An example of capacitance-type cell uses aluminum coated with  $Al_2O_3$  as part of a capacitor. The dielectric  $Al_2O_3$  film changes the capacity of the capacitor in relation to the water vapor present.

<sup>&</sup>lt;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.H0 on Liquefied Petroleum Gas.

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<sup>&</sup>lt;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.

<sup>&</sup>lt;sup>3</sup> The last approved version of this historical standard is referenced on www.astm.org.

3.1.1.2 *Discussion*—Silicone cells also operate on the same principal by reporting a capacitance change when adsorbing or desorbing water vapor.

3.1.2 *dew point, n*—the temperature, at a fixed pressure, where condensation of water first occurs.

3.1.2.1 *Discussion*—Charts of dew points versus pressure and water content are found in Test Method D1142.

3.1.2.2 *Discussion*—When water vapor is present in vaporized LPG at a constant pressure, liquid water will condense at its dew point temperature, which is directly related to the water vapor pressure.

3.1.3 *electrolytic-type cell, n*—a sensor composed of two noble metal electrode wires coated with  $P_2O_5$ .

3.1.3.1 *Discussion*—A bias voltage is applied to the electrodes, and water vapor chemically reacts, generating a current between the electrodes proportional to the water vapor present.

3.1.4 Henry's Law Constant (K), n—a factor that, when multiplied by the partial pressure of water vapor in a system, gives the mass of the dissolved water in the liquid phase hydrocarbon.

3.1.4.1 *Discussion*—Henry's Law applies only to dissolved water in a liquid. If the saturation concentration of water in the LPG is exceeded, there will be free water in the system that is outside the scope of Henry's Law.

3.1.4.2 *Discussion*—The value of K will vary with the composition of the LPG and its temperature.

3.1.5 *laser-type cell*, n—a sensor with an optical head containing a near infrared (NIR) laser, which emits light at a wavelength known to be absorbed by water molecules, and a detector.

3.1.5.1 *Discussion*—A portion of the emitted NIR light, proportional to the water molecules present, is absorbed as the light transits the sample cell and is measured by the detector.

3.1.6 *piezoelectric-type cell, n*—a sensor consisting of a pair of electrodes which support a quartz crystal (QCM) transducer, coated with a hygroscopic polymer, used to determine the amount of water vapor present in a sample.

3.1.6.1 *Discussion*—As the amount of moisture absorbed onto the polymer varies, a proportional change in the oscillation frequency of the QCM is produced which is converted into water content.

3.1.7 *saturation constant, n*—the maximum mass of water that can dissolve in a given mass of hydrocarbon or mixture of hydrocarbons at a given temperature and pressure.

3.1.8 *water content, n*—the amount of water in a fuel expressed in mg/kg.

# 4. Summary of Test Method

4.1 An LPG sample from a flowing stream of LPG is introduced to an online electronic moisture analyzer. The electronic moisture analyzer measures the dew point in either the liquid or gaseous phase. The analyzer signal is integrated over time, and the total mass of water per mass of sample is calculated from the water vapor pressure, which is functionally related to the dew point and the hydrocarbon composition of the LPG.

## 5. Significance and Use

5.1 The moisture content of LPG can be critical to the use, transportation, or processing of LPG products, especially at cold ambient temperatures and during pressure throttling, when icing or hydrate formation, or both, are most likely to occur. In order to prevent ice or hydrate formation, or both, the water content has to be low enough to prevent the formation of free water in storage tanks and/or regulators over the entire range of operating conditions (temperatures, pressures, and compositions) encountered during normal service. For example, propane and propane-propene mixtures require moisture levels below the equilibrium saturation level of water at operating temperature and pressure for these hydrocarbons to meet specifications such as Specification D1835.

5.2 The presence of free water in a propane system can lead to ice or hydrate accumulation, the blockage of vapor or liquid fuel lines, and disrupt the operation of pumps, meters, filters, valves, regulators, safety shut-off valves, and other equipment.

5.3 This test method allows continuous monitoring of process flow streams and could be applied to monitoring of product dryness during transportation operations if it is known that methanol has not been added.

# 6. Interferences

6.1 Conductive particulates that become trapped across the capacitance-type sensor leads or the sensor surface will cause erroneously high dew point readings. The most common particulates of this type are carbon, metallic particles (for example, iron scale, corrosion products, etc.), and free water droplets.

6.1.1 Interferences due to particulate contamination can be minimized by installing filters upstream of the sensor. Coalescing filters can be used to protect the sensor from free water droplets, especially in butane systems.

6.2 Alcohols such as methanol and glycols used as antiicing additives can also interfere by causing high readings.

### 7. Apparatus

7.1 Sampling System:

7.1.1 Most errors and interferences involved with moisture analysis can be eliminated with a proper sampling system. The sampling system shall meet Practice D7453.

7.1.2 A pipeline sample should be obtained with a probe per Test Method D1145. The sample temperature shall be maintained at least 2  $^{\circ}$ C (3  $^{\circ}$ F) above the dew point of the gas to prevent condensation in the sample line or analyzer. Use of insulation or heat tracing is recommended at cold ambient temperatures.

7.2 Electronic Moisture Analyzer:

7.2.1 Since electronic moister analyzers are available from various suppliers which use different technologies, review the manufacturer's manual for specific details and concerns.

7.2.2 Analyzer sensors are very sensitive to contamination. Any contaminants injurious to the sensor shall be removed from the sample stream before reaching the sensor. This shall be done with minimum impact on accuracy or time of response. 7.2.3 Protect moisture analyzers from contact with liquid water or alcohol which can deactivate some sensors. If the dew point measurement is made in the gas phase, a coalescing filter or semi-permeable membrane separator shall be used to prevent aerosols from reaching the sensor.

7.2.4 An integrated temperature sensor is necessary for moisture content determination.

## 7.3 Electronics:

7.3.1 The electronics system shall be capable of gathering and processing output from the sensor.

7.3.2 Output from the sensor will be linearized for analog or digital display in desired units. There shall be an adjustment for calibration accuracy available that can be used in the field if a suitable standard is available. (This does not apply to instruments that assume complete chemical reaction of water. Their accuracy shall be verified as described in Section 9.)

7.3.3 Saturation constants are required for calculation of milligrams of water per kilogram of LPG and are specific to the hydrocarbon composition of the LPG to be measured. Some data systems require the input of saturation values versus temperature to accommodate samples of differing composition.

7.3.4 Alternatively, data systems may require the Henry's Law Constant for the conversion of dew point of the LPG to milligrams of water per kilogram of LPG.

7.4 Power Supply:

7.4.1 Analyzers for field use require rechargeable or easily replaceable batteries. (**Warning**—Analyzers for use in hazardous locations because of flammable gas shall be certified as meeting the appropriate requirements.) The system shall incorporate calibration data specific to the sensor installed in the sample cell.

## 8. Sampling, Test Specimens, and Test Units

8.1 Analyzer cells or sampling probes shall be installed such that the sampling point provides exposure to a representative sample of the bulk fluid.

8.2 Flow and pressure shall be considered in construction of online sampling probes. Follow the manufacturer's instructions for specific limits for the system to be installed.

8.3 Analyzer cells may be installed in sample handling systems that divert some part of a flowing stream. The pressure of the stream that is sampled should never be reduced below the equilibrium vapor pressure of the stream at operating conditions.

Note 1—The API guideline for determining the minimum operating pressure in a system requires the minimum pressure on volatile hydrocarbon liquid streams to be 1.25 times the equilibrium vapor pressure of the stream at the "worst case" operating conditions, plus two times the differential pressure through the sampling device. This prevents flashing and non-representative samples.

# 9. Calibration and Standardization

9.1 Moisture sensors shall be individually calibrated using traceable standards.

9.1.1 The deviation from the certified dew point of the traceable standard shall not exceed  $\pm 3$  °C (5 °F).

9.2 Moisture sensors shall be calibrated annually and whenever maintenance is performed on the sensor or sampling system. Additional periodic calibration of measurement circuitry may be required to minimize electronic drift.

9.3 Periodic checks with a quality control sample shall be used to detect sensor drift between calibrations. Common laboratory cylinders or "20 lb barbeque" cylinders of LPG similar in composition to the samples being measured should be suitable. Consult Practice D6849 for guidance.

9.4 Consult Practices D6299 and D7808 for guidance on the statistical quality control techniques to determine fitness-foruse of the moisture analyzer system.

# 10. Procedure

10.1 If the LPG composition is unknown, determine the hydrocarbon composition using Test Method D2163 or a similar analytical method.

10.1.1 If the composition is measured in volume percent, convert to mass percent using Practice D2421.

10.2 Program the analyzer with the saturation constants or Henry's Law Constants, or both, for the LPG composition of the sample.

Note 2—Some instrument manufacturers supply the necessary data. Constants are not only specific to the hydrocarbon composition, but also to the measurement temperature. Constants for pure hydrocarbons can be found in the literature or determined experimentally. See Appendix X1 for some constants that are common to LPG.

10.3 Allow the moisture sensor time to equilibrate. The time is variable depending upon the specifics of the installation (flow, pressure), and how much volume is required to flush the sample handling system.

10.3.1 The output of some systems can be logged electronically, which is one means of determining when the sensor has stabilized.

10.4 Record the temperature and dew point in degrees Celsius (°C) to the nearest whole degree, and water content in milligrams per kilogram (mg/kg).

# 11. Report

11.1 Report the water content of the LPG in units of mg/kg to the nearest 1 mg/kg unit and reference this test method.

11.2 If a flow-proportioned average property value (FPAPV) for a batch of in-line blended product or process stream material is required, then follow Practice D6624. Report the water content of the LPG in units of mg/kg to the nearest 1 mg/kg unit, reference Practice D6624, and reference this test method.

# 12. Precision and Bias

12.1 Formal precision and bias have not yet been determined.

12.1.1 Six experiments were conducted with four LPG samples using four meters connected in series on a recirculating loop (same flow and pressure). The meters were all from a single manufacturer.<sup>4</sup> The standard deviation is as follows:

<sup>&</sup>lt;sup>4</sup> GE Panametrics model PM880 meters were used in this study.



13. Keywords

13.1 dew point; electronic moisture analyzer; liquefied petroleum gases; LPG; valve freeze; water in LPG

### APPENDIXES

#### (Nonmandatory Information)

### **X1. WATER CONTENT OF LPG MIXTURES**

X1.1 Water saturation constants for pure hydrocarbons at selected measurement temperatures are given in Table X1.1. Intermediate values can be obtained by interpolation.

X1.1.1 For mixtures of organic liquids, a saturation concentration  $(C_{mix})$  can be calculated using the percentage of each component by mass and saturation concentrations of each component.

$$C_{mix} = \sum_{i}^{n} x_i C_i \tag{X1.1}$$

Standard Deviation, mg/kg

1.042

1 9 1 7

2.192

5.811

8 6 1 2

10.698

where:

Average, mg/kg 13.547

19 480

23.414

51.076

129 484

129.970

 $x_i$  = the mass fraction of a component in the mixture, U

 $C_i$  = the saturation concentration of that component, and

n = the total number of components in the LPG mixture.

X1.2 The Henry's Law Constant, K, is determined from the water saturation concentration of the organic liquid at the

measurement temperature.

X1.2.1 The following equation can be used to calculate *K*:

$$K = C/VP_{sat} \tag{X1.2}$$

where:

 $C (or C_{mix})$  = the saturation concentration in mg/kg, and  $VP_{sat}$  = the saturation vapor pressure of water at the measurement temperature (mbar).

X1.2.2 The saturation vapor pressure of water  $(VP_{sat})$  at selected measurement temperatures is listed in Table X1.2. Intermediate values can be obtained by extrapolation.

X1.2.3 Henry's Law Constants for common LPG hydrocarbons are given as averages over common measurement temperatures in Table X1.3.

TABLE X1.1 Water Saturation Concentrations, Typical L	LPG Hydrocarbons mg/kg (ppm by weight) <sup><math>A</math></sup>
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	ASTM D8094 Temperature, °C						
	0	10	20	30	40	50	
Methane / Standar	ds.teh.a6catalog/	standar16/S1St/U	288//28408/00-4	907-9461-960	J969d19a137astm-d	8094-2210	
Ethane	31	65	130	250	400	600	
Ethylene	157	264	429	676	1035	1610	
Propane	56	93	154	240	385	580	
Propene	299	409	565	777	1150	1480	
n-Butane	20	34	60	104	185	305	
Isobutane	25	42	71	120	202	340	
Isobutylene	169	259	397	605	932	1440	
1-Butene	191	274	394	566	814	1170	
2-Butene	242	323	431	576	769	1027	
n-Pentane	29	49	81	135	226	376	

<sup>A</sup> Source: COSA Xentaur Corporation; used with permission.