Designation: D7940 – 21

Standard Practice for Analysis of Liquefied Natural Gas (LNG) by Fiber-Coupled Raman Spectroscopy[1]

This standard is issued under the fixed designation D7940; 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 practice is for both on-line and laboratory instrument-based determination of composition for liquefied natural gas (LNG) using Raman spectroscopy. Although the procedures in this practice refer specifically to liquids, the basic methodology can also be applied to other light hydrocarbon mixtures in either liquid or gaseous states, provided the data quality objectives and measurement needs are met. From the composition, gas properties such as heating value and the Wobbe index may be calculated. The components commonly determined according to this test method are CH_4, C_2H_6, C_3H_8, i-C_4H_{10}, n-C_4H_{10}, iC_5H_{12}, n-C_5H_{12}. Components heavier than C5 are not measured as part of this practice.

NOTE 1—Raman spectroscopy does not directly quantify the component percentages of noble gases; however, inert substances can be calculated indirectly by subtracting the sum of the other species from 100 %.

1.2 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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.*

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]

D1945 Test Method for Analysis of Natural Gas by Gas Chromatography

D1946 Practice for Analysis of Reformed Gas by Gas Chromatography

D3588 Practice for Calculating Heat Value, Compressibility Factor, and Relative Density of Gaseous Fuels

D4150 Terminology Relating to Gaseous Fuels

D7833 Test Method for Determination of Hydrocarbons and Non-Hydrocarbon Gases in Gaseous Mixtures by Gas Chromatography

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

2.2 *BS EN Standards:*[3]

BS EN 60079-28 Explosive Atmospheres. Protection of Equipment and Transmission Systems using Optical Radiation

BS EN 60825-1 Safety of Laser Products Part 1: Equipment Classification, Requirements and User's Guide

2.3 *ISO Standards:*[4]

ISO 6974-5 Natural Gas—Determination of Composition with Defined Uncertainty by Gas Chromatography, Part 5: Determination of Nitrogen, Carbon Dioxide and C1 to C5 and C6+ Hydrocarbons for a Laboratory and On-line Process Application Using Three Columns

ISO 6976:2016(E) Natural Gas—Calculation of Calorific Values, Density, Relative Density and Wobbe Indices from Composition

[1] This practice is under the jurisdiction of ASTM Committee D03 on Gaseous Fuels and is the direct responsibility of Subcommittee D03.12 on On-Line/At-Line Analysis of Gaseous Fuels.

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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 British Standards Institution (BSI), 389 Chiswick High Rd., London W4 4AL, U.K., http://www.bsigroup.com.

[4] Available from International Organization for Standardization (ISO), 1, ch. de la Voie-Creuse, CP 56, CH-1211 Geneva 20, Switzerland, http://www.iso.org.

3. Terminology

3.1 *Definitions:* For definitions of general terms used in D03 Gaseous Fuels standards, refer to Terminology D4150.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *accumulations, n*—the number of exposures co-added are referred to as accumulations.

3.2.1.1 *Discussion*—While the exposure time is optimized to control the amount of light entering the instrument for a single exposure, multiple exposures can be co-added to improve signal-to-noise.

3.2.2 *charge-coupled device (CCD), n*—silicon based two dimensional light sensor characterized by possessing a grid of potential energy wells where light-generated free electrons collect and then are read out sequentially.

3.2.3 *charge-coupled device binning, v*—process of combining "bins" or pixel wells on the CCD.

3.2.4 *exposure time, n*—the exposure time indicates the amount of time allocated for capturing photons.

3.2.4.1 *Discussion*—The number of electrons is counted at the end of the allotted exposure time via a binning process. The CCD converts photons to electrons over time for a measurement.

3.2.5 *incident light, λi, n*—monochromatic light illuminated into sample.

3.2.6 *Raman scattering effect, n*—an energy transfer process between photons and molecules.

3.2.6.1 *Discussion*—In this photon-molecule interaction, scattered light has a different wavelength compared to the incident wavelength. The Raman wavelength shift spectrum is unique for each molecule because the shift is dependent upon the molecular bonding structures.

3.2.7 *Raman spectroscopy, n*—a type of molecular vibration spectroscopy in which a laser is used to excite virtual energy states in the molecules being illuminated, which then decay, producing new photons that are the sum and difference between the laser and the vibrational frequencies.

3.2.7.1 *Discussion*—These new photons are then collected and analyzed to determine the vibrational spectrum of the molecules.

3.2.8 *Raman spectrum, n*—plot of intensity against Raman wavelength shift.

3.2.9 *scattered light, λs, n*—scattered light as a result of the Raman scattering effect.

3.2.10 *signal strength, n*—a measure of the amount of Raman-scattered photons reaching the CCD.

3.2.10.1 *Discussion*—Usually some scaled combination of raw areas of peaks from compounds expected to be present in LNG.

3.2.11 *wavenumber, k or v, [cm^{-1}], n*—method of specifying the number of waves per unit length of optical radiation.

3.2.11.1 *Discussion*—Raman bands are constant wavenumber shifts from the excitation source independent of the wavelength of that source.

3.3 *Acronyms:*

3.3.1 *CCD*—charge coupled device

3.3.2 *IS*—industry standard

3.3.3 *NIST*—National Institute of Standards and Technology

3.3.4 *NMI*—National Metrology Institute

3.3.5 *OH*—hydroxyl groups

3.4 *Abbreviations:*

3.4.1 *GC*—Gas chromatograph

3.4.2 *GHV*—Gross heating value

3.4.3 *LNG*—Liquefied natural gas

3.4.4 *LPG*—Liquefied petroleum gas

3.5 *Symbols:*

3.5.1 *λi*—incident light

3.5.2 *λs*—scatter light

3.5.3 *k*—coverage factor for confidence interval

4. Summary of Practice

4.1 Measurement of the volume fractions of individual molecular species contained in a liquid stream of interest such as LNG is accomplished by obtaining and analyzing Raman spectra (Fig. 1). Monochromatic light from a laser is directed down a fiber-optic cable through a sample-compatible optic probe and into the liquid to be measured. Monochromatic photons interact with the molecules of the liquid via the Raman effect to produce new photons whose wavelengths have been shifted in proportion to vibration frequencies of the molecules. These new, shifted photons are collected through the same optics that delivered the original monochromatic light and are directed down a separate fiber that is connected to a detection module. The detection module contains a spectrograph, which directs photons of different wavelengths to different pixels on a CCD detector. The CCD pixels integrate the photons falling on them into a digital signal, whose value is proportional to the number of photons. Thus, a spectrum is produced, representing a histogram charting the number of photons detected at each wavelength, corresponding to the number of molecules with particular vibrational frequencies. The spectra can be mathematically processed to yield the molecular composition of the liquid. Using standards such as Practice D3588, the energy content, and indices such as the Wobbe index, can be calculated from the composition information.

5. Significance and Use

5.1 The composition of liquefied gaseous fuels (LNG, LPG) is important for custody transfer and production. Compositional determination is used to calculate the heating value, and it is important to ensure regulatory compliance. Compositional determination is also used to optimize the efficiency of liquefied hydrocarbon gas production and ensure the quality of the processed fluids.

5.2 Alternatives to compositional measurement using Raman spectroscopy are described in Test Method D1945, Practice D1946, and Test Method D7833.

5.3 The advantage of this practice over other standards stated in 5.2, is that Raman spectroscopy can determine composition by directly measuring the liquefied natural gas. Unlike chromatography, no vaporization step is necessary.