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Standard Practice for
On-line/At-line Heating Value Determination of Gaseous Fuels by Gas Chromatography[1]

This standard is issued under the fixed designation D7164; 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 the determination of heating value in high methane content gaseous fuels such as natural gas using an on-line/at-line gas chromatograph.

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~~ safety, health, and ~~health~~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]

D1070 Test Methods for Relative Density of Gaseous Fuels
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
D3764 Practice for Validation of the Performance of Process Stream Analyzer Systems
D4150 Terminology Relating to Gaseous Fuels
D4626 Practice for Calculation of Gas Chromatographic Response Factors
D5287 Practice for Automatic Sampling of Gaseous Fuels
D5503 Practice for Natural Gas Sample-Handling and Conditioning Systems for Pipeline Instrumentation (Withdrawn 2017)[3]
D6122 Practice for Validation of the Performance of Multivariate Online, At-Line, Field and Laboratory Infrared Spectrophotometer, and Raman Spectrometer Based Analyzer Systems
D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
D6621 Practice for Performance Testing of Process Analyzers for Aromatic Hydrocarbon Materials

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[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] The last approved version of this historical standard is referenced on www.astm.org.

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

E260 Practice for Packed Column Gas Chromatography

E594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography

E1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs

2.2 *ISO Standards*[4]

ISO 6976 Natural Gas — Calculation of Calorific Values, Density, Relative Density and Wobbe Indices From Composition

ISO 7504 Gas Analysis-Vocabulary

2.3 *Gas Processors Association Standards:*[5]

GPA 2172 Calculation of Gross Heating Value, Relative Density, Compressibility and Theoretical Hydrocarbon Liquid Content for Natural Gas Mixtures for Custody Transfer

3. Terminology

~~3.1 *Definitions:*~~

~~3.1.1 *calibration gas mixture, n*—a certified gas mixture with known composition used for the calibration of a measuring instrument or for the validation of a measurement or gas analytical method.~~

~~3.1.1.1 *Discussion*—~~

~~Calibration Gas Mixtures are the analogues of measurement standards in physical metrology (reference ISO 7504 paragraph 4.1).~~

~~3.1.2 *direct sampling*—sampling where there is no direct connection between the medium to be sampled and the analytical unit.~~

~~3.1.3 *in-line instrument*—instrument with an active element installed in a pipeline, which is used to measure pipeline contents or conditions.~~

~~3.1.4 *on-line instrument*—instrument that samples gas directly from a pipeline, but is installed externally.~~

~~3.1.5 *at-line instrument*—instrumentation requiring operator interaction that samples gas directly from the pipeline.~~

~~3.1.6 *continuous fuel monitor*—instrument that samples gas directly from the pipeline on a continuous or semi-continuous basis.~~

~~3.1.7 *heating value*—in general terms, the heating value is the total energy per volume transferred as heat from the complete, ideal combustion of the gas at a specified temperature and pressure. The heating value can be reported on a net or gross basis for a gaseous stream that is assumed to be fully water vapor saturated.~~

~~3.1.8 *gross heating value*—(also called higher heating value)—the amount of energy per volume transferred as heat from the complete, ideal combustion of the gas at standard temperature in which all the water formed by the reaction condenses to liquid.~~

~~3.1.9 *net heating value*—(also called lower heating value)—the amount of energy per volume transferred as heat from the complete, ideal combustion of the gas at standard temperature in which all the water formed by the reaction remains in the vapor state.~~

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

~~3.2 *reference gas mixture, n*—a certified gas mixture with known composition used as a reference standard from which other compositional data are derived.~~

~~3.2.1 *Discussion*—~~

~~Reference Gas Mixtures are the analogues of measurement standards of reference standards (reference ISO 7504 paragraph 4.1.1).~~

4. Summary of Practice

4.1 A representative sample of the ~~Gaseous Fuel~~gaseous fuel is extracted from a process pipe or a pipeline and is transferred in

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

[5] Available from Gas Processors Association (GPA), 66 American Plaza, Suite 700, Tulsa, OK 74135, http://www.gpaglobal.org.

a timely manner to an analyzer sampling system. After appropriate conditioning steps that maintain the ~~sample~~sample's integrity are completed, a precise volume of sample is injected onto an appropriate gas chromatographic column. Excess extracted process or pipeline sample is vented to atmosphere, a flare header, or is returned to the process in accordance with applicable economic and environmental requirements and regulations.

4.2 Sample constituents are separated in the column to elute individually for identification and quantification by the detector and its data handling system. ~~The heating~~ Heating value is calculated using the results of the compositional analysis ~~using an appropriate algorithm.~~and the calculations contained in Practice D3588 or other standard algorithms.

4.3 Calibration, maintenance, and performance protocols provide a means to validate the analyzer operation.

5. Significance and Use

5.1 On-line, at-line, ~~in-line~~in-line, and other near-real time monitoring systems that measure fuel gas characteristics such as the heating value are prevalent in the natural gas and fuel gas industries. The installation and operation of particular systems vary on the specific objectives, process type, regulatory requirements, and internal performance requirements needed by the user. This protocol is intended to provide guidelines for standardized start-up procedures, operating procedures, and quality assurance practices for on-line, at-line, ~~in-line~~in-line, and other near-real time heating value monitoring systems.

6. Apparatus

6.1 *Instrument*—Any instrument of standard manufacture, with hardware necessary for interfacing to a natural gas or other fuel gas pipeline and containing all the features necessary for the intended ~~application(s)~~application(s), can be used.

6.1.1 *Chromatographic-based Systems*—The chromatographic parameters employed generally should be capable of obtaining a relative retention time repeatability of 0.05 min (3 s) for duplicate measurements. Instrumentation should satisfy or exceed other chromatographic and analytic performance characteristics for accuracy and precision for the intended application without encountering unacceptable interference or bias. In addition, components in contact with sample streams such as tubing and valving must be constructed of suitable inert materials to ensure constituents in the fuel stream do not degrade these components or alter the composition of the sampled gas. Additional information related to analyzing gaseous fuels using gas chromatography can be found in Test Method D1945 ~~and~~ , Practice D1946, and Test Method D7833.

6.2 *Sample Probes/Sample Extraction*—The location and orientation of sampling components are critical for ensuring that a representative sample is analyzed. The locations and orientation of sampling components should be selected based upon sound analytic and engineering considerations. Sampling practices for gaseous fuels can be found in Practice D5287.

6.3 *Sample Inlet System*—The siting and installation of an at-line or on-line monitor is critical for collecting representative information on heating value content. Factors that should be considered in siting an instrument include ease of calibration, ease of access for repair or maintenance, sample uniformity at the sampling point, appropriateness of samples from a sampling location, ambient conditions, and of course safety issues. An automated gas sampling valve is required in many applications. All sampling system components in contact with the fuel stream must be constructed of inert or passivated materials. Care ~~should~~must be taken to ensure that the extracted sample is maintained in ~~a single clean gaseous phase.~~ the gaseous phase throughout pressure reduction and transport throughout the expected ranges of ambient and pipeline temperatures and pressure. The addition of heat at the point of pressure reduction ~~or~~and along the sample line to the analyzer may be required to ensure that the entire sample is maintained in the gas phase during all expected operating conditions and gas compositions. When selecting sample conditioning equipment, equations of state should be used to determine whether pressure must be reduced in multiple stages to prevent a change of phase. The need for heat tracing and the extent to which it is required will be site specific. In general, considerations impacting heat tracing decisions include sample compositions and the expected variations, ambient temperature fluctuations, operating pressures, and anticipated pressure differentials in sample system components. Sample filtration should be utilized as required to remove particulate matter from the extracted ~~sample.~~ sample and to prevent any contaminating liquids such as glycol, compressor oils, and liquid water, which may form in the event of heat-tracing failure, from reaching the chromatograph. The sampling frequency relative to the process bandwidth is critical to ensuring that the reported analytical results adequately represent the process being monitored. The Nyquist-Shannon sampling criterion of a sampling frequency that exceeds twice the process bandwidth can be used to establish a minimum analytical cycle time. Sample handling and conditioning system practices can be found in Practice D5503.

6.3.1 *Carrier and Detector Gas Control*—Constant flow ~~control of~~ carrier and detector ~~gases~~ gas control is critical for optimum and consistent analytical performance. Control is achieved by use of pressure ~~regulators~~ regulators, mass flow controllers, and fixed flow restrictors. Temperature control is generally vital for ensuring consistent operation of these devices. The gas flow is measured by appropriate means and adjusted as necessary. ~~Mass flow~~ Most chromatographs automatically control their gas flow rates which reduces a user's responsibility for ensuring the proper gas pressure is provided to the chromatograph. Should a chromatograph require external gas flow control, mass flow controllers, capable of maintaining gas flow constant to ±1 % at the flow rates necessary for optimal instrument performance, are generally used.

6.3.2 *Detectors*—A thermal conductivity detector (TCD) is commonly used. Other detectors, such as the flame ionization detector (FID), Practice E594, can be used but should at least meet TCD linearity, sensitivity, and selectivity in the selected application.

6.4 *Columns*—A variety of columns, ranging from packed columns to open tubular capillary columns, can be used in the determination of the ~~Heating Value~~heating value of a gaseous fuel. Packed columns and open tubular capillary columns are covered in Practices E260 and E1510 respectively. Columns should be conditioned in accordance with the manufacturer's recommendations. The selected column must provide retention and resolution characteristics that satisfy the intended application. The column must be inert and non-absorptive towards gaseous fuel components. If the selected column utilizes a liquid phase, bleeding at high temperatures must be sufficiently low ~~so as~~ to avoid the loss of instrument response during high temperature operation.

6.5 *Data Acquisition*—Data acquisition and storage can be accomplished using a number of devices and media. Following are some examples.

6.5.1 *Recorder*—A 0 to 1 mV range recording potentiometer or equivalent, with a full-scale response time of 2 s or less, can be used.

6.5.2 *Integrator*—An electronic integrating device or computer can be used. ~~For GC-based systems, it~~ It is suggested that the device and software have the following capabilities:

6.5.2.1 Graphic presentation of chromatograms.

6.5.2.2 Digital display of chromatographic peak areas.

6.5.2.3 Identification of peaks by retention time or relative retention time, or both.

6.5.2.4 Calculation and use of response factors.

6.5.2.5 External standard calculation and data presentation.

6.5.2.6 Site-appropriate archives up to one month of all runs. Archives could include raw data, derived component values or heating value results or both. Hourly, daily, and monthly averages are included as required.

6.5.3 *Communications Systems*—Efficient communications between the analyzer and the host depend on resolving any and all interface issues. Signals to and from the host are typically optically isolated from each other.

7. Reagents and Materials

NOTE 1—**Warning:** Compressed gas standards should only be handled in well ventilated locations away from sparks and flames. Improper handling of compressed gas cylinders containing calibration standards, air, nitrogen, hydrogen, argon, or helium can result in explosion. Rapid release of nitrogen or helium can result in asphyxiation. Compressed air supports combustion.

7.1 *Standards*—The components ~~in~~within the reference standard cylinder should be representative of the monitored ~~gas.~~ gas and possess a current certified component accuracy that meets or exceeds the needs of the user and application. Concentrations of major components are typically selected between one half and twice their expected concentration in the monitored gas. ~~Standards~~ Standard cylinders must ~~be maintained as close as practicable to a constant temperature within the temperature range~~ always be maintained above their dew point temperature as specified by the ~~manufacturer to ensure accuracy and stability.~~standard's manufacturer throughout its transportation, storage, and use. Should a standard be suspected of falling below its dew point temperature, cease using the standard and consult its manufacturer for guidance. Cylinder heating blankets or cabinets are commonly used to ensure a standard's gas cylinder is kept above its dew point during use.

8. Equipment Siting and Installation

8.1 A ~~sample inlet~~ sampling (extraction, conditioning, and transport) system capable of operating continuously ~~at or~~ above the

~~maximum column operating~~natural gas' maximum dew point temperature is necessary. The location of the ~~sample inlet to the analyzer~~ chromatograph relative to the sample extraction ~~point is~~ point, and the internal volume of the sample conditioning and transport system, are critical to obtaining timely analytical results. Ideally, the ~~analyzer~~chromatograph is installed close ~~coupled~~ to the sample extraction point and ~~there is~~ sample conditioning system using the smallest diameter tubing recommended by the manufacturer resulting in an insignificant sampling lag time. ~~Normally, the analyzer~~However, it is common that the chromatograph is mounted at some distance away from the sample extraction point. This increased distance represents increased lag time between when a sample is extracted from a process and when an analytical result is reported. The maximum allowable lag time depends on the specifics of the sampling location relative to the process being sampled. ~~A fast loop sweep~~ Lag time can be minimized by reducing the pressure of the sampled gas at, or near, the sample extraction point. In addition, a bypass loop can be used to ~~minimize~~ further reduce the lag time by ~~creating a bypass loop that flows sample from the process to the analyzer and is then~~increasing the volume, and therefore velocity, of the sample being transported from the extraction point to the chromatograph. The bypassed gas flow is either returned to the process or ~~is vented.~~vented in a safe manner.

8.2 The sample should flow continuously without impediment through the ~~instrument~~ sampling system. The sampling system should be capable of delivering a representative sample to the ~~detection system within the cycle time of the analyzer. Shorter times may be required to meet the intended need.~~chromatograph faster than the chromatograph's cycle time. Some applications may require even shorter lag times.

8.3 A monitoring system pretest of both sampling and analysis functions is critical to determining monitoring system characteristics, identify unforeseen factors affecting measurement and to determine optimal operating conditions for the intended use. This pretest is performed before the system is placed in continuous service and may be performed in a variety of ways including a comparison of results to another instrument already in service, analysis of a known gaseous sample etc.

9. Performance Tests

9.1 The following performance tests are suggested as part of an overall QA program. This list is not inclusive. The use of some, or all, of these performance tests, as well as tests not specified, may be required or deemed appropriate and optional by local, regional, state, and federal regulations, or a combination thereof. Also, the user's judgment, manufacturer's recommendations, and application requirements, or a combination thereof, apply. For analyzers installed in remote locations, a sub-set of site and application specific diagnostic tests and checks, which can be completed during a ~~one day~~ visit to the site, can be performed to verify that the analyzer is operating correctly. A full set of performance tests on the analyzer should be performed at least annually, or more frequently, as required.

9.2 *Standard Operating Procedure*—Maintain a current and readily available Standard Operating Procedure (SOP) and maintenance log.

9.3 *System Blank Test*—Periodically perform a system blank test to evaluate the presence of contamination, system leaks or wear on sample valves and related components, or a combination thereof. As necessary, replace components to restore the analytical system to nominal function.

9.4 *Daily Calibration Check*—It is recommended that instruments possessing auto calibration capability are calibrated daily. If the analyzer is equipped with an auto-verification feature, a calibration check, done biannually, daily, or at some other interval consistent with the intended use of the analyzer, using an appropriate ~~Calibration Gas Mixture~~ calibration gas mixture as discussed under 7.1 should be performed. A calibration check can be performed as follows:

9.4.1 Perform consecutive triplicate injections using the appropriate ~~Calibration Gas Mixture.~~calibration gas mixture.

9.4.2 Discard the first injection as a conditioning and purging step.

9.4.3 Record the second injection as the initial data point.

9.4.4 Compare the third injection against the second injection. The individual component results of the third injection should agree with the results of the initial data point to within 5 %.

9.4.4.1 For components heavier than C6 or with concentrations <50 ppmv, a larger variation may be allowed.