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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 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 and health practices and determine the applicability of regulatory limitations prior to use.*

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

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

D6122 Practice for Validation of the Performance of Multivariate Online, At-Line, and Laboratory Infrared Spectrophotometer 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

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*[3]

ISO 7504 Gas Analysis-Vocabulary

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

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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] 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.

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.

3.2 *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 is extracted from a process pipe or a pipeline and is transferred in a timely manner to an analyzer sampling system. After appropriate conditioning steps that maintain the sample 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 value is calculated using the results of the compositional analysis using an appropriate algorithm.

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 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 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) 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.

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 be taken to ensure that the extracted sample is maintained in a single clean gaseous phase. The addition of heat at the point of pressure reduction or along the sample line to the analyzer may be required to ensure that the sample is maintained in the gas 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. 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 is critical for optimum and consistent analytical performance. Control is achieved by use of pressure regulators 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 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 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 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 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 the reference standard should be representative of the monitored gas. Concentrations of major components are typically selected between one half and twice their expected concentration in the monitored gas. Standards must be maintained as close as practicable to a constant temperature within the temperature range specified by the manufacturer to ensure accuracy and stability.

8. Equipment Siting and Installation

8.1 A sample inlet system capable of operating continuously at or above the maximum column operating temperature is necessary. The location of the sample inlet to the analyzer relative to the sample extraction point is critical to obtaining timely analytical results. Ideally, the analyzer is close coupled to the sample extraction point and there is an insignificant sampling lag time. Normally, the analyzer 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 can be used to minimize the lag time by creating a bypass loop that flows sample from the process to the analyzer and is then returned to the process or is vented.

8.2 The sample should flow continuously without impediment through the instrument sampling system. The sampling system should be capable of delivering a sample to the detection system within the cycle time of the analyzer. Shorter times may be required to meet the intended need.

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 should be performed. A calibration check can be performed as follows:

9.4.1 Perform consecutive triplicate injections using the appropriate 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 %.

9.4.5 If the third injection satisfies criteria under 9.4.4, record the result of the third injection.

9.4.6 If the third injection does not satisfy criteria under 9.4.4, initiate mitigation steps.

9.4.7 Repeat steps 9.4.1 through 9.4.6, as required, for the low-span and high-span Calibration Gas Mixtures.

9.5 *7-Day Calibration Error Test*—At least annually, more frequently as required, and if appropriate for the installation, periodically evaluate the system performance over seven consecutive days. The calibration drift should not exceed 10 percent of the full-scale range for each calibrant. Alternatively, it is possible to specify an appropriate percentage of detector response for each calibrant component, such as a maximum 10 % change in the calibrant response during the course of one week.

9.6 *Linearity Check*—On a regular basis or as needed and when practicable, perform a three point linearity check. Linearity at the midpoint should not exceed 5% of the expected value.

9.7 *Drift Test*—It is suggested that a control or drift test be performed on a daily, as practicable or as required basis. Verify that the system response drift for individual species in the test gas does not consistently exceed 10 % of its daily historical value, control chart information, or the most recent validation or control sample results. Adequate system performance is demonstrated by recoveries of 90% to 110% of the theoretical amounts for the individual species in the test gas. Adjustments made to compensate for successive drifts exceeding 10 % of the daily historical value may be indicative of an operational problem. As necessary, examine the retention time for each individual sulfur specie of interest. Verify that the retention time drift for individual species in the test gas does not consistently exceed 5% for minor components or 2% for major components, such as methane and nitrogen, of its daily historical value, control chart information, or the most recent validation or control sample results. Compare retention times to system programming parameters, such as time gates, to ensure compatibility. These parameters, including the analysis time, on occasion may need to be updated. A drift passing a zero drift test but exceeding the lesser of 10% at the full scale range, or the published manufacturer's specification, may be indicative of an operational problem.

9.8 *Carrier Flow Rates*—The carrier flow rates should be verified on an as needed basis.

9.9 *Audit Test*—Calibration, precision, calibration error, and performance audit tests are conducted to determine performance of the monitor. Periodic calibration and maintenance methodology are also specified.

9.10 *Validation Test*—The validation of a process analyzer is covered in Practices D3764, D6122, and D6621. Application of statistical quality assurance techniques to the performance evaluation of an analytical measurement system is covered in Practice D6299. The Additional Reading section contains a list of practices, guides, and procedures related to the performance and validation of analytical measurement systems.

9.11 *Lab vs. Process Comparison Test*—At start-up and on an annual basis, or on an as-necessary basis, perform a comparison of results from the on-line/at-line/in-line monitor and a laboratory-based analysis of a spot sample. Under certain operational conditions, direct comparison of the analyzer's result to a laboratory-based method may not be valid. In these cases, verification of the analyzer may be performed by comparing the analyzer's results with an appropriate Calibration Gas Mixture or a Reference Gas Mixture. Results consistent with those obtained at instrument start-up constitute acceptable instrument performance.

10. System Maintenance

10.1 System maintenance is critical for ensuring accuracy and consistency of measurements. A maintenance program following but not limited to manufacturer's guidelines is a good practice. After performing maintenance or after a system shut down exceeding several hours, a prudent practice is to re-perform the monitoring system pretest procedure stated in 8.3 to ensure the system is performing acceptably.

11. Calculation

11.1 The heating value is calculated using the analyzed gas composition and Practice D3588. Methods related to determining the relative density of gaseous fuels can be found in Practice D1070. Response factor calculation is covered in Practice D4626.

12. Keywords

12.1 at-line monitor; continuous fuel monitor; heating value; on-line monitor

ADDITIONAL READING

(1) American Gas Association, *Gas Measurement Manual*, Part 11, Measurement of Gas Properties, Washington, DC.

(2) American Petroleum Institute, *API 14.1*, Chapter 14, Natural Gas Fluids Measurement; Section 1, Collecting and Handling of Natural Gas Samples for Custody Transfer, Fifth Edition, June 2001.

(3) Clevett, Kenneth J., *Process Analyzer Technology*, Wiley-Intercourse, New York, 1986.

(4) Gas Processors Association, *Engineering Data Book*, Tenth Edition, Gas Processors Suppliers Association, Tulsa, 1994.

(5) Gas Processors Association, GPA-2166 Obtaining Natural Gas Samples for Analysis by Gas Chromatography, Tulsa.

(6) Green , Don W., editor, *Perry's Chemical Engineer's Handbook*, Sixth Edition, McGraw-Hill Book Company, New York, 1984.

(7) International Organization for Standardization, ISO 10715 Natural Gas Sampling Guide.

(8) McMillan, Gregory K., and Considine, Douglas M., *Process Instruments and Controls Handbook*, 5th Edition, McGraw-Hill Professional, New York, 1999.

(9) Nyquist, Harry, "Certain Topics in Telegraph Transmission Theory," *Trans. AIEE*, Vol 47, Apr. 1928, pp. 617-644.

(10) Shannon, Claude E., "Communication in the Presence of Noise," *Proc. Institute of Radio Engineers,* Vol 37 , no.1, Jan. 1949, pp. 10-21.

(11) Sherman, R. E., editor, *Analytical Instrumentation*, Instrument Society of America, Research Triangle Park, 1996.

(12) Skoog, Douglas A., Holler, F. James, and Nieman, Timothy A., *Principles of Instrumental Analysis*, Fifth Edition, Harcourt Brace College Publishers, Philadelphia, 1998.

ASTM Standards

(13) C1068 Standard Guide for Qualification of Measurement Methods by a Laboratory Within the Nuclear Industry

(14) D3764 Standard Practice for Validation of the Performance of Process Stream Analyzer Systems

(15) D6122 Standard Practice for Validation of the Performance of Multivariate Process Infrared Spectrophotometers

(16) D6299 Standard Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

(17) D6621 Standard Practice for Performance Testing of Process Analyzers for Aromatic Hydrocarbon Materials

(18) E1866 Standard Guide for Establishing Spectrophotometer Performance Tests

(19) E2027 Standard Practice for Performing Proficiency Tests

(20) E2093 Standard Guide for Optimizing, Controlling and Reporting Test Method Uncertainty

(21) E2165 Standard Practice for Establishing an Uncertainty Budget for the Chemical Analysis of Metals, Ores and Related Materials—performance methods need an uncertainty budget which includes the variance caused by sampling, sample prep and analysis (withdrawn)

(22) E2437 Standard Practice for Designing and Validating Performance Based Test Methods

(23) E2438 Standard Procedure for Implementing Standard Performance Test Methods