



Standard Practice for Determination of the Heating Value of Gaseous Fuels using Calorimetry and On-line/At-line Sampling¹

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1. Scope

1.1 This practice is for the determination of the heating value measurement of gaseous fuels using a calorimeter. Heating value determination of sample gasses containing water vapor will require vapor phase moisture measurements of the pre-combustion sample gas as well as the non-condensed gasses exiting the calorimeter. Instruments equipped with appropriate conditioners and algorithms may provide heating value results on a net or gross and dry or wet basis.

1.2 This practice is applicable to at-line and in-line instruments that are operated from time to time on a continuous basis.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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
- D1826 Test Method for Calorific (Heating) Value of Gases in Natural Gas Range by Continuous Recording Calorimeter
- 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

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.

D4150 Terminology Relating to Gaseous Fuels

D4891 Test Method for Heating Value of Gases in Natural Gas Range by Stoichiometric Combustion

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 Process 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

D7164 Practice for On-line/At-line Heating Value Determination of Gaseous Fuels by Gas Chromatography

2.2 ISO Standards:³

ISO 14532 Natural gas – Vocabulary

ISO 7504 Gas analysis – Vocabulary

3. Terminology

3.1 Definitions:

3.1.1 *at-line instrument, n*—See Terminology D4150, Section 3.

3.1.2 *auto-verification, n*—an automated means of introducing Calibration Gas Mixtures or Reference Gas Mixtures into an analyzer for the purposes of verifying the analyzer response without making any adjustments to the calibration parameters of the analyzer.

3.1.3 *bypass line, n*—Line ultimately vented to the atmosphere that is used where it is impractical to provide a sufficient pressure differential.

3.1.3.1 *Discussion*—The flowrate and pressure loss in the open-ended line needs to be controlled so as to ensure that the sample accuracy is not affected from any cooling and condensation or both (reference ISO 14532 paragraph 2.3.2.9).

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>.

3.1.4 *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.

3.1.4.1 *Discussion*—Calibration Gas Mixtures are the analogues of measurement standards in physical metrology (reference **ISO 7504** paragraph 4.1)

3.1.5 *calorimeter, n*—See Terminology **D4150**, Section 3.

3.1.6 *continuous fuel monitor, n*—an instrument that samples gas directly from a source continuously and provides an analytical result on a continuous or semi-continuous basis.

3.1.7 *direct sampling, adj*—sampling where there is a direct connection between the sample source and the analytical unit, that is, in-line or on-line instrument.

3.1.8 *dry gas, n*—See Terminology **D4150**, Section 3.

3.1.9 *fast loop/hot loop, n*—Bypass loop that returns sampled gas to the process line in a closed configuration and used for environmental and safety considerations.

3.1.9.1 *Discussion*—The loop requires a pressure differential from the collection point to the discharge point so as to ensure a constant and steady flowrate through the sampling equipment located in the loop (reference **ISO 14532** paragraph 2.3.2.8)

3.1.10 *gross heating value (also called higher heating value), n*—See Terminology **D4150**, Section 3.

3.1.11 *heating value, n*—the amount of energy per volume transferred as heat from the complete, ideal combustion of the gas at standard temperature.

3.1.12 *in-line instrument, n*—See Terminology **D4150**, Section 3.

3.1.13 *net heating value (also called lower heating value), n*—See Section 3 entitled Terminology, of **D4150**.

3.1.14 *on-line instrument, n*—See Terminology **D4150**, Section 3.

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

3.1.15.1 *Discussion*—Reference Gas Mixtures are the analogues of reference standards (**ISO 7504** paragraph 4.1.1)

3.1.16 *wet gas, n*—See Terminology **D4150**, Section 3.

3.2 *Acronyms:*

3.2.1 *SOP, n*—Standard Operating Procedure.

3.2.2 *QA, n*—Quality Assurance.

4. Summary of Practice

4.1 A representative sample of the gaseous fuel is extracted from a process pipe, a pipeline, or other gaseous fuel stream and is transferred to an analyzer sampling system. After conditioning that maintains the sample integrity, the sample is introduced into a calorimeter. Excess extracted process or sample gas is vented to the atmosphere, a flare header, or is returned to the process in accordance with applicable economic and environmental requirements and regulations. Post-combustion gasses from the calorimeter are typically vented to the atmosphere.

4.2 The heating value is calculated based upon the instrument's response to changes in the heating value of the sample gas using an algorithm.

4.3 Calibration (7.1), maintenance (Section 10), and performance (Section 9) protocols provide a means to validate and assess operation of the analyzer.

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 heating value are prevalent in various gaseous fuel industries and in industries either producing or using gaseous fuel in their industrial processes. The installation and operation of particular systems vary depending on process type, regulatory requirements, and the user's objectives and performance requirements. This practice is intended to provide guidance for standardized start-up procedures, operating procedures, and quality assurance practices for calorimeter based on-line, at-line, in-line and other near-real time heating value monitoring systems. Users employing gas chromatographic based instrumentation for measurement of gaseous fuel heating value are referred to Practice **D7164**.

6. Apparatus

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

6.1.1 *Combustion System*—Operating parameters employed must be capable of converting all of the volatile combustible chemical species in the sample into carbon dioxide, water, nitrogen, nitrogen dioxide, and/or sulfur dioxide, using a dry, hydrocarbon-free oxidant which is typically air. A change of less than or equal to 1,000 ppm/wt in the moisture content of instrument air between calorimeter calibrations is acceptable to maintain a statistically insignificant $\pm 0.1\%$ heating value accuracy as denoted in Practice **D4891**. The less than 1,000 ppm/wt moisture content control value is easily achieved using desiccant or refrigerant air dryers when the air dryers are maintained according to the manufacturer's recommendations. Instrumentation must satisfy or exceed 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 or passivated materials to ensure that the composition of the sampled gas is not altered.

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*—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.

6.3.1 *Combustion Air, Sample, and Carrier Gas Control*—Constant flow control of combustion air, sample gas, and carrier gas, if required by the measurement application, is necessary for optimum and consistent analytical performance. Control is typically achieved by use of pressure regulators and fixed flow restrictors. Ambient, combustion air, sample, and carrier gas temperature control is generally vital for ensuring consistent operation of flow control devices. The gas flow is measured and verified by appropriate means and adjusted as necessary.

6.3.2 *Detectors*—Common calorimetry heating value detection systems include stoichiometric combustion (Test Method [D4891](#)), continuous recording calorimeters (Test Method [D1826](#)), non-stoichiometric combustion, and residual oxygen detection calorimeters. Other detectors can be used provided they have appropriate linearity, accuracy, sensitivity and measurement range for the selected application. In selecting a detector, the user should consider the linearity and sensitivity of a particular detection system prior to installation. The user should also consider potential sample compositional effects that may influence the reported heating value.

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

6.4.1 *Recorder*—A 0 to 1 millivolt or a 4-20 milliamp range recording potentiometer or equivalent, with a full-scale response time of 2 s or less can be used mounted locally or remotely.

6.4.2 *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 isolated from each other in an appropriate manner.

7. Reagents and Materials

7.1 **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 or air can result in explosion. Compressed air supports combustion.

7.1.1 *Standards*—Components in the Calibration Gas Mixture should be representative of the monitored gas. The heating value is either determined instrumentally or is calculated using a certified gas composition of the standard. Practice [D3588](#) or other methods as required for regulatory purposes can be used to calculate the heating value of a gas mixture. Other heating value calculational algorithms can be used so long as all interested parties are advised of and are in agreement with the calculational methodology employed, or both. Methods related to determining the relative density of gaseous fuels can be found in Practice [D1070](#). Mixtures of major components are typically specified to achieve the desired heating value. A minimum of major representative components is frequently

used. The number of components used is frequently minimized for economical reasons and to reduce the probability of error during the preparation of the Calibration Gas Mixture. In order to ensure their accuracy and stability by preventing condensation and degradation, Calibration Gas Mixtures must be maintained within the temperature range specified by the manufacturer. If there is any doubt concerning the validity of the Calibration Gas Mixture, a Reference Gas Mixture should be used to verify the validity of the Calibration Gas Mixture.

8. Equipment Siting and Installation

8.1 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 hazardous area rating, 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. A sample inlet system capable of operating continuously at or above the maximum operating sample 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 will result in 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 or by-pass line can be used to minimize the lag time. 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](#).

8.2 The sample should flow continuously 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. Sample system transport times may require optimization to meet the intended need.

8.3 A monitoring system pretest of both sampling and analysis functions performed as part of a Site Acceptance Test (SAT) prior to initial use 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 If the analyzer is equipped with an auto-verification feature, a calibration check, done biannually, daily or at some other interval using a gas standard can be preformed as follows:

9.4.1 Perform consecutive triplicate analysis using the calibration gas .

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

9.4.3 Record the second analysis as the initial data point.

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

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

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

9.4.7 If the analyzer is not equipped with an auto-verification feature, a calibration check can be done following the steps indicated in 9.4 on an as needed basis.

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 or detector area counts.

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 the manufacturer's specification.

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. 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 either re-perform the monitoring system pretest procedure stated in 8.3, or an appropriate sub-set of the system pretest procedure deemed appropriate based on the user's judgement of site-specific application requirements for system performance to ensure the system is performing acceptably.

11. Calculation

11.1 The heating value is calculated from the response of the detector to changes in the heating value of the sample gas using an appropriate algorithm or the appropriate ASTM method, such as Test Method D1826 and D4891. The heating value can be reported on a net or gross basis. If reported on a gross basis the gaseous stream is typically assumed to be fully water vapor saturated. Software included with the instrumentation may perform the calculation. The user should be satisfied that the software is working properly and is accurately performing calculations. Methods related to determining the relative density of gaseous fuels can be found in Test Methods D1070.

12. Keywords

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

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) Cleve, Kenneth J., *Process Analyzer Technology*, Wiley-Interscience, 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 (with-drawn)
- (22) E2437 Standard Practice for Designing and Validating Performance Based Test Methods
- (23) E2438 Standard Procedure for Implementing Standard Performance Test Methods

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