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Standard Practice for
Determination of the Heating Value of Gaseous Fuels using Calorimetry and On-line/At-line Sampling[1]

This standard is issued under the fixed designation D7314; 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 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 *Units*—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.*~~

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1.5 *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
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
D4150 Terminology Relating to Gaseous Fuels
D4891 Test Method for Heating Value of Gases in Natural Gas and Flare Gases 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 (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

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

2.2 *ISO Standards:*[4]

ISO 14532 Natural ~~gas—Vocabulary~~Gas—Vocabulary

ISO 7504 Gas ~~analysis—Vocabulary~~Analysis—Vocabulary

3. Terminology

3.1 Refer to Terminology D4150 for general definitions related to gaseous fuels. Definitions specific to this standard follow.

3.2 ~~Definitions:~~Definitions of Terms Specific to This Standard:

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

3.2.1 *auto-verification, n*—an automated means of introducing ~~Calibration Gas Mixtures or Reference Gas Mixtures~~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.

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

3.2.2.1 *Discussion*—
~~The~~Flowrate—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).

3.2.2.2 *Discussion*—
Loop—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).

3.2.2.3 *Discussion*—
Reference Gas—Reference gas mixtures are the analogues of reference standards (ISO 7504, paragraph 4.1.1).

~~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)~~

3.2.3 *~~wet gas,~~ fast loop/hot loop, n—*~~See Terminology~~bypass loop ~~D4150, Section 3.~~that returns sampled gas to the process line in a closed configuration and used for environmental and safety considerations.

3.3 *Acronyms:*

3.3.1 *SOP, n*—Standard Operating Procedure.

3.3.2 *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~~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~~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)~~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~~or sulfur dioxide, or a combination thereof, using a dry, hydrocarbon-free oxidant, which is typically air. A change of less than or equal to ~~1,000~~1000 ppm/wt in the moisture content of instrument air between calorimeter calibrations is acceptable to maintain a statistically insignificant ~~± 0.1%~~±0.1 % heating value accuracy as denoted in Practice D4891. The less than ~~1,000~~1000 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~~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.~~calibration gas mixture. In order to ensure their accuracy and stability by preventing condensation and degradation, ~~Calibration Gas Mixtures~~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~~calibration gas mixture, a reference gas mixture should be used to verify the validity of the ~~Calibration Gas Mixture.~~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 .~~gas.