



# Standard Practice for Validation of the Performance of Process Stream Analyzer Systems<sup>1</sup>

This standard is issued under the fixed designation D 3764; 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.

<sup>e1</sup> NOTE—Updated Fig. 5 editorially in November 2006.

## INTRODUCTION

Operation of a process stream analyzer system typically involves four sequential activities. (1) **Analyzer Calibration**—When an analyzer is initially installed, or after major maintenance has been performed, diagnostic testing is performed to demonstrate that the analyzer meets the manufacturer's specifications and historical performance standards. These diagnostic tests may require that the analyzer be adjusted so as to provide predetermined output levels for certain reference materials. (2) **Correlation**—Once the diagnostic testing is completed, process stream samples are analyzed using the analyzer system. For application where the process analyzer system results are required to agree with results produced from an independent (primary) test method (PTM), a mathematical function is derived that relates the analyzer results to the primary test method results (PTMR). The application of this mathematical function to an analyzer result produces a predicted primary test method result (PPTMR). (3) **Probationary Validation**—After the correlation relationship between the analyzer results and primary test method results has been established, a probationary validation is performed using an independent but limited set of materials that were not part of the correlation activity. This probationary validation is intended to demonstrate that the PPTMRs agree with the PTMRs to within user-specified requirements for the analyzer system application. (4) **General and Continual Validation**—After an adequate amount of PPTMRs and PTMRs have been accrued on materials that were not part of the correlation activity, a comprehensive statistical assessment is performed to demonstrate that the PPTMRs agree with the PTMRs to within the tolerances established from the correlation activities. Subsequent to a successful general validation, quality assurance control chart monitoring of the differences between PPTMR and PTMR is conducted during normal operation of the process analyzer system to demonstrate that the agreement between the PPTMRs and PTMRs established in the General Validation is maintained. This practice deals with the third and fourth of these activities.

## 1. Scope

1.1 This practice describes procedures and methodologies based on the statistical principles of Practice D 6708 to validate whether the degree of agreement between the results produced by a total analyzer system (or its subsystem), versus the results produced by an independent test method that purports to measure the same property, meets user-specified requirements. This is a performance-based validation, to be conducted using a set of materials that are not used a priori in the development

of any correlation between the two measurement systems under investigation. A result from the independent test method is herein referred to as a Primary Test Method Result (PTMR).

1.2 This practice assumes any correlation necessary to mitigate systemic biases between the analyzer system and PTM have been applied to the analyzer results.

1.3 This practice requires that both the primary method against which the analyzer is compared to, and the analyzer system under investigation, are in statistical control. Practices described in Practice D 6299 should be used to ensure this condition is met.

1.4 This practice applies if the process stream analyzer system and the primary test method are based on the same measurement principle(s), or, if the process stream analyzer

<sup>1</sup> This practice is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.25 on Performance Assessment and Validation of Process Stream Analyzer Systems for Petroleum and Petroleum Products.

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system uses a direct and well-understood measurement principle that is similar to the measurement principle of the primary test method. This practice also applies if the process stream analyzer system uses a different measurement technology from the primary test method, provided that the calibration protocol for the direct output of the analyzer does not require use of the PTMRs (see Case 1 in [Note 1](#)).

1.5 This practice does not apply if the process stream analyzer system utilizes an indirect or mathematically modeled measurement principle such as chemometric or multivariate analysis techniques where PTMRs are required for the chemometric or multivariate model development. Users should refer to Practice [D 6122](#) for detailed validation procedures for these types of analyzer systems (see Case 2 in [Note 1](#)).

**NOTE 1**—For example, for the measurement of benzene in spark ignition fuels, comparison of a Mid-Infrared process analyzer system based on Test Method [D 6277](#) to a Test Method [D 3606](#) gas chromatography primary test method would be considered Case 1, and this practice would apply. For each sample, the Mid-Infrared spectrum is converted into a single analyzer result using methodology (Test Method [D 6277](#)) that is independent of the primary test method (Test Method [D 3606](#)). However, when the same analyzer uses a multivariate model to correlate the measured Mid-Infrared spectrum to Test Method [D 3606](#) reference values using the methodology of Practice [E 1655](#), it is considered Case 2 and Practice [D 6122](#) applies. In this case 2 example, the direct output of the analyzer is the spectrum, and the conversion of this multivariate output to an analyzer result require use of Practice [D 6122](#), hence it is not independent of the primary test method.

1.6 Performance Validation is conducted by calculating the precision and bias of the differences between results from the analyzer system (or subsystem) after the application of any necessary correlation, (such results are herein referred to as Predicted Primary Test Method Results (PPTMRs)), versus the PTMRs for the same sample set. Results used in the calculation are for samples that are not used in the development of the correlation. The calculated precision and bias are statistically compared to user-specified requirements for the analyzer system application.

1.6.1 For analyzers used in product release or product quality certification applications, the precision and bias requirement for the degree of agreement are typically based on the site or published precision of the Primary Test Method.

**NOTE 2**—In most applications of this type, the PTM is the specification-cited test method.

1.6.2 This practice does not describe procedures for establishing precision and bias requirements for analyzer system applications. Such requirements must be based on the criticality of the results to the intended business application and on contractual and regulatory requirements. The user must establish precision and bias requirements prior to initiating the validation procedures described herein.

1.7 Two procedures for validation are described: the line sample procedure and the validation reference material (VRM) injection procedure.

1.8 Only the analyzer system or subsystem downstream of the VRM injection point or the line sample extraction point is being validated by this practice.

1.9 The line sample procedure is limited to applications where material can be safely withdrawn from the sampling point of the analyzer unit without significantly altering the property of interest.

1.10 Validation information obtained in the application of this practice is applicable only to the type and property range of the materials used to perform the validation.

1.11 Two types of validation are described: General Validation, and Level Specific Validation. These are typically conducted at installation or after major maintenance once the system mechanical fitness-for-use has been established.

1.11.1 General Validation is based on the statistical principles and methodology of Practice [D 6708](#). In most cases, General Validation is preferred, but may not always be possible if the variation in validation materials is insufficient. General Validation will validate analyzer operation over a wider operating range than Level Specific Validation.

1.11.2 When the variation in available validation materials is insufficient to satisfy the requirements of Practice [D 6708](#), a Level Specific Validation is done to validate analyzer operation over a limited range.

1.11.3 The validation outcome are considered valid only within the range covered by the validation material Data from several different Validations (general or level-specific) can potentially be combined for use in a General Validation.

1.12 Procedures for the continual validation of system performance are described. These procedures are typically applied at a frequency commensurate with the criticality of the application.

1.13 This practice does not address procedures for diagnosing causes of validation failure.

1.14 *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:<sup>2</sup>

- [D 1265](#) Practice for Sampling Liquefied Petroleum (LP) Gases, Manual Method
- [D 3606](#) Test Method for Determination of Benzene and Toluene in Finished Motor and Aviation Gasoline by Gas Chromatography
- [D 4057](#) Practice for Manual Sampling of Petroleum and Petroleum Products
- [D 4177](#) Practice for Automatic Sampling of Petroleum and Petroleum Products
- [D 5842](#) Practice for Sampling and Handling of Fuels for Volatility Measurement
- [D 6122](#) Practice for Validation of the Performance of Multivariate Process Infrared Spectrophotometers
- [D 6277](#) Test Method for Determination of Benzene in

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

Spark-Ignition Engine Fuels Using Mid Infrared Spectroscopy

**D 6299** Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance

**D 6708** Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material

**E 456** Terminology Relating to Quality and Statistics

**E 1655** Practices for Infrared Multivariate Quantitative Analysis

**F 307** Practice for Sampling Pressurized Gas for Gas Analysis

2.2 *ASTM Adjuncts:*

Software Program CompTM, adjunct to Practice D 6708<sup>3</sup>

### 3. Terminology

3.1 *Definitions:*

3.1.1 *accepted reference value (ARV), n*—a value that serves as an agreed-upon reference for comparison, and which is derived as: (1) a theoretical or established value, based on scientific principles, (2) an assigned or certified value, based on experimental work of some national or international organization, or (3) a consensus or certified value, based on collaborative experimental work under the auspices of a scientific or engineering group. **E 456**

3.1.2 *cross-method reproducibility ( $R_{XY}$ ), n*—a quantitative expression of the random error associated with the difference between two results obtained by different operators using different apparatus and applying the two methods *X* and *Y*, respectively, each obtaining a single result on an identical test sample, when the methods have been assessed and an appropriate bias-correction has been applied in accordance with this practice; it is defined as the 95 % confidence limit for the difference between two such single and independent results. **D 6708**

3.1.2.1 *Discussion*—Within the context of this practice,  $R_{XY}$  is interpreted to be the 95 % confidence limit for the prediction deviation between any single Primary Test Method Result (PTMR) and the Predicted Primary Test Method Result (PPTMR) produced by the analyzer system that is deemed acceptable on the assumption that both the analyzer system and primary test method are in statistical control, and that the correlation relationship applied to the analyzer results to produce the PPTMR is fit-for-purpose.

3.1.3 *precision, n*—the closeness of agreement between independent test results obtained under stipulated conditions. **E 456**

3.1.4 *repeatability conditions, n*—conditions where independent test results are obtained with the same method on identical test items in the same laboratory by the same operator using the same equipment within short intervals of time. **E 456**

3.1.5 *reproducibility conditions, n*—conditions where test results are obtained with the same method on identical test

items in different laboratories with different operators using different equipment. **E 456**

3.1.6 *site precision conditions, n*—conditions under which test results are obtained by one or more operators in a single site location practicing the same test method on a single measurement system using test specimens taken at random from the same sample of material, over an extended period of time spanning at least a 15 day interval. **D 6299**

3.1.6.1 *Discussion*—A measurement system may comprise multiple instruments being used for the same test method.

3.1.7 *site precision, n*—2.77 times the standard deviation of results obtained under site precision conditions. **D 6299**

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *Analyzer System Items:*

3.2.1.1 *analyzer output, n*—a signal (pneumatic, electrical, or digital), proportional to the property being measured that is suitable for readout or control instrumentation external to the analyzer system.

3.2.1.2 *analyzer system result, n*—the measured property reading, in the accepted property measurement units, that is displayed by the analyzer unit readout instrumentation or transmitted to end user of the analyzer system.

3.2.1.3 *analyzer unit, n*—the instrumental equipment necessary to automatically measure the physical or chemical property of a process or product stream sample using either an intermittent or a continuous technique.

3.2.1.4 *analyzer unit repeatability, n*—2.77 times the standard deviation of results obtained from repetitive analysis of the same material directly injected into the analyzer unit under repeatability conditions.

3.2.1.5 *continuous analyzer unit, n*—an analyzer that measures the property value of a process or product stream on a continuous basis and dynamically displays the instantaneously updated analyzer output.

3.2.1.6 *intermittent analyzer unit, n*—a cyclic type analyzer that performs a measurement sequence on samples from a process or product stream and displays a new analyzer output at the conclusion of each cycle.

3.2.1.7 *total analyzer system, n*—the complete analyzer system inclusive of the sample loop, sample conditioning unit, analyzer unit, readout instrumentation, and excess sample return system (see Fig. 1).

3.2.1.8 *line sample, n*—an aliquot of material taken from the process stream that is intended to be used to perform analyzer system validation as per this standard.

3.2.2 *Time Unit Items—General Terms:*

3.2.2.1 *analyzer unit cycle time, n*—for intermittent analyzers, the time interval between successive updates of the analyzer output.

3.2.2.2 *analyzer unit dead time, n*—the time interval between the introduction of a step change in property characteristic at the inlet of the analyzer unit and the initial indication of analyzer response to this change.

(1) *Discussion*—For intermittent analyzers, if the analyzer dead time is less than one analyzer unit cycle time, the analyzer unit dead time cannot be directly measured.

<sup>3</sup> Available from ASTM International Headquarters. Order Adjunct No. ADJD6708. Original adjunct produced in 2005.