Designation: D3764 – 09

Standard Practice for Validation of the Performance of Process Stream Analyzer Systems[1]

This standard is issued under the fixed designation D3764; 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.

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 D6708 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 D6299 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 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

[1] 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.

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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 D6122 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 D6277 to a Test Method D3606 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 D6277) that is independent of the primary test method (Test Method D3606). However, when the same analyzer uses a multivariate model to correlate the measured Mid-Infrared spectrum to Test Method D3606 reference values using the methodology of Practice E1655, it is considered Case 2 and Practice D6122 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 D6122, 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 D6708. 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 D6708, 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:*[2]

D1265 Practice for Sampling Liquefied Petroleum (LP) Gases, Manual Method

D3606 Test Method for Determination of Benzene and Toluene in Finished Motor and Aviation Gasoline by Gas Chromatography

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D5842 Practice for Sampling and Handling of Fuels for Volatility Measurement

D6122 Practice for Validation of the Performance of Multivariate Process Infrared Spectrophotometer Based Analyzer Systems

D6277 Test Method for Determination of Benzene in Spark-Ignition Engine Fuels Using Mid Infrared Spectroscopy

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

[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.

D6708 Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material
E456 Terminology Relating to Quality and Statistics
E1655 Practices for Infrared Multivariate Quantitative Analysis
F307 Practice for Sampling Pressurized Gas for Gas Analysis

2.2 *ASTM Adjuncts:*
Software Program CompTM, adjunct to Practice D6708[3]

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. **E456**

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. **D6708**

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. **E456**

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. **E456**

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. **E456**

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. **D6299**

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. **D6299**

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.

3.2.2.3 *analyzer unit response time, n*—(see Fig. 2) the time interval between the introduction of a step change in property characteristic at the inlet of the analyzer unit and when the analyzer output indicates a value corresponding to 99.5 % of the subsequent change in analyzer results.

[3] Available from ASTM International Headquarters. Order Adjunct No. ADJD6708. Original adjunct produced in 2005.

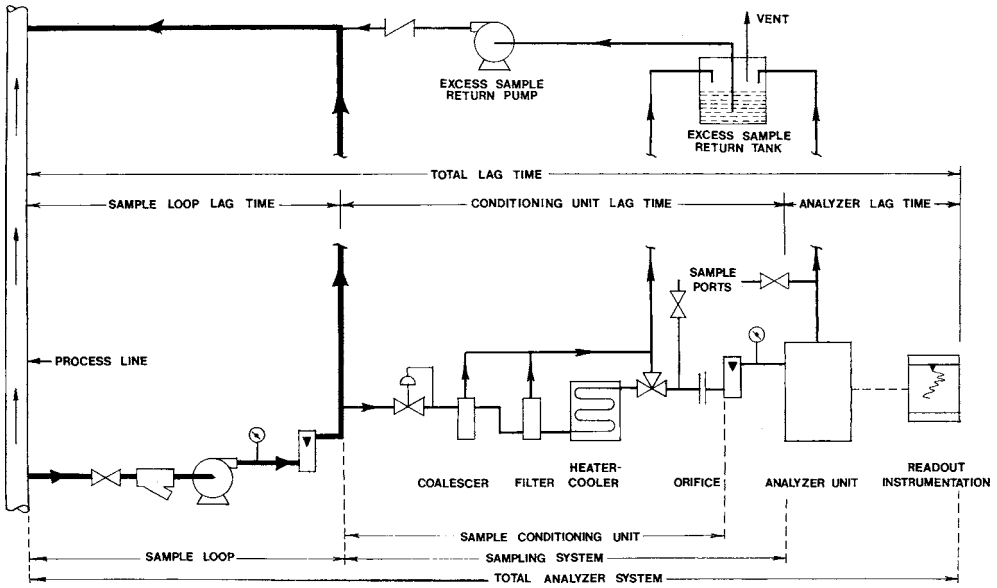

FIG. 1 Total Analyzer System

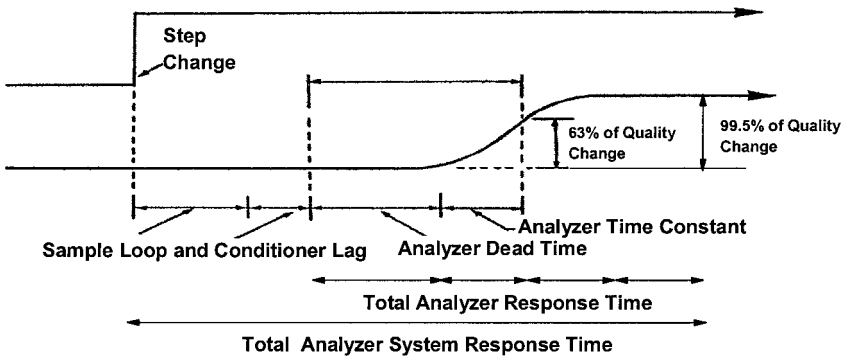

FIG. 2 Analyzer Time Units

(1) Discussion—For continuous and intermittent analyzers with sufficiently short cycle times, the total analyzer response time is the analyzer dead time plus three times the analyzer unit time constant. For intermittent analyzers with long cycle times, the analyzer unit response time is effectively equal to the analyzer unit cycle time. For intermittent analyzers with intermediate cycle times, the analyzer unit response time should be defined as the multiple of the analyzer unit cycle time needed to exceed 99.5 % response.

3.2.2.4 *analyzer unit time constant, n*—(see Fig. 2) the time interval between the initial response of the analyzer unit to a step change in property characteristic and when the analyzer output indicates a value corresponding to 63 % of the subsequent change in analyzer results.

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

3.2.2.5 *lag time, n*—the time required for material to travel from Point A to Point B in the total analyzer system (Points A and B are user-defined).

(1) Discussion—Lag time is a function of an analyzer system design parameters such as length and diameter of lines, number of fittings, flow restrictions, and the flow rate of the material (process or product stream) through the analyzer system (see Figs. 2 and 1).

3.2.2.6 *sample conditioning unit lag time, n*—the time required for material to travel from the start of the sample conditioning unit to the analyzer unit inlet.

3.2.2.7 *sample loop lag time, n*—the time required for material to travel from the process takeoff point of the sample loop to start of the sample conditioning unit.

3.2.2.8 *total analyzer system response time, n*—(see Fig. 2) The time interval between when a step change in property characteristic at the sample loop inlet and when the analyzer output indicates a value c corresponding to the 99.5 % of the subsequent change in analyzer results; the total analyzer system response time is the sum of the sample loop lag time, the same conditioning loop lag time, and the total analyzer response time.

3.2.3 *General Terms:*

3.2.3.1 *composition-specific VRM, n*—a validation reference material consisting of a single, pure compound, or a known, reproducible mixture of compounds for which an accepted reference value or site assigned value can be calculated or measured.

(1) Discussion—A composition-specific VRM may be a commercial standard reference material (SRM) having a certified accepted reference value.

3.2.3.2 *continual validation, n*—the quality assurance process by which the bias and precision performance determined during initial validation are shown to be sustained.

3.2.3.3 *direct measurement, n*—a quantitative measurement result obtained using a principle or principles that express the characteristic property of interest in its defining units.

3.2.3.4 *indirect measurement, n*—a correlated quantitative measurement result obtained using a measurement principle that produces values that do not express the desired characteristic property but which can be modified empirically, using mathematical modeling techniques, to estimate the necessary defining units of the property of interest.

(1) Discussion—Methods that utilize chemometric or multivariate analysis are indirect measurements for generating correlative characteristic property measurement results.

3.2.3.5 *line sample, n*—process material that can be safely withdrawn from a sample port and associated facilities located anywhere in the total analyzer system without significantly altering the property of interest.

3.2.3.6 *prediction deviations* (Δ)*, n*—calculated differences (including algebraic sign) between predicted primary test method result and primary test result, defined as (PPTMR – PTMR).

(1) Discussion—This is also referred to as prediction residuals in Practice D6708.

3.2.3.7 *primary test method results (PTMR), n*—test results produced from an ASTM or other established standard test method that are accepted as the reference measure of a property.

3.2.3.8 *predicted Primary Test Method Results (PPTMR), n*—results from the analyzer system, after application of any necessary correlation, that is interpreted as predictions of what the primary test method results would have been, if it was conducted on the same material.

3.2.3.9 *process-derived VRM, n*—a validation reference material derived from an isolated batch of process or product stream material with chemical or physical characteristics, or both, that is suitable for determination of an accepted reference value or site assigned value for the property of interest.

3.2.3.10 *site assigned value (SAV), n*—a property value of a reference material that is based on multiple results from either the analyzer unit or a primary test method, obtained under site precision conditions.

3.2.3.11 *validation, n*—the statistically quantified judgment that the analyzer system or subsystem, in conjunction with any correlation applied, can produce acceptable precision and bias performance on the prediction deviations (Δ) for materials that were not used to develop the correlation.

3.2.3.12 *validation reference material (VRM), n*—for validation and quality assurance testing, a material having an accepted reference value or site assigned value for the property of interest.

4. Summary of Practice

4.1 PPTMRs from the total analyzer system or its subsystem are compared to the corresponding PTMRs on at least 15 materials. PPTMR and PTMR are statistically assessed relative to each other using the methodology of Practice D6708, recognizing that this is only a preliminary Practice D6708 assessment. Precision and bias statistics on the prediction deviations (Δ) are generated and the bias is assessed against pre-specified performance criteria. The system or subsystem performance is considered to be probationary validated for materials and property ranges representative of those used in the validation if the prediction deviations are in statistical control, and bias performance statistic meets pre-specified criterion.

4.2 After probationary validation is achieved, continued statistical quality control chart monitoring and analyses on Δ are carried out with new production samples to ensure ongoing prediction performance of the PPTMR meets the levels established from the probationary validation.

4.3 Once the total number of samples with completed datasets (PPTMR , PTMR , Δ) from probationary and continual validation reaches 30, a general validation is conducted using the statistical methodology of Practice D6708. The objective of the general validation is to demonstrate performance with at least 30 samples over a wider operating envelope, or, to confirm outcome from probationary validation with more accrued data.

4.4 If the variation among the 30 samples is inadequate to conduct the Practice D6708 assessment, a level specific validation may be performed to validate the agreement between PPTMR and PTMR over a narrow operating range. As additional (PPTMR / PTMR / Δ) datasets are collected covering a wider operating range, the general validation may again be attempted.

4.5 After general validation has been achieved, continue to monitor Δ using statistical quality control charts at a frequency commensurate with the criticality of the application.

5. Significance and Use

5.1 This practice can be used to quantify the performance of a process stream analyzer system or its subsystem in terms of precision and bias relative to those of a primary test method for the property of interest.

5.2 This practice provides developers or manufacturers of process stream analyzer systems with useful procedures for evaluating the capability of newly designed systems for industrial applications that require reliable prediction of measurements of a specific property by a primary test method of a flowing component or product.

5.3 This practice provides purchasers of process stream analyzer systems with some reliable options for specifying acceptance test requirements for process stream analyzer systems at the time of commissioning to ensure the system is

capable of making the desired property measurement with the appropriate precision or bias specifications, or both.

5.4 PPTMR from Analyzer Systems validated in accordance with this practice can be used to predict, with a specified confidence, what the PTMR would be, to within a specified tolerance, if the actual primary test method was conducted on the materials that are within the validated property range and type.

5.5 This practice provides the user of a process stream analyzer system with useful information from on-going quality control charts to monitor the variation in Δ over time, and trigger update of correlation relationship between the analyzer system and primary test method in a timely manner.

5.6 Validation information obtained in the application of this practice is applicable only to the material type and property range of the materials used to perform the validation. Selection of the property levels and the compositional characteristics of the samples must be suitable for the application of the analyzer system. This practice allows the user to write a comprehensive validation statement for the analyzer system including specific limits for the validated range of application. This practice does not recommend extrapolation of validation results beyond the material type and property range used to obtain these results. In addition, users are cautioned that for measurement systems that show matrix dependencies, bias information determined from pure compounds or simple mixtures of pure compounds may not be representative of that achieved on actual process or product samples.

6. System Components

6.1 Fig. 1 illustrates a total analyzer system incorporating a selection and arrangement of components that are typical but not specific for any particular analyzer system. A total analyzer system design addresses the chemical and physical properties of the process or product stream to be measured, provides a representative sample, and handles it without adversely affecting the value of the specific property of interest. Included are a sample loop, piping, hardware, a sampling port, sample conditioning devices, an analyzer unit instrumentation, any data analysis computer hardware and software, and a readout display.

6.2 *Sample Loop*—Piping connected to the main process stream to deliver a portion of the stream to a location close to the analyzer system with minimum lag time and return the unused material to the main process stream.

6.3 *Sampling System*—Sample probes, valves, lines, containers, pressure regulator, and gages that constitute the equipment employed to obtain a proper sample from the sample loop and introduce either it or a validation standard sample to the analyzer.

6.4 *Sample Conditioning Unit*—A collection of devices to properly treat a portion of the sample from the sample loop so that it meets the requirements for testing by the process analyzer. These components can incorporate temperature or pressure adjustment, change of state (liquid, vapor), or removal of contaminants.

6.5 *Inlet Port*—Appropriate piping with selector valve(s) for placement either at the inlet to the analyzer unit or, when dictated by the measurement specifications, at the inlet to the sample conditioning unit. The purpose of this inlet port is to allow injection of validation standards or other calibration material into the analyzer system with quick switching between these typically containerized materials and the flowing process stream.

6.5.1 For many analyzer systems the inlet port requires a manifold arrangement for validation or quality assurance studies. Such a manifold, with suitable valving, provides a means to use a containerized supply of standby material when a flowing process stream is not available for the purpose. It also permits quick switching between different validation standards when that is desirable.

6.6 *Sample Port*—An appropriate probe or fitting in the piping to permit collection of representative samples for laboratory analyses using a primary test method.

6.7 *Analyzer Unit*—Instrumentation designed to automatically measure the chemical or physical property of a process or product stream sample and provide either an intermittent or a continuous output signal representing the measurement result.

6.8 *Readout Instrumentation*—If it is not an integral component of the analyzer system, a device to display or record or both, the property measurement analyzer result.

7. Preparation of Analyzer System

7.1 Implementation of this practice requires that the process stream analyzer system operates under conditions specified:

7.1.1 Meets all applicable electrical and safety codes.

7.1.2 Meets the supplier's recommendation.

7.1.3 Complies with operating conditions specified by the manufacturer.

7.1.4 Includes a predicted PTM algorithm, if necessary.

7.2 After installation or major maintenance, conduct such diagnostic tests as recommended by the manufacturer to demonstrate that the analyzer meets the manufacturer's specifications or historical performance levels, or both. If necessary, adjust the analyzer system components so as to obtain recommended analyzer output levels for specified reference materials.

7.3 Inspect the entire analyzer system to ensure it is installed properly, is in operating condition, and is properly adjusted after completion of the initial commissioning procedures.

8. Pre-Validation Analyzer Calibration Check

8.1 When an analyzer is initially installed, and after major maintenance has been preformed, diagnostic tests should be conducted to demonstrate that the analyzer meets 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. Such adjustment may be done in hardware, software or both.

8.2 Description of specific calibration procedures for the numerous analyzer types is beyond the scope of this practice.

9. Validation Procedure

9.1 The objective of the validation procedures is to quantify the precision and bias performance of prediction deviations (Δ)

between PPTMR produced by a process stream analyzer system (or its subsystem) versus PTMR for materials spanning the intended operating range for the analyzer system. The user must specify acceptable precision and bias performance criteria before initiating the validation. These criteria will be dependent on the intended use of the analyzer.

9.1.1 For analyzer systems used in product certification, precision performance acceptance criteria for Δ will typically be based directly on the published reproducibility (R) of the primary test method. Bias criteria will typically be based on regulatory or contractual requirements. It is a general performance expectation that no bias correction can further improve the precision of Δ statistically.

9.1.2 For analyzer systems used in other types of service, precision and bias criteria must be developed based on the intended use of the analyzer results.

9.1.3 This practice recommends articulation of precision performance of Δ as a cross method reproducibility (R_{XY}).

9.2 The line sample procedure directly fulfills the validation objective since the validation results for both the process system and the primary test method are obtained on process samples. However, if line samples covering the composition and property range of interest cannot be acquired within a reasonable length of time once the validation process begins, consider using either process-derived or composition-specific validation reference materials (VRMs) to extend the composition and property range of the validation sample set. A suitable process-derived VRM may simply be a batch of material obtained at a time prior to the start of the validation procedure but that was not used in calibrating either the analyzer or the primary test method. In general, the composition of a VRM used for validation should be similar to a composition that is anticipated for the process stream at some future time.

9.2.1 In cases where it is necessary to include the sample loop or the sample conditioning unit (Fig. 1), or both, in the validation procedure, VRMs should not be used to the exclusion of lines sample unless it is practical to use the VRMs to validate both sample system and analyzer (this is generally not practical). The sample system can be excluded from the validation procedure if it is known that the sample system does not materially alter the composition or condition of the sample presented to the analyzer and if the sample system response time can be estimated with reasonable certainty. Guidance on how to meet these conditions is beyond the intended scope of this practice. If these conditions cannot be met and if VRMs are needed to extend the property and composition range of the validation set, it is recommended that the user conduct two probationary validations, one using line samples and the other using VRMs, to demonstrate that VRM procedure adequately reflects corresponding performance for actual process materials. Once demonstrated, the statistical quality control charting for continual validation can be done using VRM procedures, with a periodic line sample procedure mixed in over time to demonstrate that both procedures continue to provide similar and acceptable performance.

NOTE 3—If the process analyzer system is not based on identically the same measurement principle as the primary test method, then the analyzer system may react differently to variations in the sample matrix than does the primary test method. In such case, analyzer results for process samples might be biased relative to primary test method results even when the VRM procedure results shown no such bias unless the VRM is process-derived. The bias can be minimized by using a process stream (test) sample for which an ARV or SAV was determined as the VRM. The test sample used in this fashion should be representative of the current process stream.

NOTE 4—If, due to differences in sample pretreatment, the sample analyzed by the process stream analyzer and the sample analyzed by the primary test method are not identically the same, then the use of the VRM procedure may not accurately reflect agreement between the process analyzer and the primary test method. The VRM may not be affected in the same manner as process samples by the different sample pretreatments. Again, this effect can be minimized by using current process stream (test) samples as VRMs.

9.3 *Probationary, General and Level Specific Validation using the Line Sample Procedure*:

9.3.1 This procedure is applicable for analyzer systems that are equipped with sample ports anywhere within the system that can facilitate the safe collection of material intended for analysis by the analyzer unit without significantly altering the property of interest. The subsystem from the sample port up to and including the analyzer subsystem (see Fig. 1) is considered to be validated for current process stream samples if the Δ results are in statistical control, and the precision and bias statistics meet user-specified requirements.

9.3.2 *Line Sample Procedure Requirements:*

9.3.2.1 Select point of line sample withdrawal.

9.3.2.2 Determine the total lag time of the system or subsystem from the sample withdrawal point (see Figs. 2 and 1 for guidance) up to and including the analyzer.

9.3.3 *Procedure*—Collect analyzer unit results from at least 15 implementations of the line sample procedure under site precision conditions, with at least 8 to 12 h between each implementation, as follows:

9.3.3.1 Observe the analyzer unit output until the change between readings over at least three lag times for the subsystem (associated with the sample port) to be validated. Ensure the manufacturing process is at steady state by confirming the maximum difference between results observed does not exceed the known repeatability of the analyzer unit. If steady state conditions cannot be achieved, the line sample validation procedure should not be executed at this time. In the event that the process stream composition typically changes at a rate great enough to prevent this condition from being met, either *(1)* accept the generally inflated differences between PPTMRs and PTMRs that would be a consequence of the fact that the samples presented to the analyzer would not match exactly those presented to the primary test method, or, *(2)* perform the validation with VRMs, recognizing that the effects due to sample composition matrix differences may not be included in the performance statistics. If the analyzer system repeatability is unknown, the repeatability of the primary test method can be used as the reference for data comparison.

9.3.3.2 After steady state has been verified, begin collecting the process line sample from the sample port. Refer to Practices D1265, D4057, D4177, D5842, or F307 for procedures for sample collection. Record the time, t_s, corresponding to the start of sample collection. Record the analyzer system

result $A_0(t_s)$ observed at t_s. Collect the volume of sample required for PTM analysis. Record the time, t_e, when sample collection ends.

9.3.3.3 If the sample collection interval $t_e - t_s$ is less than the lag time of the subsystem to be validated (Fig. 3), record the analyzer result $A_1(t_e)$ at a time one subsystem lag time interval after t_s. If $A_1(t_e)$ and $A_0(t_s)$ agree to within known analyzer system repeatability, assign the average of these two results as the PPTMR for the collected line sample. Otherwise, the line sample and results are discarded. Wait until steady state is re-established before beginning the line sample procedure again.

9.3.3.4 If the sample collection interval $t_e - t_s$ is longer than the subsystem lag time (Fig. 4), then record analyzer results $A_0(t_s)$ and $A_1(t_e)$ at times corresponding to one total analyzer response interval after t_s and t_e respectively. If $A_0(t_s)$ and $A_1(t_e)$ agree to within the known repeatability of the analyzer system, assign the average of these two results as the PPTMR for the collected line sample. Otherwise, the line sample and results are discarded. Wait until steady state is re-established before beginning the line sample procedure again.

9.3.3.5 Obtain a PTMR for the line sample collected.

9.3.3.6 For each line sample collected, calculate Δ, where Δ = (PPTMR – PTMR).

9.3.3.7 After a minimum 15 line sample datasets are collected, conduct a preliminary Practice D6708 assessment, using the PPTMR, PTMR, and site precision standard deviations for the PPTMR and PTMR which have been established using control charts on suitable quality control materials as per Practice D6299.

NOTE 5—Site precision standard deviation is not to be confused with standard deviation of the PPTMR results for the line samples.

9.3.3.8 Follow the Practice D6708 outcome decision flowchart in Fig. 5. If the outcome is a "fail," then, the system that produced the PPTM results is deemed to have failed the validation requirements of this practice.

NOTE 6—The Practice D6708 assessment is most easily conducted using the ADJD6708 software adjunct to the practice.

NOTE 7—In the Practice D6708 assessment, an Anderson-Darling test is used to determine if the distribution of the prediction deviations (residuals), including sample specific biases and other errors, is nominally Gaussian (normal). If the PTMR or PPTMR are not reported to a sufficient number of significant digits, then the Anderson-Darling test may not be applicable. If the Practice D6708 assessment fails because the prediction deviations (D) fail the Anderson-Darling test, visually inspect the prediction deviations (Δ) to determine how many unique values are present. If there are fewer than 4 unique values, the Anderson-Darling test is not applicable, and the range of the deviations (max-min) should be compared to user requirements to determine if the analyzer passes validation. If there are 4 or more unique values, the Anderson-Darling test is applicable, and the analyzer fails validation.

9.3.3.9 If the Practice D6708 outcome decision from above is a "pass," follow the instructions in Practice D6299 (section on Procedure for Pretreatment, Assessment, and Interpretation of Test Results) and assess all Δ following the quality control (QC) sample results protocol. Interpret the control chart generated and determine whether the Δ exhibit in statistical control behavior. Investigate the out-of-control points and take appropriate corrective actions to address the root cause(s). Replace the out-of-control points by repeating the line sampling procedure.

9.3.3.10 If the Δ exhibit in statistical control behavior, the system that produced the PPTMR is deemed to have passed probationary validation.

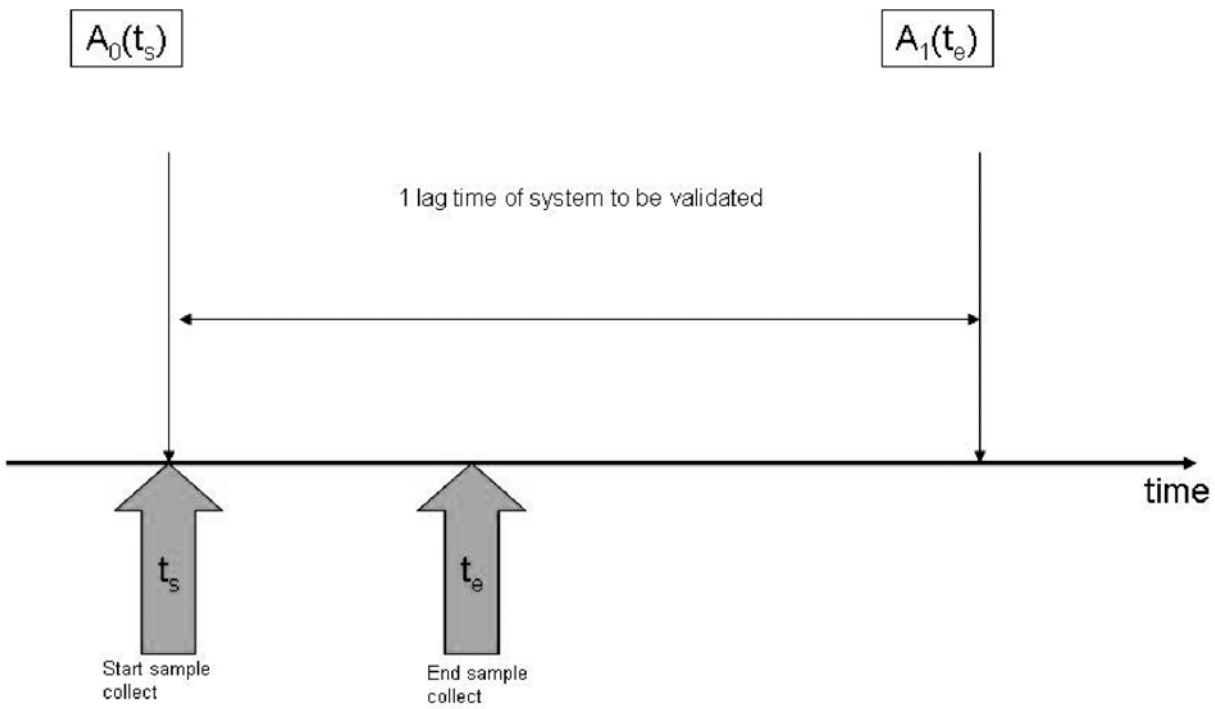

FIG. 3 Guidance for Recording Analyzer Result During Line Sampling (see 9.3.3.3)

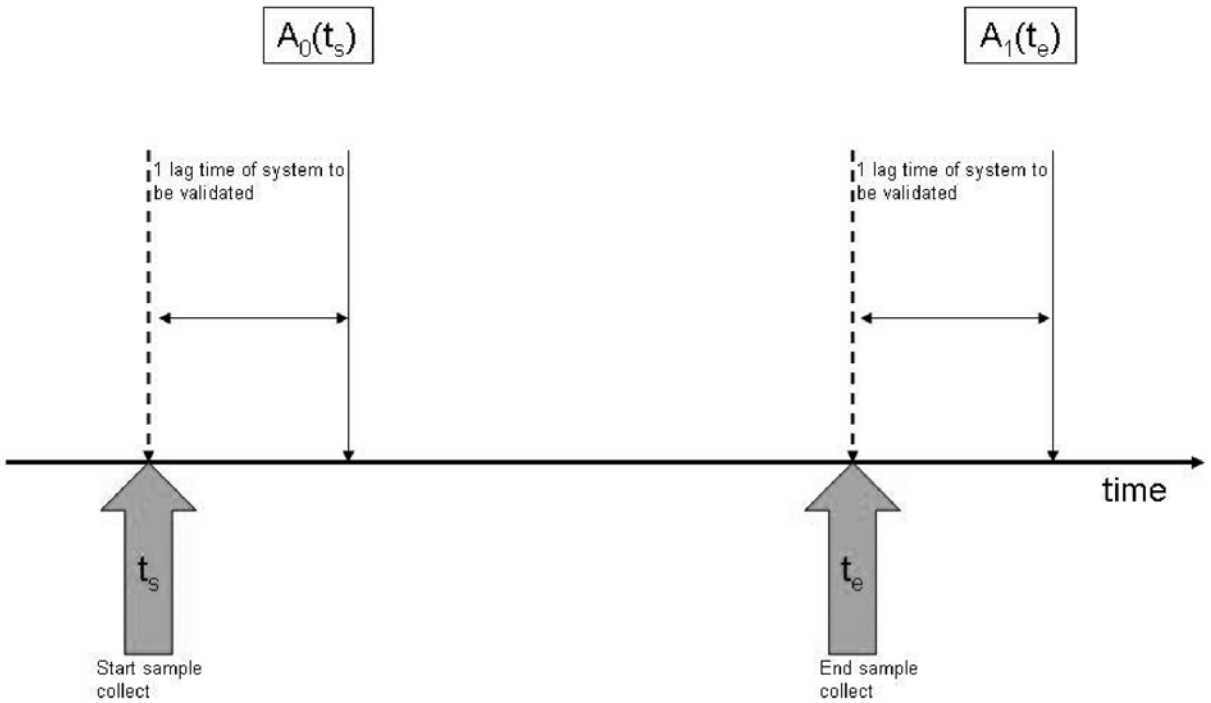

FIG. 4 Guidance for Recording Analyzer Result During Line Sampling (see 9.3.3.4)

9.3.3.11 Continue to collect validation samples and populate the statistical control chart for Δ.

9.3.3.12 A reassessment using Practice D6708 techniques as described above shall be conducted when data from a total of 30 line samples have been accrued (including the probationary data).

9.3.3.13 If the Practice D6708 reassessment outcome (Fig. 5) is a "pass," and, if all Δ results exhibit in-statistical-control behavior, compare R_{XY} from the Practice D6708 outcome to the required precision performance. Ensure the comparison is carried out on the same unit basis (that is, compare reproducibility to reproducibility, not standard deviation). The analyzer system is deemed to have met the General Validation requirements of this practice if the precision performance criteria is met. A failure of the Practice D6708 outcome, or, out of control behavior of the Δ results, or failure to meet the precision performance criteria will be deemed as a failure to meet the General Validation requirements of this practice.

9.3.3.14 If the Practice D6708 assessment concludes that there is insufficient variation in the sample set, proceed with a level-specific validation later in this section.

9.3.4 *Level-Specific Validation Using the Line Sample Procedure*:

9.3.4.1 For each of the 15 line samples collected, calculate the prediction deviation (Δ).

9.3.4.2 Follow the instructions in Practice D6299 (section on Procedure for Pretreatment, Assessment, and Interpretation of Test Results) and assess all the Δ results following the quality control (QC) sample results protocol. Interpret the control chart generated and determine if the Δ results exhibit in statistical control behavior.

NOTE 8—The system that generated the Δ results comprises the analyzer subsystem being validated, the PTM, and the process of obtaining the line samples.

9.3.4.3 If the Δ results are in statistical control, proceed with calculation of system precision and bias statistics. Otherwise, investigate the out-of-control points and take appropriate corrective actions to address the root cause(s). Replace the out-of-control points by repeating the line sampling procedure.

9.3.4.4 Assess the bias by performing a one-sample t-test using all the Δ results in accordance with Practice D6299. If the bias is not statistically significant, the system that produced the PPTMR is deemed to have passed probationary validation, limited to materials representative of the line samples used in the assessment.

9.3.4.5 If a statistically significant bias is observed, and is of a magnitude that exceeds user's requirement, for the purpose of this practice, the system that generated the PPTM results is considered to have failed to meet the probationary validation requirements. However, the average of the Δ results may be interpreted as the best estimate of the bias between the PTM and the analyzer system at the specific property level. Users may choose to re-establish the correlation, thus changing the PPTM process, and repeat the aforementioned probationary validation procedures.

9.3.5 Continue to collect validation samples and populate the control chart with new Δ results.

9.3.6 When the total number of validation sample sets reaches 30, conduct a Practice D6708 assessment as per the protocol described under General Validation earlier in this practice. If there is still insufficient variation for a successful Practice D6708 assessment, then, the dataset is considered insufficient for a General Validation. Compare the precision

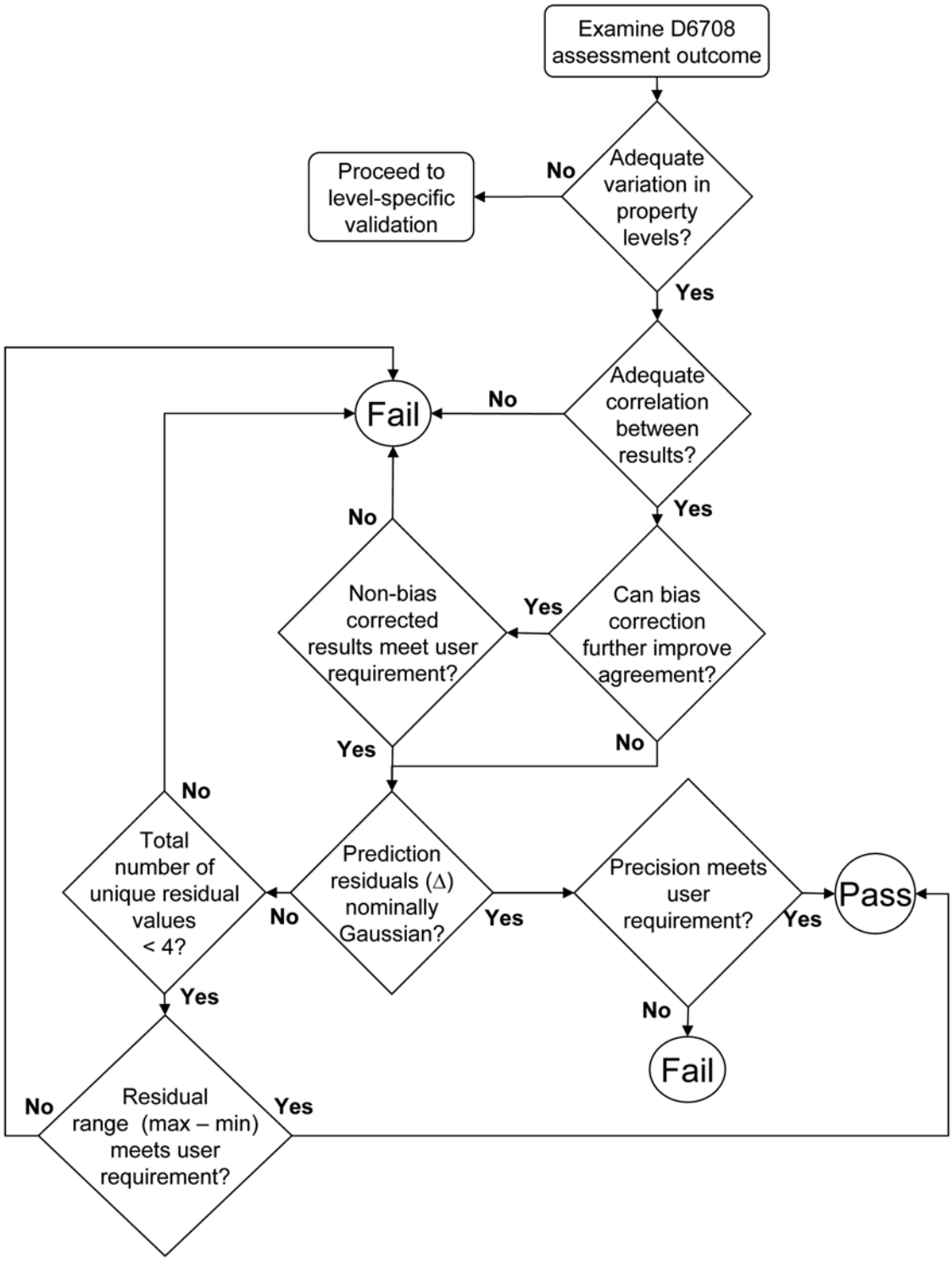

FIG. 5 Practice D6708 Outcome Assessment

and bias statistics to user specified requirements to form a conclusion for a level-specific validation outcome as follows:

9.3.6.1 Compare the precision (2× standard deviation) of the Δ results to the user-specified precision requirement (expressed as a reproducibility) to determine if the precision meets performance requirement.

9.3.6.2 Compare the bias (mean of the) to the precision via a one-sample *t*-test to determine if the bias is statistically

significant. If the bias is statistically significant, compare the bias value to user-specified bias requirement to determine if it is of practical significance.

9.3.6.3 If the precision meets user-specified precision requirements, and the bias is not of practical significance relative to user specified bias requirements, the analyzer passes level-specific validation and may be employed for analysis of materials within the narrow range covered by the level-specific validation materials.

9.3.6.4 If the analyzer precision does not meet user-specified precision requirements, or if the bias is practically significant, the analyzer fails level-specific validation. The cause of the failure should be investigated and corrected and validation can be restarted at the probationary level.

9.4 *Level-Specific Validation using the VRM Injection Procedure*:

9.4.1 This procedure requires analyzer system to be equipped with storage and injection facilities designed for the delivery of a VRM into the analyzer unit. The subsystem downstream of the VRM injection point is considered to be validated if validation results are in statistical control, and the predicted PTM results are in agreement with actual PTM results within satisfactory precision and bias limits. The validation applies only for analyses of materials of the same type as the VRM.

9.4.2 *Injection Procedure Requirements*:

9.4.2.1 Select the point of injection.

9.4.2.2 Determine the total lag time of the subsystem downstream of the injection point (use Fig. 1 for guidance).

9.4.3 *Procedure*—Collect analyzer unit results from at least 15 implementations of the VRM injection procedure for each selected VRM under site precision conditions, with nominally 8 to 12 h between each implementation, as follows:

9.4.3.1 Isolate the subsystem to be validated from the regular process stream sample flow.

9.4.3.2 Commence injection of the VRM.

9.4.3.3 Observe the analyzer unit output until the change between readings over at least three subsystem lag times does not exceed the known repeatability of the analyzer unit (that is, steady state has been reached). If the analyzer system repeatability is unknown, the repeatability of the primary test method can be used as the reference for data comparison.

9.4.3.4 Record the steady state analyzer unit output as the result for one implementation of VRM injection procedure.

9.4.3.5 Pretreat and assess the collected data in accordance with Practice D6299, including the construction of the I/MR control charts, using the protocol for a single check standard. Use the SAV instead of the ARV for VRMs that do not have ARVs.

9.4.3.6 If the data exhibits in statistical control behavior, follow the procedure in Practice D6299 to estimate the site precision and bias of the analyzer subsystem for the specific VRM. For the bias test use the protocol for a single check standard.

9.4.3.7 Assess the standard deviation of results for each VRM against the appropriate site standard deviation of the PTM. For product certification applications, the subsystem is expected to meet or better the site precision of the PTM. For other applications, the standard deviation of the results should exceed the pre-specified precision criteria for the intended use.

9.4.3.8 If the one-sample *t*-test for bias is statistically significant, assess the bias magnitude against the application requirement for practical significance.

9.4.3.9 If both the precision and bias meet the application requirements, the subsystem is considered to have met the validation requirements for materials of the same type and property range as the VRMs used in the assessment on a probationary basis.

9.4.4 Obtain additional results using the VRM injection procedure at a frequency commensurate with the criticality of the analyzer application (typically at least once a week). Plot results on control charts. Assess control chart status in accordance with procedures in Practice D6299. The frequency of VRM injection can be reduced if the subsystem stability and precision is monitored by way of other QC material in accordance with Practice D6299.

9.4.5 *General Validation using the VRM Injection Procedure*—General validation will not typically be possible using the VRM injection procedure unless at least 6 different VRMs are available spanning a range that is at least twice the larger of the site precisions of the analyzer and PTM. If a sufficient number and variation of VRMs is available, the General Validation can be attempted once the total number of results from initial and continual validation reaches 30. Follow the General Validation procedure described in the Line Sample Protocol.

9.5 *Validation of Total Process Analyzer System*:

9.5.1 The complete analyzer system, inclusive of the sample loop, can be validated by a combination of line sample and VRM procedure where:

9.5.1.1 The Line sample procedure is deployed to validate the entire system using current production material by sampling from a location located in close proximity to the process takeoff point of the sample loop.

9.5.1.2 The VRM procedure is deployed to validate the analyzer unit for material that is not currently available from the process.

ANNEX

(Mandatory Information)

A1. PROCEDURE FOR DEVELOPING A VALIDATION REFERENCE MATERIAL

A1.1 Determine the number of validation standards and the quantity of each that is appropriate for the proposed validation and quality assurance testing uses for the specific analyzer system application.

A1.1.1 If the analyzer system is known or suspected to produce nonlinear results, at least three validation standards having different accepted reference values can be required.

A1.1.2 The desired quantity of each validation standard shall be sufficient to sustain necessary analyzer system operation long enough to determine the data for initial validation of the system. In addition, it is recommended that enough material be included in a given lot, to permit on-going statistical quality control (SQC) testing after the validated system is placed in service. The quantity of validation standard selected for such SQC testing will depend on the stability of the material, available storage capacity, and so forth.

A1.1.3 Obtain the validation reference material(s) and store them under conditions that will ensure essentially no degradation of the critical property accepted reference value once it is established.

A1.1.4 Commercial standard reference materials are often available for use as a designated validation reference material. The property and the accepted reference value are available from the supplier.

A1.2 When commercial standard reference material is not available, the validation standard may be prepared from on-site process or product material meeting the desired specifications. Utilization of this type of material requires testing by a primary test method, preferably under reproducibility conditions, to establish the accepted reference value of the selected property.

A1.2.1 Collect and store the appropriate quantity of an on-site process or product material for use as a validation standard. Prepare and fill the necessary number of individual containers of validation standard for primary test method analyses to determine the ARV or SAV of the desired property.

A1.2.2 For each validation standard, obtain a minimum of ten primary test method results.

A1.2.2.1 More than ten primary test method results can be necessary to provide an average value having acceptable confidence limits. This can vary significantly for different primary test methods and validation standard properties.

A1.2.2.2 The controlling factors in defining the number of test results required are: degree of precision desired, testing costs, precision of the primary test method, and the criticality of the analyzer system accuracy and precision.

A1.2.3 For guidance in determining the number of primary test method results required to establish desired confidence limits for the ARV or SAV of the validation standard, refer to instructions provided in A1.4.

A1.2.4 To establish an ARV, it is necessary that the primary test method results be obtained under reproducibility conditions, to minimize effects of inter-laboratory bias and test variability.

A1.3 To establish an SAV, it is recommended that different operators and apparatus combinations be utilized to the maximum extent possible so the data are representative of site precision conditions.

A1.3.1 If it is considered necessary to obtain the multiple determinations in a single laboratory that has only one piece of apparatus available, make the multiple determinations over an extended period of time using multiple operators and testing other samples between the validation standard measurements. This approach will provide data obtained in a manner that is closest to site precision conditions.

A1.3.2 If the validation standard primary test method results are determined in a single laboratory, it is recommended that the laboratory maintain records verifying their bias status, based on participation in an industry-wide round-robin exchange sample testing program.

A1.4 *Calculating the Accepted Reference Value (ARV) or Site Assigned Value (SAV) for the Validation Reference Material*:

A1.4.1 Tabulate the primary test method results for the validation standard and visually screen for extreme values or outliers, or both, by an accepted statistically based rejection criterion.[4] Remove the outliers to further analyze the data. No more than 10 % of the data points should be removed through this process.

A1.4.2 Determine the arithmetic average (X_r) and the variance (S_r^2) of the acceptable validation standard data.

A1.4.2.1 Calculate the arithmetic average value using the following equation:

$$\bar{X}_r = \frac{\sum X_r}{N_r} \tag{A1.1}$$

where:

X_r = individual test results on the validation standard, and
N_r = number of test results.

A1.4.2.2 Calculate the variance by either of the following equations:

$$S_r^2 = \frac{\left[\sum X_r^2 - \frac{(\sum X_1)^2}{N_r}\right]}{(N_{r-1})} \tag{A1.2}$$

$$S_r^2 = \frac{\sum (X_r - \bar{X}_r)^2}{(N_r - 1)} \tag{A1.3}$$

[4] Supporting data are available from ASTM International Headquarters. Request RR: D02-1481.

A1.4.3 Compare the calculated validation standard data variance to that used to establish the reproducibility precision statement of the applicable primary test method. The statistical criteria for this judgment is the *F*-Test, which requires determination of the ratio of the variances as follows:

$$F = \frac{S_r^2}{\sigma_t^2} \quad \text{(A1.4)}$$

where:

S_r^2 = variance of validation standard data, and
σ_t = historical reproducibility standard deviation of the primary test method.

A1.4.3.1 This standard deviation can be obtained by dividing the reproducibility (*R*) given in the precision statement of the primary test method by 2.772.

A1.4.4 Determine the limiting *F* value from the statistical *F* Distribution (5 % error level) tables for $(N_r - 1)$ degrees of freedom in the numerator and 30 degrees of freedom in the denominator. (See Table A1.1 for a condensed portion of the *F* Distribution table.

A1.4.5 Compare the calculated *F* value to the limiting *F* value obtained from the *F* Distribution table and interpret as follows:

A1.4.5.1 If the calculated *F* value is equal to or less than the limiting *F* value, the variance of the validation standard data is not significantly worse than that of the expected primary test method precision and the validation standard data are qualified and acceptable.

A1.4.5.2 If the calculated *F* value is larger than the limiting *F* value, the variance of the validation standard data is not as good as the expected primary test method precision and the difference is statistically significant.

A1.4.6 When a significant difference between the variances occurs, the reason(s) for the substandard validation standard primary test method data requires investigation. Make any needed changes to the procedure or apparatus, or both, and then obtain a new set of validation standard primary test method data for comparison of the variances once again. Repeat the process until the precision of the primary test method data is acceptable.

A1.4.7 Assign the accepted reference value (ARV) and appropriate confidence limits for the property of the validation standard material tested as follows:

A1.4.7.1 Use the arithmetic average result of the validation standard primary test method data as the property ARV.

A1.4.7.2 Calculate the 95 % confidence interval limits for the ARV based on the validation standard test data using the following equation:

$$95\ \%\ \text{confidence limits} = X_r \pm t\frac{S_r}{\sqrt{N_r}} \quad \text{(A1.5)}$$

Where: t = students t value for the 95th percentile from standard *t*-tables for n-1 degrees of freedom. (See Table A1.2 for a condensed portion of the *t*-table).

A1.4.7.3 If the confidence interval width (magnitude between the upper and lower confidence limits) is too far apart to be considered useful, mathematically increase *N* and recalculate until the desired confidence interval width is obtained. Proceed and collect the additional results to meet the increased *N* requirement.

A1.4.8 Confirm the validation standard accepted reference value at periodic intervals because storage conditions and the factors that affect the stability of the material can change with time. The analyzer system user best determines the frequency of confirmation.

TABLE A1.1 *F*-Distribution
Degrees of freedom for numerator

	1	2	3	4	5	6	7	8	9	10	12	15	20
1	161	200	216	225	230	234	237	239	241	242	244	246	248
2	18.5	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4	19.4	19.4	19.4	19.4
3	10.1	9.55	9.28	9.12	9.01	8.94	8.87	8.85	8.81	8.79	8.74	8.70	8.66
4	7.71	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.91	5.86	5.80
5	6.61	5.79	5.41	5.19	5.05	4.95	4.88	4.81	4.77	4.74	4.68	4.62	4.56
6	5.99	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	4.00	3.94	3.87
7	5.59	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.57	3.51	3.44
8	5.32	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.28	3.22	3.15
9	5.12	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.07	3.01	2.94
10	4.96	4.10	3.70	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.91	2.85	2.77
11	4.84	3.98	3.59	3.36	3.20	3.09	3.01	2.95	2.90	2.85	2.79	2.72	2.65
12	4.75	3.89	3.49	3.26	3.11	3.00	2.91	2.85	2.80	2.75	2.69	2.62	2.54
13	4.67	3.81	3.41	3.18	3.03	2.92	2.83	2.77	2.71	2.67	2.60	2.53	2.46
14	4.60	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65	2.60	2.53	2.46	2.39
15	4.54	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.48	2.40	2.33
16	4.49	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54	2.49	2.42	2.35	2.28
17	4.45	3.59	3.20	2.96	2.81	2.70	2.61	2.55	2.49	2.45	2.38	2.31	2.23
18	4.41	3.55	3.16	2.93	2.77	2.66	2.58	2.51	2.46	2.41	2.34	2.27	2.19
19	4.38	3.52	3.13	2.90	2.74	2.63	2.54	2.48	2.42	2.38	2.31	2.23	2.16
20	4.35	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.28	2.20	2.12
∞	3.84	3.00	2.60	2.37	2.21	2.10	2.01	1.94	1.88	1.83	1.75	1.67	1.57

TABLE A1.2 Table of *t* at 5 % Probability Level

Degrees of Freedom (*N*-1)	*t*
1	12.706
2	4.303
3	3.182
4	2.776
5	2.571
6	2.447
7	2.365
8	2.306
9	2.262
10	2.228
11	2.201
12	2.179
13	2.160
14	2.145
15	2.131
16	2.120
17	2.110
18	2.101
19	2.093
20	2.086

APPENDIX

(Nonmandatory Information)

X1. ASSESSMENT OUTCOME EXAMPLES

X1.1 *Example 1*—A successful Practice D6708 assessment outcome using process in Fig. 5 and ADJD6708:

PPTM and PTM Dataset			
VP Analyzer	Site Precision Std Dev for VP Analyzer	PTM (D5191)	Site Precision Std Dev for PTM
90.7	0.5	90.55	0.7
91.96	0.5	92.3	0.7
95.34	0.5	94.3	0.7
92.2	0.5	92.9	0.7
90.42	0.5	91.4	0.7
90.75	0.5	91.7	0.7
91.92	0.5	93.0	0.7
96.69	0.5	96.05	0.7
102.6	0.5	101.9	0.7
101.11	0.5	100.95	0.7
99.09	0.5	100.8	0.7
97.17	0.5	97.8	0.7
102.37	0.5	102.3	0.7
99.09	0.5	99.0	0.7
106.4	0.5	104.1	0.7
99.51	0.5	100.1	0.7
98.72	0.5	97.7	0.7
108.56	0.5	109.6	0.7
102.32	0.5	101.6	0.7
94.12	0.5	94.2	0.7
100.82	0.5	99.9	0.7
100.02	0.5	101.3	0.7
103.17	0.5	103.05	0.7

CompTM—Results
CompTM v. 1.0.26, 20 Oct 2005, 15:15—Summary

TM X: VP analyzer	
Can Test Method X distinguish among the samples?	Yes
TM Y: D5191	
Can Test Method Y distinguish among the samples?	Yes
Are the TMs correlated?	Yes
Selected bias correction, where Y = a + bx: a = 0, b =1	Class 0
Will a bias correction significantly improve their agreement?	No
Are there sample-specific biases?	No
Cross Method Reproducibility:	
Rxy (D6708, Eq. 22) = 1.7032e00	

X1.2 *Example 2*—A failed Practice D6708 assessment outcome using process in Fig. 5 and ADJD6708:

PPTM and PTM Dataset

Bz Analyzer	Site Precision Std Dev for Bz Analyzer	PTM (D3606)	Site Precision Std Dev for PTM
1.03	0.0125	0.93	0.013
1.04	0.0125	0.945	0.013
0.44	0.0125	0.419	0.013
1.04	0.0125	0.923	0.013
1.04	0.0125	0.968	0.013
1.03	0.0125	0.945	0.013
0.63	0.0125	0.574	0.013
1.25	0.0125	1.18	0.013
1.05	0.0125	0.977	0.013
0.49	0.0125	0.439	0.013
1.25	0.0125	1.171	0.013
1.13	0.0125	1.033	0.013
0.62	0.0125	0.561	0.013
1.15	0.0125	1.091	0.013
0.98	0.0125	0.892	0.013
0.87	0.0125	0.771	0.013
1.17	0.0125	1.082	0.013
1.24	0.0125	1.142	0.013
0.64	0.0125	0.608	0.013
0.79	0.0125	0.667	0.013
0.68	0.0125	0.555	0.013
1.16	0.0125	1.091	0.013
1.18	0.0125	1.129	0.013
0.69	0.0125	0.571	0.013
0.9	0.0125	0.819	0.013
0.91	0.0125	0.827	0.013
0.92	0.0125	0.824	0.013
1.15	0.0125	1.1	0.013
0.91	0.0125	0.831	0.013
0.9	0.0125	0.813	0.013
0.92	0.0125	0.84	0.013
0.93	0.0125	0.84	0.013
0.9	0.0125	0.83	0.013
1.22	0.0125	1.15	0.013

(Failure due to bias detection)
CompTM—Results
CompTM v. 1.0.26, 20 Oct 2005, 15:28—Summary

TM X: Siemens FID	
Can Test Method X distinguish among the samples?	Yes
TM Y: D3606	
Can Test Method Y distinguish among the samples?	Yes
Are the TMs correlated?	Yes
Selected bias correction, where Y = a + bx: a = -7.9765e-02, b =1	Class 1a
Will a bias correction significantly improve their agreement?	Yes
Are there sample-specific biases?	Yes
Are they random?	Yes
A-D test: A2* = 0.263, A2*Crit = 1.035	Not significant