

# Standard Practice for Determining the Site Precision of a Process Stream Analyzer on Process Stream Material<sup>1</sup>

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### INTRODUCTION

When a process stream analyzer is used to monitor or control a process, the results produced by the analyzer are typically used as surrogates for values that would otherwise have been obtained via analyses of process samples using a Primary Test Method (PTM). Successful application of the analyzer requires that the Predicted Primary Test Method Result (PPTMR) produced by the analyzer agrees with the Primary Test Method Result (PTMR) to within some user specified accuracy (bias and precision). To achieve this goal, it is typically necessary to develop a correlation that relates raw, Uncorrected Analyzer Results (UARs) to PTMRs. The correlation and the analyzers performance are then assessed during the analyzer validation to establish the expected agreement between the PPTMR and PTMR. In establishing the correlation, and assessing the performance, it is necessary to know the precision of both the PPTMR and the PTMR. The precision of the PTMRs is established through statistical quality control procedures described in D6299. The precision of the PPTMRs is established via procedures described herein. The techniques used to determine process analyzer site precision can also be used for ongoing quality control of the analyzer measurement system.

### 1. Scope

1.1 This practice describes a procedure to quantify the site precision of a process analyzer via repetitive measurement of a single process sample over an extended time period. The procedure may be applied to multiple process samples to obtain site precision estimates at different property levels

1.1.1 The site precision is required for use of the statistical methodology of D6708 in establishing the correlation between analyzer results and primary test method results using Practice D7235.

1.1.2 The site precision is also required when employing the statistical methodology of D6708 to validate a process analyzer via Practices D3764 or D6122.

1.2 This practice is not applicable to in-line analyzers where the same quality control sample cannot be repetitively introduced. 1.3 This practice is meant to be applied to analyzers that measure physical properties or compositions.

1.4 This practice can be applied to any process analyzer system where the feed stream can be captured and stored in sufficient quantity with no stratification or stability concerns.

1.4.1 The captured stream sample introduction must be able to meet the process analyzer sample conditioning requirements, feed temperature and inlet pressure.

1.4.2 This practice is designed for use with samples that are single liquid phase, petroleum products whose vapor pressure, at sampling and sample storage conditions, is less than or equal to 110 kPa (16.0 psi) absolute and whose D86 final boiling point is less than or equal to  $400^{\circ}$ C (752°F).

Note 1—The general procedures described in this practice may be applicable to materials outside this range, including multiphase materials, but such application may involve special sampling and safety considerations which are outside the scope of this practice.

1.5 The values for operating conditions are stated in SI units and are to be regarded as the standard. The values given in parentheses are the historical inch-pound units for information only.

1.6 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the

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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>

- D86 Test Method for Distillation of Petroleum Products at Atmospheric Pressure
- D3764 Practice for Validation of the Performance of Process Stream Analyzer Systems
- D6122 Practice for Validation of the Performance of Multivariate Online, At-Line, and Laboratory Infrared Spectrophotometer Based Analyzer Systems
- D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
- D6708 Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material
- D7235 Guide for Establishing a Linear Correlation Relationship Between Analyzer and Primary Test Method Results Using Relevant ASTM Standard Practices
- D7278 Guide for Prediction of Analyzer Sample System Lag Times

# 3. Terminology

3.1 Definitions:

3.1.1 *aliquot*, n—portion of sample being tested that is a representative portion of the whole.

3.1.2 *analyzer*, *n*—all piping, hardware, computer, software, instrumentation and calibration model required to automatically perform the analysis of a process or product stream. D6122

3.1.3 *site precision* (R'), n—the value below which the absolute difference between two individual test results obtained under site precision conditions may be expected to occur with a probability of 0.95 (95%). It is defined as 2.77 times the standard deviation of results obtained under site precision conditions. **D6299** 

3.1.4 *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 which may comprise multiple instruments, 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

3.1.5 process analyzer system, n—see analyzer.

3.2 Acronyms:

3.2.1 LPG—liquefied petroleum gas

3.2.2 *PPTMR(s)*—predicted primary test method result(s)

3.2.3 PTM -- primary test method

- 3.2.4 *PTMR(s)*—primary test method result(s)
- 3.2.5 QC-quality control
- 3.2.6 UAR(s)—uncorrected analyzer result(s)

# 4. Significance and Use

4.1 The analyzer site precision is an estimate of the variability that can be expected in a UAR or a PPTMR produced by an analyzer when applied to the analysis of the same material over an extended time period.

4.2 For applications where the process analyzer system results are required to agree with results produced from an independent PTM, a mathematical function is derived that relates the UARs to the PPTMRs. The application of this mathematical function to an analyzer result produces a predicted PPTMR. For analyzers where the mathematical function, that is, a correlation, is developed by D7235, the analyzer site precision of the UARs is a required input to the computation.

4.3 After the correlation relationship between the analyzer results and primary test method results has been established, a probationary validation (see D3764 and D6122) 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. The analyzer site precision is a required input to the probationary validation procedures.

4.3.1 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 PTM then validation is done via D3764. Practice D3764 also applies if the process stream analyzer system uses a different measurement technology from the PTM, provided that the calibration protocol for the direct output of the analyzer does not require use of the PTM.

4.3.2 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 development of the chemometric or multivariate model, then validation of the analyzer is done using Practice D6122.

4.3.3 Both the D3764 and D6122 validation practices utilize the statistical methodology of Practice D6708 to conduct the probationary validation. This methodology requires that the site precision for the PTM and the analyzer site precision be available.

4.4 The procedures described herein also serve as the basis for a process analyzer quality control system. A representative sample of the QC material is introduced into the analyzer system in a repeatable fashion. Such sample introduction permits capturing the effect of the analyzer system operating variables on the UAR and PPTMR output signal from the process analyzer. By comparing the observed analyzer responses to the expected response for the QC sample, the fitness for use of the analyzer system can be determined.

<sup>&</sup>lt;sup>2</sup> 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.