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Standard Practice for Determining the Site Precision of a Process Stream Analyzer on Process Stream Material[1]

This standard is issued under the fixed designation D7808; 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

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 typically 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.

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, 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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***A Summary of Changes section appears at the end of this standard**

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 °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 responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.7 *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]

D86 Test Method for Distillation of Petroleum Products and Liquid Fuels 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, 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
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*—see *analyzer system.*

3.1.3 ~~*analyzer,*~~ *analyzer system, n*—*for equipment used in the analysis of liquid petroleum products and fuels,* all piping, hardware, computer, software, ~~instrumentation and calibration~~ instrument, linear correlation or multivariate model required to ~~automatically perform the analysis of~~ analyze a process or product ~~stream.~~sample; the analyzer system may also be referred to as the analyzer, or the total analyzer system.

3.1.3.1 *Discussion—*
Online analyzers that utilize extractive sampling include sample loop, sample conditioning system and excess sample return system (see Fig. 1 in D3764 for example). Online analyzers that utilize insertion probes include fiber optics and sample probes.

3.1.3.2 *Discussion—*
At-line, field and laboratory analyzers include the instrument and all associated sample introduction apparatuses. ~~D6122~~

3.1.4 *site precision (R'), n*—the value below which the absolute difference between two individual test results obtained under site

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

precision conditions ~~may be~~ is 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.~~exceed about 5 % of the time (one case in 20 in the long run) in the normal and correct operation of the method.

3.1.4.1 *Discussion—*
It is defined as 2.77 times $\sigma_{R'}$, the standard deviation of results obtained under site precision conditions. **D6299**

3.1.5 *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**

3.1.5.1 *Discussion—*
Site precision conditions should include all sources of variation that are typically encountered during normal, long term operation of the measurement system. Thus, all operators who are involved in the routine use of the measurement system should contribute results to the site precision determination. In situations of high usage of a test method where multiple QC results are obtained within a 24 h period, then only results separated by at least 4 h to 8 h, depending on the absence of auto-correlation in the data, the nature of the test method/instrument, site requirements, or regulations, should be used in site precision calculations to reflect the longer term variation in the system. **D6299**

3.1.6 *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* —~~*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.

5. Procedure

5.1 *QC Sample Collection*—The intent of this procedure is to capture samples that are representative of the process stream so that these QC samples can be used to establish and monitor the precision of the analyzer system.

5.1.1 Preferably, capture two QC samples whose property levels represent the bottom and top of the range of analyzer service.

5.1.2 For applications where the sample being analyzed is intended to be free of sediment and water, then the QC sample being analyzed should also be free of sediment and water.

5.1.2.1 Capture the QC sample from a point in the analyzer system after filtration and coalescing have been done

NOTE 2—Ideally, sample capture should be at the boundary between the process analyzer and the local ambient environment, that is, at the exterior wall where the sample enters the process analyzer. Sample capture at the exterior wall of the process analyzer ensures that all variations attributable to the sample conditioning system are accounted for. If sample capture at the exterior wall of the process analyzer is not possible, sample capture should occur as close to the exterior wall of the process analyzer as possible.

5.1.2.2 If filtering and coalescing that is part of the normal treatment for process samples is not done when the QC sample is captured, it needs to be done when the QC sample is introduced into the analyzer. A larger volume of sample will be needed to account for the volume of the filter and coalescer and the required size of the QC sample storage vessel will be increased.

5.1.2.3 Removal of water and other contaminants can improve the QC sample's storage stability.

NOTE 3—Care must be exercised that removal of water and other contaminants does not compromise the integrity of the sample with respect to the measured parameter(s) of interest.

5.1.2.4 Entrained and free water can adversely affect some sample vessel materials of construction.

NOTE 4—Sample vessel used to store QC materials shall be constructed of materials that do not interact with the sample so as to alter measured parameter(s) of interest.

5.1.3 For applications where the sample being analyzed is intended to include sediment or water, or both, then the QC sample should also include sediment or water, or both.

5.1.3.1 For such multiphase QC samples, the sample must be homogenized prior to introduction into the analyzer.

5.1.3.2 A common application of this type would be the measurement of sediment or water, or both, in crude and fuel oil.

5.1.4 The process analyzer system should include a line sample collection facility to permit capture of aliquots of the process stream for analysis by the PTM.

5.1.4.1 The line samples shall be used to assess the validity of the sample collected before starting the process analyzer site precision data collection process.