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

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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 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.

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*

[1] This test method 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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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]

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.

[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.

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 can be used to assess the validity of the sample collected before starting the process analyzer site precision data collection process.

5.1.4.2 Using the line samples permits the PTM site precision determination using the same sample as the process analyzer.

5.1.4.3 The line samples can be used to test the stability of the sample stream during the sample collection process.

5.1.5 This practice assumes the delivery of a stable representative sample from the process through the sample delivery system to the sample vessel.

5.1.6 It is highly preferred to have the process stream quality held constant during the QC sample collection process.

5.1.6.1 If the sample quality collected from a process unit can change during the sample collection process then the QC sample vessel must be equipped with mixers to ensure that the QC sample is homogeneous.

5.1.6.2 Systems where the QC sample is obtained from a finished homogeneous blend stock or other bulk homogeneous QC sample may not require mixing.

5.1.6.3 This practice assumes that post-mixed QC samples do not stratify during storage.

5.1.7 In general, sample shall be collected as close as possible to ambient temperatures.

5.1.8 Collect a minimum QC sample volume sufficient for 20 valid process analyzer analyses for each measured parameter of interest. Twenty (20) valid analyses for each measured parameter of interest translate into 19 degrees of freedom. The collected volume shall take into account any required replicate individual quality control measurements needed to generate a valid result.

NOTE 5—The size of the collected volume is directly related to the introduction flow rate to be employed and the expected sample flush volume required to ensure that the reported process analyzer result represents the introduced sample. The size of the collected volume is also related to the lag time between the sample introduction point and the process analyzer as well as the process analyzer cycle time and response time. See Guide D7278 for details.

NOTE 6—Pure compounds are not recommended for use as site precision samples since they do not represent the inherent variability in sampling of a process stream.

NOTE 7—Quality control samples containing stability additives can potentially impact the process analyzer or laboratory test method, or both.

5.2 *QC Sample Storage:*

5.2.1 The sample storage vessel shall be designed and used so as to have no effect on the measured parameter(s) of interest.

NOTE 8—Knowledge of the process analyzer and PTM test principle is critical when selecting the type and design of the sample vessel.

5.2.1.1 Samples stored above or within 14°C (26°F) of its flash point shall use a zero headspace storage vessel under positive pressure.

5.2.1.2 Samples shall not be exposed to nitrogen or any other blanket gases at a pressure greater than atmospheric pressure.

NOTE 9—This prevents the sample absorbing the blanket gas while in storage and then releasing gases during the analysis. Such outgassing may affect the analytical results obtained.

5.2.1.3 Sample shall be stored at a minimum of 14°C (26°F) above its cloud point.

5.3 *QC Sample Introduction:*

5.3.1 The ideal sample introduction location is the same place where the sample was collected. The ideal sample introduction conditions, such as temperature, pressure, and flow rate, are the same as the collection conditions.

5.3.1.1 Sample volume considerations may necessitate that the sample introduction location is different from the sample collection location.

5.3.1.2 Use of a sample introduction location that differs from the sample collection location shall not introduce any material changes to the sample.

5.3.2 In general, the sample phase during introduction shall be the same as the sample phase during sample collection.

5.3.2.1 At the introduction point samples shall be a single phase, that is, liquid or vapor.

5.3.2.2 For high vapor pressure liquid samples, such as LPG, that are analyzed in the vapor phase, it may be more convenient to collect the required sample volume as a liquid phase sample and then introduce the sample in the vapor phase. A vaporizing apparatus will then be connected between the sample vessel and the sample introduction location. The vaporizing apparatus shall have no material effect on the measuring parameter of interest.

5.3.3 In general, sample shall be collected as close as possible to ambient temperatures.

5.3.3.1 During storage, samples with initial temperatures that differ from the ambient will either heat or cool to the ambient temperature.

5.3.3.2 As samples heat or cool, it is possible that some sample property or properties will change and that these changes may make a material difference in the measurement of the parameter of interest. Such property changes need to be assessed as to their reversibility, or lack thereof, and the feasibility of replicating the collection temperature during introduction. If it is not possible to replicate the sample collection temperature, an effort should be made to determine how the temperature variance biases the results obtained.

5.3.4 In general, the pressure of a liquid sample under storage conditions may be less than the sample pressure at collection.

5.3.4.1 The application of a blanket gas at a pressure exceeding atmospheric pressure may be required so that the sample can be introduced into the process analyzer system.

NOTE 10—Use of blanket gas as a QC sample motive force may adversely affect the precision of volatility property measurements and hence is not recommended.

5.3.4.2 The choice of blanket gas shall be inert to the sample.

5.3.4.3 The application of the blanket gas pressure shall occur immediately before the sample introduction process is to begin. This minimizes the potential for the sample to absorb the blanket gas that could be released during the analysis.

5.3.5 In general, it is desirable to introduce the sample at the same flow rate that the sample is introduced to the process analyzer during normal operating conditions.

5.3.5.1 Sample volume considerations may necessitate the use of a slower sample introduction flow rate. If it is not possible to replicate the normal operating condition sample flow rate introduction flow rate, an effort should be made to determine how the slower introduction flow rate biases the results obtained.

5.4 *QC Data Collection and Analysis:*

5.4.1 QC sample is introduced into the analyzer and analyzed once a day for a period of at least 20 days. A total of 20 valid analyzer results must be collected. If practical, the time of day should be varied so as to randomize any diurnal dependence of analyzer performance.

5.4.2 After introduction of QC sample, allow the analyzer to operate until it reaches steady state (see Practice D3764), that is, until results for consecutive analyses are within the analyzer repeatability. Use the final analyzer result as the daily value for use in calculation of analyzer site precision.

5.4.2.1 If the analyzer precision is being calculated to provide data for use in establishing the correlation between UAR and PTMR using Guide D7235, then the UAR values are used in the calculation of the analyzer site precision.

5.4.2.2 If the analyzer precision is being used to validate the analyzer performance using practices D3764 or D6122, then the PPTMR is used in the calculation of analyzer site precision.

NOTE 11—Once the D7235 correlation is established, the UAR values can be converted to PPTMR values for use in validation via D3764.

5.4.3 Use the procedures described in D6299 to assess the analyzer results for the QC sample. Begin the assessment once 20 results have been obtained.

5.5 *Calculation of Analyzer Site Precision:*

5.5.1 Once 20 valid results have been collected, calculate the mean of the results, and the standard deviation, σ_R>. The analyzer site precision is $2.77*_{\sigma R}$>.

5.5.2 Calculate the analyzer precision for the QC samples at the top and bottom of the analyzer property range. For other property levels, assume the analyzer site precision varies linearly with property level.

5.5.2.1 If μ_t and μ_b are the average values for the top and bottom of range QC samples, and R_t' and R_b' are the corresponding analyzer site precisions, then the analyzer site precision at level p, R_p' is estimated as:

$$m = \frac{R_t' - R_b'}{\mu_t - \mu_b} \Rightarrow b = R_t' - m\mu_t \Rightarrow R_p' = mp + b \quad (1)$$

6. Keywords

6.1 analyzer quality control; analyzer site precision; process analyzer