Designation: D3764 – 22

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. *(2a)* **Correlation for the Same Material**—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), for the same material. *(2b)* **Correlation for Material including Effect from Additional Treatment to the Material**—The PPTMR in *(2a)* can be used as an input to a mathematical model to predict the effect of an additive and/or a blendstock added to a basestock material as measured by a PTM. *(3)* **Probationary Validation**—After the correlation(s) 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.

"Correlation for material including effect from additional treatment to the material" as outlined in this standard is intended primarily to be applied to biofuels where the biofuel material is added at a terminal or other facility and not included in the process stream material sampled by the analyzer at the basestock manufacturing facility. The correlation shall be specific for a constant percentage addition of the biofuels material to the basestock for each model. This practice may not apply for physical properties where the source material for the biofuel material or the denaturant/diluent material used with the biofuel material can significantly affect the finished biofuel's physical property. The user of the standard should investigate the effect of changes to biofuels material blend ratios, biofuels material source material, and blendstock material composition when using this practice. Limits to any of these may need to be applied when the correlation is used.

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).

1.1.1 The degree of agreement described in 1.1 can be either for PPTMRs and PTMRs measured on the same materials, or for PPTMRs measured on basestocks and PTMRs measured on these same basestocks after constant level additivation.

1.1.2 In some cases, a two-step procedure is employed. In the first step, the analyzer and PTM are applied to the measurement of the same blendstock material. If the analyzer employed in Step 1 is a multivariate spectrophotometric analyzer, then Practice D6122 is used to access the agreement between the PPTMRs and the PTMRs for this first step. Otherwise, this practice is used to compare the PPTMRs to the PTMRs measured for this blendstock to determine the degree of agreement. In a second step, the PPTMRs produced in Step 1 are used as inputs to a second model that predicts the results obtained when the PTM is applied to the analysis of the finished blended product. Since this second step does not use analyzer readings, the validation of the second step is done independently. Step 2 is only performed on valid Step 1 results. Note that the second model might accommodate variable levels or multiple material additions to the blendstock.

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. See Guide D7235 for procedures for establishing such correlations.

1.3 This practice assumes any modeling techniques employed have the necessary tuning to mitigate systemic biases between the analyzer PPTMR and PTMR have been applied to the model results. Model form and tuning is not covered by this practice, only the validation of the model output.

1.4 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.

1.5 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 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).

1.6 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.

1.7 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.

1.7.1 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.

1.7.2 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.

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

1.9 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] This practice 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.

Current edition approved April 1, 2022. Published June 2022. Originally approved in 1980. Last previous edition approved in 2019 as D3764 – 19. DOI: 10.1520/D3764-22.