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Standard Practice for Validation of the Performance of Multivariate Online, At-Line, Field and Laboratory Infrared Spectrophotometer, and Raman Spectrometer Based Analyzer Systems¹

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INTRODUCTION

Operation of a laboratory or process stream analyzer system typically involves five sequential activities. (1) **Correlation**—Prior to the initiation of the procedures described in this practice, a multivariate model is derived which relates the spectrum produced by the analyzer to the Primary Test Method Result (PTMR). (1a) **If the analyzer and Primary Test Method (PTM) measure the same material**, then the multivariate model directly relates the spectra to PTMR collected on the same samples. Alternatively (1b) **if the analyzer measures the spectra of a material that is subjected to treatment prior to being measured by the PTM**, then the multivariate model relates the spectra of the untreated sample to the PTMR for the same sample after treatment. (2) **Analyzer Qualification**—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 (3) **Local Validation**—A local validation is performed using an independent but limited set of materials that were not part of the correlation activity. This local validation is intended to demonstrate that the agreement between the Predicted Primary Method Test Results (PPTMRs) and the PTMRs are consistent with expectations based on the multivariate model. (4) **General Validation**—After an adequate number of PPTMRs and PTMRs have been accrued on materials that were not part of the correlation activity and which adequately span the multivariate model compositional space, a comprehensive statistical assessment can be performed to demonstrate that the PPTMRs agree with the PTMRs to within user-specified requirements. (5) **Continual Validation**—Subsequent to a successful local or 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 the PTMRs established during the General Validation is maintained. This practice deals with the third, fourth, and fifth of these activities.

“Correlation where analyzer measures a material which is subjected to treatment before being measured by the PTM” as outlined in this practice can 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 “treatment” shall be a constant percentage addition of the biofuels material to the basestock material. The correlation is deemed valid only for the specific percentage addition and type of biofuel material used in its development.

1. Scope*

1.1 This practice covers requirements for the validation of measurements made by laboratory, field, or process (online or at-line) infrared (near- or mid-infrared analyzers, or both), and Raman analyzers, used in the calculation of physical, chemical, or quality parameters (that is, properties) of liquid petroleum

products and fuels. The properties are calculated from spectroscopic data using multivariate modeling methods. The requirements include verification of adequate instrument performance, verification of the applicability of the calibration model to the spectrum of the sample under test, and verification that the uncertainties associated with the degree of agreement between

*A Summary of Changes section appears at the end of this standard

the results calculated from the infrared or Raman measurements and the results produced by the PTM used for the development of the calibration model meets user-specified requirements. Initially, a limited number of validation samples representative of current production are used to do a local validation. When there is an adequate number of validation samples with sufficient variation in both property level and sample composition to span the model calibration space, the statistical methodology of Practice **D6708** can be used to provide general validation of this equivalence over the complete operating range of the analyzer. For cases where adequate property and composition variation is not achieved, local validation shall continue to be used.

1.1.1 For some applications, the analyzer and PTM are applied to the same material. The application of the multivariate model to the analyzer output (spectrum) directly produces a PPTMR for the same material for which the spectrum was measured. The PPTMRs are compared to the PTMRs measured on the same materials to determine the degree of agreement.

1.1.2 For other applications, the material measured by the analyzer system is subjected to a consistent additive treatment prior to being analyzed by the PTM. The application of the multivariate model to the analyzer output (spectrum) produces a PPTMR for the treated material. The PPTMRs based on the analyzer outputs are compared to the PTMRs measured on the treated materials to determine the degree of agreement.

1.1.3 In some cases, a two-step procedure is employed. In the first step, the analyzer and PTM are applied to the measurement of a blendstock material. 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 produced by addition to the blendstock. If the analyzer used in the first step is a multivariate spectroscopic based analyzer, then this practice is used to access the degree of agreement between PPTMRs and PTMRs. Otherwise, Practice **D3764** is used to compare the PPTMRs to the PTMRs for this blendstock to determine the degree of agreement. Since this second step does not use spectroscopic data, the validation of the second step is done using Practice **D3764**. If the first step uses a multivariate spectrophotometric analyzer, then only samples for which the spectra are not outliers relative to the multivariate model are used in the second step. Note that the second model might accommodate variable levels of additive material addition to the blend stock.

1.2 Multiple physical, chemical, or quality properties of the sample under test are typically predicted from a single spectral measurement. In applying this practice, each property prediction is validated separately. The separate validation procedures for each property may share common features, and be affected by common effects, but the performance of each property

prediction is evaluated independently. The user will typically have multiple validation procedures running simultaneously in parallel.

1.3 Results used in analyzer validation are for samples that were not used in the development of the multivariate model, and for spectra which are not outliers or nearest neighbor inliers relative to the multivariate model.

1.4 When the number, composition range or property range of available validation samples do not span the model calibration range, a local validation is done using available samples representative of current production. When the number, composition range and property range of available validation samples becomes comparable to those of the model calibration set, a general validation can be done.

1.4.1 *Local Validation:*

1.4.1.1 The calibration samples used in developing the multivariate model must show adequate compositional and property variation to enable the development of a meaningful correlation, and must span the compositional range of samples to be analyzed using the model to ensure that such analyses are done via interpolation rather than extrapolation. The Standard Error of Calibration (SEC) is a measure of how well the PTMRs and PPTMRs agree for this set of calibration samples. SEC includes contributions from spectrum measurement error, PTM measurement error, and model error. Sample (type) specific biases are a part of the model error. Typically, spectroscopic analyzers are very precise, so that spectral measurement error is small relative to the other types of error.

1.4.1.2 During initial analyzer validation, the compositional range of available samples may be small relative to the range of the calibration set. Because of the high precision of the spectroscopic measurement, the average difference between the PTMRs and PPTMRs may reflect a sample (type) specific bias which is statistically observable, but which are less than the uncertainty of PPTMR, $U(PPTMR)$. Therefore, the bias and precision of the PTMR/PPTMR differences are not used as the basis for local validation.

1.4.1.3 Based on SEC, and the leverage statistic, the uncertainty of each PPTMR, $U(PPTMR)$ is calculated. During validation, for each non-outlier sample, a determination is made as to whether the absolute difference between PPTMR and PTMR, $|δ|$, is less than or equal to $U(PPTMR)$. Counts are maintained as to the total number of non-outlier validation samples, and the number of samples for which $|δ|$ is less than or equal to $U(PPTMR)$. Given the total number of non-outlier validation samples, an inverse binomial distribution is used to calculate the minimum number of results for which $|δ|$ must be less than $U(PPTMR)$. If the number of results for which $|δ|$ is less than $U(PPTMR)$ is greater than or equal to this minimum, then the results are consistent with the expectations of the multivariate model, and the analyzer passes local validation. The calculations involved are described in detail in Section **11** and **Annex A4**.

1.4.1.4 The user must establish that results that are consistent with the expectations based on the multivariate model will be adequate for the intended application. A 95 % probability is recommended for the inverse binomial distribution calculation.

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.

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