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Standard Practice for Performance-Based Qualification of Spectroscopic Analyzer Systems¹

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INTRODUCTION

Successful use of spectroscopic analyzers involves several activities, including sample introduction, analyzer calibration, and analyzer validation. Many of these activities are covered in separate existing documents, but not necessarily tied together therein. There are also activities not captured in existing documents that are essential for spectroscopic methods. This practice is intended to pull these together for users to employ and show the confidence in an analyzer system.

This practice is not limited to specific analyzers or applications. It does provide certain requirements that analyzers, associated systems, and software must meet.

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1. Scope*

1.1 This practice covers requirements for establishing performance-based qualification of vibrational spectroscopic analyzer systems intended to be used to predict the test result of a material that would be produced by a Primary Test Method (PTM) if the same material is tested by the PTM.

1.1.1 This practice provides methodology to establish the lower/upper prediction limits associated with the Predicted Primary Test Method Result (PPTMR) in 1.1 with a specified degree of confidence that would contain the PTM result (if tested by the PTM).

1.1.2 The prediction limits in 1.1.1 can be used to estimate the confidence that product released using the analyzer system based on a PPTMR that meets PTM-based specification limits will meet PTM-based specification limits when tested by a PTM.

1.2 The practice covers the qualification of on-line, at-line, or laboratory infrared or Raman analyzers used to predict physical, chemical, or performance properties of liquid petroleum products and fuels. Infrared analyzers can operate in the near-infrared (NIR) region, mid-infrared (MIR) region, or both.

1.2.1 This practice applies to all analyzer systems that can meet the performance requirements defined within.

1.2.2 This practice is not limited to analyzers designed by any specific instrument manufacturer.

1.2.3 This practice allows for multiple calibration techniques to create a multivariate model which relates the spectra produced by the analyzer to the corresponding property determined by a PTM. Spectra can be used to predict multiple properties, but the analyzer system performance of each predicted property is qualified individually.

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

1.3 The practice describes procedures for establishing performance requirements for analyzer system applications. The user of this practice must establish written protocols to confirm the procedures are being followed.

1.4 This practice makes use of standard practices, guides, and methods already established in ASTM. Additional requirements are listed within this practice.

1.5 Any multivariate model that meets performance requirements and detects when the spectrum of a sample is an outlier (analysis that represents an extrapolation of the model) or a nearest neighbor distance inlier (a spectrum residing in a gap in the multivariate space) can be used.

1.6 This practice can be used with methods for determining properties of biofuel blends. Three alternative procedures can be used. In all three cases, the qualification of the predicted values for the blend are established and monitored as part of a continual program by application of Practice [D6122](#) or by combined application of Practices [D6122](#) and [D3764](#) (see definition in section 3.2.3).

1.6.1 If the analyzer is used to directly predict a property of the biofuel blend, and both the Primary Test Method Result (PTMR) and Predicted Primary Test Method Result (PPTMR) are measured on the same material, then the analyzer is validated using Practice [D6122](#).

1.6.2 If the analyzer is used to directly predict a property of a blend stock to which a fixed level of biofuel material is added prior to measurement by the PTM, and if the multivariate model correlates the spectrum of the blend stock to the PTMR for the fixed level blend, then the analyzer is validated using Practice [D6122](#).

1.6.3 If the analyzer directly predicts a property of a blend stock to which some amount of biofuel material is later added, then Practice [D6122](#) is used to validate the analyzer performance. If the PPTMR produced by the analyzer is input into a second model to predict the property value for the final blend, based on the PPTMR for the blend stock and the blend level for the biofuel material, then the performance of this second model is validated using Practice [D3764](#).

1.7 *Disclaimer of Liability as to Patented Inventions—Neither ASTM International nor an ASTM committee shall be responsible for identifying all patents under which a license is required in using this document. ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.*

1.8 *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.*

1.9 *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](#)
- [D1265 Practice for Sampling Liquefied Petroleum \(LP\) Gases, Manual Method](#)
- [D2699 Test Method for Research Octane Number of Spark-Ignition Engine Fuel](#)
- [D2700 Test Method for Motor Octane Number of Spark-Ignition Engine Fuel](#)
- [D3764 Practice for Validation of the Performance of Process Stream Analyzer Systems](#)
- [D4057 Practice for Manual Sampling of Petroleum and Petroleum Products](#)
- [D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products](#)
- [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](#)

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.

- D6596 Practice for Ampulization and Storage of Gasoline and Related Hydrocarbon Materials
- D6624 Practice for Determining a Flow-Proportioned Average Property Value (FPAPV) for a Collected Batch of Process Stream Material Using Stream Analyzer Data
- D6708 Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material
- D6792 Practice for Quality Management Systems in Petroleum Products, Liquid Fuels, and Lubricants Testing Laboratories
- D7235 Guide for Establishing a Linear Correlation Relationship Between Analyzer and Primary Test Method Results Using Relevant ASTM Standard Practices
- D7453 Practice for Sampling of Petroleum Products for Analysis by Process Stream Analyzers and for Process Stream Analyzer System Validation
- D7808 Practice for Determining the Site Precision of a Process Stream Analyzer on Process Stream Material
- D7825 Practice for Generating a Process Stream Property Value through Application of a Process Stream Analyzer
- D8146 Guide for Evaluating Test Method Capability and Fitness for Use
- D8321 Practice for Development and Validation of Multivariate Analyses for Use in Predicting Properties of Petroleum Products, Liquid Fuels, and Lubricants based on Spectroscopic Measurements
- E131 Terminology Relating to Molecular Spectroscopy
- E1655 Practices for Infrared Multivariate Quantitative Analysis
- E1866 Guide for Establishing Spectrophotometer Performance Tests

3. Terminology

3.1 Definitions:

- 3.1.1 For definitions of terms and symbols relating to IR spectroscopy, refer to Terminology **E131**.
- 3.1.2 For definitions of terms and symbols relating to multivariate calibration, refer to ~~Practices~~ Practice **E1655** and **D8321**.
- 3.1.3 *accepted reference value (ARV), n*—value that serves as an agreed-upon reference for comparison and that is derived as (1) a theoretical or established value, based on scientific principles, (2) an assigned value, based on experimental work of some national or international organization, such as the U.S. National Institute of Standards and Technology (NIST), or (3) a consensus value, based on collaborative experimental work under the auspices of a scientific or engineering group. **D6596**
- 3.1.4 *analysis, n*—*in the context of this practice*, the process of applying the calibration model to a spectrum, preprocessed as required, so as to estimate a component concentration value or property. **E1655**
<https://standards.iteh.ai/catalog/standards/sist/89601160-7d3a-4550-824a-10edaa1319a7/astm-d8340-21>
- 3.1.5 *analyzer, n*—all piping, hardware, computer, software, instrumentation and calibration model required to automatically perform the analysis of a process or product stream. **D6122**
- 3.1.6 *analyzer system, n*—the complete analyzer system inclusive of the sample loop, sample conditioning unit, analyzer unit, readout instrumentation, and excess sample return system (see Fig. 1 from Practice **D3764** for example). **D3764**
- 3.1.7 *calibration samples, n*—the set of reference samples used for creating a calibration model. Reference component concentration or property values are known (measured by reference method) for the calibration samples and a calibration model is found which relates these values to the spectra during the calibration. **E1655**
- 3.1.8 *check sample, n*—a single pure compound, or a known, reproducible mixture of compounds whose spectrum is constant over time such that it can be used in a performance test. **D6122**
- 3.1.9 *control limits, n*—limits on a control chart that are used as criteria for signaling the need for action or for judging whether a set of data does or does not indicate a state of statistical control. **D6299**
- 3.1.10 *estimate, n*—the value for a component concentration or property obtained by applying the calibration model for the analysis of an absorption spectrum. **E1655**
- 3.1.11 *fit for use, n*—an expression of the adequacy of a test method to provide a precise estimate of the intended parameter with a desired level of confidence at the level of a corresponding specification, regulatory, or manufacturing limit to support compliance decision. **D8146**

3.1.11.1 Discussion—

Fit for use is the effectiveness of an analytical measurement system to adequately meet the precision requirements for the intended application relative to specific limits.

3.1.12 flow-proportioned average property value (FPAPV), *n*—average property value of the collected material in the tank or vessel, calculated by using the flow-proportioned average technique described in the practice of all measurements performed on aliquots of the material while it is flowing into the tank or vessel. **D6624**

3.1.12.1 Discussion—

The term *property* as used in this practice can be the physical, chemical, or performance property measurements as provided by on-line, at-line analyzer systems, or, can be the deviation of such measurements from a desired value.

3.1.13 general validation, *n*—a comprehensive evaluation of the agreement between the PPTMR and the PTMR done on a set of samples that adequately span the multivariate model composition. **D6122**

3.1.14 line sample—a process or product sample which is withdrawn from a sample port in accordance with Practices **D1265**, **D4057**, **D4177**, or **D7453**, whichever is applicable, during a period when the material flowing through the analyzer is of uniform quality and the analyzer result is essentially constant. **D6122**

3.1.14.1 Discussion—

Line Samples are not limited to the sampling practices mentioned in the definition given in Practice **D6122**.

3.1.15 linearly mixable, *adj*—property is deemed to be linearly mixable in a mass or volume measurement unit if the property of the mixed material can be calculated from the quantities and properties of the materials used to produce the mixture. **D6624**

3.1.15.1 Discussion—

The general equations describing this linearly mixable attribute are as follows:

$$P_{MIXED} = \frac{A_1 \cdot P_1 + A_2 \cdot P_2 + A_3 \cdot P_3 + A_4 \cdot P_4 + \dots + A_N \cdot P_N}{A_1 + A_2 + A_3 + A_4 + \dots + A_N} \quad (1)$$

$$A_{MIXED} = A_1 + A_2 + A_3 + A_4 + \dots + A_N \quad (2)$$

where:

A_N = quantity of material, N,

P_N = property of material, N,

P_{MIXED} = property of mixed material, and

A_{MIXED} = quantity of mixed material.

3.1.15.2 Discussion—

The material being mixed can be from the same process stream over time.

3.1.16 local validation, *n*—an evaluation of the agreement between the PPTMR and PTMR done on a set of samples that do not necessarily span the compositional space of the multivariate model so as to demonstrate that the agreement is consistent with expectations based on the multivariate model. **D6122**

3.1.17 multivariate calibration, *n*—an analyzer calibration that relates the spectrum at multiple wavelengths or frequencies to the physical, chemical, or quality parameters. **D6122**

3.1.18 multivariate model, *n*—the mathematical expression or the set of mathematical operations that relates component concentrations or properties to spectra for a set of calibration samples. **D8321**

3.1.19 outlier detection methods, *n*—statistical tests which are conducted to determine if the analysis of a spectrum using a multivariate model represents an interpolation of the model. **D6122**

3.1.20 post-processing, *v*—performing a mathematical operation on an intermediate analyzer result to produce the final result, including correcting for temperature effects, adding a mean property value of the analyzer calibration, and converting into appropriate units for reporting purposes. **D6122**

3.1.21 pre-processing, *v*—performing mathematical operations on raw spectral data prior to multivariate analysis or model

development, such as selecting wave length regions, correcting for baseline, smoothing, mean centering, and assigning weights to certain spectral positions. **D6122**

3.1.22 *primary test method (PTM), n*—the analytical procedure used to generate the reference values against which the analyzer is both calibrated and validated. **D7235**

3.1.23 *primary test method result (PTMR), n*—test result produced from an ASTM or other established standard test method that is accepted as the reference measure of a property. **D6122**

3.1.24 *predicted primary test method result (PPTMR), n*—result from the analyzer system, after application of any necessary correlation, that is interpreted as predictions of what the primary test method results would have been, if it was conducted on the same material. **D6122**

3.1.25 *validation, n*—statistically quantified judgment that the analyzer system or subsystem being assessed can produce predicted PTM results with acceptable precision and bias performance when compared to actual results from a primary test method measurement system for common materials. **D7453**

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *calibration, n*—the practice of creating a univariate or multivariate linear relationship between one or more wavelengths (or wavenumbers) from a set of spectra and a physical, chemical, or a performance property.

3.2.2 *chemical property, n*—the concentration of a select component per unit volume or unit mass of a sample.

3.2.2.1 *Discussion—*

Example: volume percent total aromatics in gasoline.

3.2.3 *liquid petroleum product and fuels, n—for the purposes of this standard, any single-phase liquid material that is produced at a facility in the petroleum and petrochemical industries and will be in whole or in part of a petroleum product; it is inclusive of biofuels, renewable fuels, blendstocks, alternative blendstocks, and additives.*

3.2.4 *performance property, n*—a rating value determined by a test method for a specified characteristic related to the intended use of the sample being tested.

3.2.4.1 *Discussion—*

Example: octane ratings of gasoline. <https://standards.sist/89601160-7d3a-4550-824a-10edaa1319a7/astm-d8340-21>

3.2.5 *physical property, n*—a measurable property that relates a condition of the sample.

3.2.5.1 *Discussion—*

Example: relative density of diesel fuel.

3.3 *Acronyms:*

3.3.1 *ARV*—accepted reference value

3.3.2 *Mid-IR or MIR*—mid-infrared

3.3.3 *MLR*—multiple linear regression

3.3.4 *NIR*—near-infrared

3.3.5 *PCR*—principle component regression

3.3.6 *PLS*—partial least squares regression

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

3.3.8 *PTM*—primary test method

3.3.9 *PTMR(s)*—primary test method result(s)

3.3.10 *SEC*—standard error of calibration

3.3.11 *SQC*—statistical quality control

3.3.12 *VRM*—validation reference material

3.4 *Symbols:*

3.4.1 *h*—leverage statistic

3.4.2 *SEC*—standard error of calibration; *SEC(m)* indicates *SEC* at property level *m*.

3.4.3 *t(p, dof)*—student's T-value at probability *p* for *dof* degrees of freedom.

4. Summary of Practice

4.1 Procedures in existing ASTM standard practices and additional prescriptive requirements are combined, allowing the user to qualify the use of vibrational spectroscopic-based analyzers to predict property values of applicable materials within a specified confidence.

4.1.1 The spectroscopic measurements covered by this practice are not limited to those in standardized test methods.

4.2 The primary purpose of the qualification is to show at a specified confidence that the results from the analyzer system will be within limits when tested by the PTM.

4.3 Statistical tests shall be applied to spectra to detect outliers (samples that are outside the dataset used to create the multivariate model, that is, when samples extrapolate the multivariate model by having compositions outside the calibration range, by having new unmodeled components, or a spectrum is collected at significantly different temperature), and to detect nearest neighbor distance inliers (samples whose spectra are in voids in the multivariate calibration space). PPTMRs for leverage and spectral outliers and nearest neighbor inliers are considered invalid and not included in the performance evaluation. A limit on the amount of invalid results is set. Practice **D6624** requires valid PPTMRs for at least 90 % of the material collected during the batch/blend, and gives direction for estimating property values for the balance of the volume (up to 10 %) that did not have valid data.

4.4 Validation via Practice **D6122** is required to show the degree of agreement between the Primary Test Method Results (PTMR) and Predicted Primary Test Method Result (PPTMR) is consistent with the expectations based on the multivariate model Standard Error of Calibration (SEC).

4.4.1 Validation is required before initial use and as part of a continual program.

5. Significance and Use

5.1 This practice is intended for use by parties interested in releasing product by use of vibrational spectroscopic analyzer systems. It is expected to meet the industry need for a written practical reference describing a scientifically systematic approach to show the degree of confidence and degree of uncertainty in analyzer predicted values in relation to the PTM.

5.2 This is a performance-based practice that relies on the demonstrated quality of the test result and on strict adherence to the referenced standards and the additional requirements in this practice.

5.3 As part of demonstrating performance, this practice incorporates by reference other ASTM standardized practices as key steps in the process.

5.4 There are prescriptive requirements included for this practice.

5.4.1 The practice requires sample temperature to be carefully controlled in analyzer system hardware or that effects of temperature change be compensated in modeling or software.

5.4.2 Outlier detection capability is required for demonstrating the multivariate calibration model is applicable for the analysis of the sample spectrum, that is, that the analysis interpolates the model, that the sample does not contain a statistically significant amount of unmodeled components above a certain limit based on spectral residual statistic and that the sample spectrum does not fall within gap in the multivariate calibration space.

5.5 In order to follow this practice, all criteria must be met.

5.5.1 The user shall investigate the cause of not meeting the practice requirements.

5.5.2 For any nonconformities noticed, the user shall make corrections to the analyzer system or procedures to conform to the requirements of this practice.

6. Apparatus and Considerations for Spectroscopy Measurements

6.1 This practice is applicable to:

6.1.1 Spectroscopic analyzers measuring molecular vibrations by infrared absorption (NIR or mid-IR, or both) and Raman scattering.

6.1.2 Dispersive or Fourier-transform analyzers.

6.2 Analyzer spectral resolution and signal-to-noise (S/N) affect multivariate model performance, and the user needs to consider these in determining the analyzer requirements based on the intended use. The analyzer resolution and S/N must be sufficient to produce PPTMR with adequate precision and accuracy to pass the validation requirements.

6.3 The analyzer shall include a means of demonstrating that it is operating within the vendor's specification.

6.3.1 The analyzer shall incorporate instrument performance tests to demonstrate that it is operating within historically expected limits. <https://standards.iteh.ai/catalog/standards/sist/89601160-7d3a-4550-824a-10edaa1319a7/astm-d8340-21>

6.3.2 The analyzer shall have a means of validating wavelength/frequency precision and accuracy relative to the calibration analyzer.

6.3.2.1 The wavelength/frequency precision must be sufficient to allow spectra to be collected and used in creating a multivariate model that meets or exceeds user's specifications.

6.3.2.2 The wavelength/frequency precision of the analyzer used for calibration and the between analyzer wavelength frequency relative accuracy and reproducibility for any analyzer the model is transferred to must be sufficient to allow analyzers to be validated by Practice [D6122](#).

6.3.3 Ambient temperature changes may affect some spectroscopic measurements. Users may need to maintain constant environments around some analyzers.

6.4 Sample system requirements for on-line and at-line analyzers are as follows.

6.4.1 The sample system shall be designed to provide a representative sample to the analyzer system.

6.4.2 Sample lag time/sample delivery system should be considered if lab sample station and analyzer have a significant lag difference. Practice [D7453](#) is suggested for guidance.

6.4.3 The sample system shall be designed to maintain the sample stream at a single phase and sufficient fluid velocity to make it through the sample system with a reasonable lag time. Practice [D7453](#) is suggested for guidance.