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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 [3-2-33.1.18](#)).

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](#)

[D3700 Practice for Obtaining LPG Samples Using a Floating Piston Cylinder](#)

[D3764 Practice for Validation of the Performance of Process Stream Analyzer Systems](#)

[D4057 Practice for Manual Sampling of Petroleum and Petroleum Products](#)

[D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants](#)

[D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products](#)

[D5842 Practice for Sampling and Handling of Fuels for Volatility Measurement](#)

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.

- 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
- 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~~D8009 Guide for Evaluating Test Method Capability and Fitness for UsePractice for Manual Piston Cylinder Sampling for Volatile Crude Oils, Condensates, and Liquid Petroleum Products
- 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 used in this practice, refer to Terminology D4175.
- 3.1.2 For definitions of terms and symbols relating to IR spectroscopy, refer to Terminology E131.
- 3.1.3 For definitions of terms and symbols relating to multivariate calibration, refer to Practice D8321.
- 3.1.4 *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**
- 3.1.5 *analysis, n*—~~in the context of this practice,~~multivariate spectroscopic measurement, the process of applying the ~~calibration~~multivariate model to a spectrum, preprocessed as required, ~~so as to estimate~~predict a component concentration value or ~~property.~~ property, the prediction being referred to herein as a Predicted Primary Test Method Result (PPTMR). **E1655**D8321
- 3.1.6 *analyzer, n*—~~all see piping, hardware, analyzer system.~~ computer, software, instrumentation and calibration model required to automatically perform the analysis of a process or product stream. **D6122**
- 3.1.7 *analyzer system, n*—~~the complete for equipment in the analysis of liquid petroleum products and fuels,~~ analyzer system inclusive of the sample loop, sample conditioning unit, analyzer unit, readout instrumentation, and excess sample return system (see Fig. 1 from Practice all piping, hardware, computer, software, instrument, linear correlation or multivariate model required to analyze a process or product sample; the analyzer system may also be referred to as the analyzer, or the total analyzer system. **D3764** for example). **D3764**
- 3.1.7.1 *Discussion*—
Online analyzers that utilize extractive sampling include sample loop, sample conditioning system and excess sample return system.
- 3.1.7.2 *Discussion*—
At-line, field and laboratory analyzers include the instrument and all associated sample introduction apparatuses.

3.1.8 calibration, *n*—in multivariate spectroscopic measurement, a process for creating a multivariate model relating component concentrations or sample properties to spectra for a set of known samples, referred to as calibration samples. **D8321**

3.1.9 calibration samples, *n*—in multivariate spectroscopic measurement, the set of reference samples used for creating a calibration model. Reference component concentration or property values are samples with 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; the (PTM) component concentrations or property values that are used for creating a multivariate model. **E1655D8321**

3.1.10 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**

3.1.11 chemical property—a property of a material associated with its elemental or molecular composition. **D8321**

3.1.11.1 Discussion—

Examples of chemical properties include, but are not limited to sulfur content, benzene content, and aromatics content. **D8321**

3.1.12 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**

3.1.13 fit for use, *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; product, system, or service that is suitable for its intended use. **D8146D6624**

3.1.13.1 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. A fit-for-use measurement system provides an estimate of a property with a desired level of confidence that meets the intended use.

3.1.14 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**

3.1.14.1 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.

3.1.15 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:composition space using the statistical methodology of Practice D6708 to demonstrate all required criteria in D6708 are met, and Rxy meets user requirements. **D6122**

3.1.16 line sample—a process or product sample which is process material that can be safely withdrawn from a sample port or associated facilities without significantly altering the property of interest so that the material can be used to perform analyzer system validation; the material is withdrawn in accordance with Practices D1265, D3700, D4057, D4177, D5842 or, D7453, or D8009, whichever is applicable, during a period when the material flowing through the analyzer is of uniform quality and the analyzer result is essentially results are practically constant. **D6122D3764**

3.1.16.1 Discussion—

Line Samples are not limited to the sampling practices mentioned in the definition given in Practice **D6122D3764**.

3.1.17 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**

3.1.17.1 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.

3.1.17.2 Discussion—

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

3.1.18 liquid petroleum product and fuels, n —in relation to multivariate spectroscopic analyzers and process analyzers, 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.

3.1.19 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**

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

3.1.21 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**

3.1.21.1 Discussion—

The multivariate model includes any preprocessing done to the spectra or concentration or properties prior to the development of the correlation between spectra and properties, and any post-processing done to the initially predicted results. **D8321**

3.1.22 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**

3.1.23 performance property, n —a property of a material which measures how well the material functions in its intended use. **D8321**

3.1.23.1 Discussion—

Examples of performance properties include research and motor octane numbers. **D8321**

3.1.24 physical property, n —a property of matter not involving in its manifestation a chemical change. **D8321**

3.1.24.1 Discussion—

Examples of physical properties include, but are not limited to density, melting point, boiling point, vapor pressure, flash point, cloud point, and pour point. **D8321**

3.1.25 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**

3.1.26 pre-processing, v —performing mathematical operations on raw spectral data prior to multivariate analysis or model development, such as selecting wave-length spectral regions, correcting for baseline, smoothing, mean centering, and assigning weights to certain spectral positions. **D6122**

3.1.27 predicted primary test method result(s) (PPTMR), n —result(s) 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. **D3764**

3.1.28 prediction, n —see predicted primary test method result (PPTMR).

3.1.29 *primary test method (PTM)*, *n*—the analytical procedure used to generate the reference values against which the analyzer is both calibrated and validated. **D7235D3764**

3.1.30 *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. **D6122D3764**

~~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**~~

~~3.1.31 *validation*, *n*—for equipment in the analysis of liquid petroleum products and fuels, the statistically quantified judgment that the analyzer system or subsystem being assessed can produce predicted PTM results with subsystem, in conjunction with any correlation applied, can produce acceptable precision and bias performance when compared to actual results from a primary test method measurement system for common materials on the prediction deviations (δ for materials that were not used to develop the correlation). **D7453D3764**~~

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.~~

~~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.~~

3.2 *Acronyms:*

3.2.1 *ARV*—accepted reference value

3.2.2 *Mid-IR or MIR*—mid-infrared

3.2.3 *MLR*—multiple linear regression

3.2.4 *NIR*—near-infrared

3.2.5 *PCR*—principle component regression

3.2.6 *PLS*—partial least squares regression

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

3.2.8 *PTM*—primary test method

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

3.2.10 *SEC*—standard error of calibration

3.2.11 *SQC*—statistical quality control

3.2.12 *VRM*—validation reference material

3.3 *Symbols:*

3.3.1 *h*—leverage statistic

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

3.3.3 *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.