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Standard Practice for
Performance-Based Qualification of Spectroscopic Analyzer Systems[1]

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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.

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.

1.3 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 3.1.18).

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)

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[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**

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
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
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
D8009 Practice 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
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**

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[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.

3.1.5 *analysis, n—in multivariate spectroscopic measurement*, the process of applying the multivariate model to a spectrum, preprocessed as required, to predict a component concentration value or property, the prediction being referred to herein as a Predicted Primary Test Method Result (PPTMR). **D8321**

3.1.6 *analyzer, n*—see *analyzer system.*

3.1.7 *analyzer system, n—for equipment in the analysis of liquid petroleum products and fuels*, 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**

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 samples with known (measured by the PTM) component concentrations or property values that are used for creating a multivariate model. **D8321**

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**

3.1.13 *fit-for-use, n*—product, system, or service that is suitable for its intended use. **D6624**

3.1.13.1 *Discussion*—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 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*—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, D7453, or D8009, whichever is applicable, during a period when the material flowing through the analyzer is of uniform quality and the analyzer results are practically constant. **D3764**

3.1.16.1 *Discussion*—Line Samples are not limited to the sampling practices mentioned in the definition given in Practice D3764.

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:

$$P_{MIXED} = \frac{A_1 \cdot P_1 + A_2 \cdot P_2 + A_3 \cdot P_3 + A_4 \cdot P_4 + \ldots + A_N \cdot P_N}{A_1 + A_2 + A_3 + A_4 + \ldots + A_N} \tag{1}$$

$$A_{MIXED} = A_1 + A_2 + A_3 + A_4 + \ldots + A_N \tag{2}$$

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 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. **D3764**

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. **D3764**

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, in conjunction with any correlation applied, can produce acceptable precision and bias performance on the prediction deviations (δ for materials that were not used to develop the correlation). **D3764**

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.

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.

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.

6.4.4 The optical system of the analyzer can be either of a cell or probe type.

NOTE 1—Some analyzers may not have an associated sample system.

6.5 Sample temperature is critical to vibrational spectroscopic analyzer performance and shall be addressed by one of the following options. Changes in temperature can affect the measured spectral intensities, resulting in changes to property values predicted. Some intensity changes may be compensated for in modeling.

6.5.1 The user needs to establish the effects of temperature for their application. The sample stream is conditioned to within the determined acceptable temperature difference limits from the user-defined specified temperature for the application, according to user-defined accessories for the test. Some analyzer systems or applications, or both, may require tighter temperature control in order to pass Practice D6122 validation.

6.5.1.1 A mathematical correction can be developed to correct spectra or PPTMRs for temperature deviations from a specified temperature. For that sort of correction being applied to the calibration spectra used during model development, the same temperature correction is applied to spectra of samples being analyzed. Corrections can be applied to spectra or PPTMRs when using a model developed using spectra of samples collected at a specified temperature.

6.5.1.2 Effects of temperature fluctuations may be compensated for in the modeling.

6.5.1.3 A study may be conducted to generate data to demonstrate no significant temperature dependence above a user-defined limit.

6.5.2 Proof of the ability to compensate for temperature fluctuations is that Practice D6122 validation passes.

NOTE 2—Temperature differences may affect molar ratios in sample path for infrared or affect the Raman shift.

NOTE 3—Temperature affects both band position and absorptivity for vibrational spectroscopy of condensed material owing to changes in the interactions among the components of the material and due to expansion and contraction (density changes of the assayed volume by the equipment).

NOTE 4—Small temperature differences effect the amount of sample in the IR cell or Raman scattering volume (volumetric expansion/contraction). Large temperature changes cause spectral bandwidth changes and can cause sample phase changes.

NOTE 5—For temperature effect on vibrational spectrum, the density effect can be relatively easily compensated for. But there are other significant effects such as conformational equilibrium (determined by Boltzmann distribution and degeneracy) and hydrogen bonding (consider spectra collected with ethanol, avgas with significant amount of aniline, etc.), which are virtually impossible to compensate for in a fundamental way.

7. Expected Agreement

7.1 The spectroscopic test method precision qualification must be conducted in the form of reproducibility for agreement between the PTMR and PPTMRs.

7.1.1 For analyzers qualified by Practice D6122 general validation, the between-method limits used for comparisons shall be within user-specified agreement to the PTM reproducibility.

7.1.2 For analyzers qualified by Practice D6122 local validation, the uncertainty in the predicted value would have to be within user-specified agreement to the PTM reproducibility.

7.2 Demonstrate performance by meeting Practice D6122 requirements.

7.2.1 For initial validation, the local validation and general validation are both acceptable options.

7.2.1.1 For the local validation, the examples in Practice D6122 Annex A4 is to guide the users in performing preliminary validation, as well as continuing validation.

7.2.1.2 The use of $t * SEC(m) * \sqrt{1+h}$ for local validation is scientifically and statistically sound manner of defining the acceptable limits when comparing results from the spectroscopic method and the PTMR. See Practice D6122 for information on C_{min} for validation.

7.2.2 For Practice D6708, site precision for "fit-for-use" methods can be determined by interlaboratory exchange sample results (example: Test Method D2699).

7.2.2.1 Use the differences from the interlaboratory exchange ARV for a given location calculate the site precision value.

7.2.2.2 Practice D6708 will identify if sufficient variation exists in the general validation sample set.

7.2.3 Analyzer precision is established per Practice D7808 for on-line process analyzers. For laboratory or at-line analyzers, precision would be established by Practice D6299 methodologies. Analyzer precision can be input into Practice D6708 for establishing linear relationship between the PTM and analyzer system.

7.2.3.1 If a bias correction is made due to improve the linear relationship, the validation process starts over.

7.2.4 Practice D7825 provides the workflow related to generating a property value from the process analyzer.

7.2.5 Practice D6122 requires periodic line samples or validation reference materials (VRM) representative of current production to be analyzed for continual validation of the system.

7.2.6 Retained VRMs can be used for initial validation.

7.3 *Acceptance:*

7.3.1 If a user can demonstrate that the performance of the analyzer system and procedures meet the preliminary and continual validation requirements of Practice D6122 in an acceptable manner, and the differences between the PPTMR and the PTMR are within acceptable limits as required, the performance is deemed satisfactory.

7.3.2 If the performance and procedures do not meet the preliminary and continual validation requirements of Practice D6122, or the results are outside the acceptable limits, the performance is not satisfactory.

7.3.2.1 The user shall investigate and bring the system back into control with acceptable performance.

7.3.3 Records of performance shall be maintained and readily available.

7.3.4 Records of testing pertaining to temperature effects demonstrated or no temperature effects is to be maintained and readily available.

NOTE 6—Practice D6792 Section 7 has been suggested for guidance on records.

NOTE 7—See Practice D6122 spreadsheet for an example on local validation.

NOTE 8—See Practice D6708 for an example on general validation.

8. Multivariate Models

8.1 Calibration is the process of developing a multivariate model relating a material's spectral information to the primary test data.

8.1.1 Calibration includes the use of a set of samples to create a model for use with the analyzer system. The size of the sample set is dependent upon the complexity of the sample matrix. See Practice D8321 for guidance on the number of samples needed for the calibration.

8.1.1.1 The user shall validate the performance of the analyzer system for each property per Practice D6122.

8.1.2 Recalibration typically includes the use of a smaller set of samples needed to adjust an analyzer after maintenance has been performed.

8.1.2.1 Recalibration is not the same for each analyzer system. For some, it may add a smaller set of samples to the initial calibration set to expand upon the range of the multivariate model. For others, it can be a model adjustment that does not require the model to be developed again.

8.1.2.2 The user shall validate the performance of each model after recalibration per Practice D6122.

8.1.3 Validation of the analyzer performance for each model after calibration/recalibration shall follow Practice D6122 guidance.

8.1.4 The user should define a period of time for retain samples used for calibration or recalibration, or both. Retained samples shall be stored in a manner to maintain sample integrity to sustain the property of interest. In addition, they should be stored to meet requirements of regulatory bodies.

8.2 Multivariate models can be as a linear regression.

8.2.1 Examples of linear regression include multivariate techniques of multiple linear regression (MLR), partial least squares regression (PLS), and principal component regression (PCR) which develop correlations between spectral data and PTM data.

8.2.2 The multivariate model can be that of a standardized test method, a user/vendor-created global multivariate model, or a user-created site-specific multivariate model.

8.2.2.1 A global multivariate model is one developed by use of samples and data that may represent materials produced at multiple facilities or locations.

NOTE 9—Some locations may start with a global model and add site-specific sample to it.

8.2.2.2 A site-specific multivariate model is one developed by use of samples and data that is limited to a single facility or location.

8.3 Techniques typically applied to developing models can be found in Practice D8321. Alternate techniques that yield results meeting the performance criteria (agreement with PTM and outlier detection) set forth in this practice may also be used.

8.4 All pre- and post-processing steps are considered to be part of the model. The same pre- and post-processing steps must be applied to both the calibration and the analysis spectra.

8.5 Multivariate regression may utilize the complete set of spectra and data. Cross validation can allow for assessing model performance. Cross validation includes options of leave-one-out and leaving multiple spectra out. Cross validation is not a substitution for the validations in Practice D6122.

8.6 *Model Updates:*

8.6.1 Model update frequency is dependent upon model performance.

8.6.1.1 The passing validation procedure is one measure of performance.

8.6.1.2 The frequency of outliers is also a limiting factor, as a maximum of 10 % is allowed as pointed out in 13.3.

8.6.2 When a model update occurs, the validation starts over.

9. Outlier Statistics

9.1 Identification and handling of outliers is important to the success of meeting this performance-based practice. See Practice D8321 for information on outliers, as outliers are to be considered for elimination from the calibration set, and in Practice D6122 where outliers are not used in analyzer validation.

9.2 *Spectral Outliers:*

9.2.1 A spectral outlier is recognized as a sample whose spectrum differs from the spectra of samples in the calibration set by certain criteria. (for example, leverage, spectral residuals, nearest neighbor).

9.2.2 The spectra of the calibration samples define a set of variables that are used in the multivariate model. If, when unknown samples are analyzed, the variables calculated from the spectrum of the unknown sample lie within the range of the variables for the calibration, the predicted value for the unknown sample is obtained by interpolation of the model. If any variable for the unknown sample is outside the range of the variables in the calibration model, the prediction represents an extrapolation of the model. Various related statistics are used to determine whether the spectrum of the unknown sample interpolates or extrapolates the model. These statistics include leverage, Mahalanobis Distance and Hoteling's T-Squared. Outlier limits are set based on the chosen statistic for the calibration set such that any spectrum that exceeds this limit is considered a spectral outlier.

9.2.3 If the spectrum of the sample under test contains spectral features that were not present in the spectra of the calibration samples, then these features represent variables that were not included in the calibration, and the analysis of the sample spectrum represents an extrapolation of the model. Various related spectral residual statistics are in common use. A spectral residuals outlier limit is based on the statistics for the calibration set such that any spectrum that exceeds this limit is considered a spectral outlier.

9.2.4 In some instances, the calibration samples may not be uniformly distributed across the variable space of the model. The calibration may include clusters of samples in variable space as well as voids where there are no samples. A nearest neighbor distance statistic is used to determine if a spectrum being analyzed falls within the clusters or voids in the calibration variable space. Outlier limits are based on the nearest neighbor distance statistic for the calibration set such that any analysis that exceeds this limit is considered a spectral outlier.

9.3 It is permissible for the identification and handling of outliers to be performed by the same software used for generating PPTMR from spectra, if the capabilities are present.

9.4 It is permissible for the identification and handling of outliers to be performed by a separate software package than that used for applying the model to unknown spectra for generation of PPTMRs.

9.5 For analysis of a sample (grab or process on-line) for the purposes of determining property values, the software shall indicate whether the spectrum is identified as an outlier, based on the criteria set by the user. The sample analysis may indicate that expected performance is not reached for a sample identified as an outlier.

NOTE 10—For on-line analyzers, when material is identified as an outlier, locations may want to consider collecting a sample that can be used to learn information on why it is an outlier or for inclusion into a model update.

10. Analytical Approach

10.1 For the lab, all sample handling, testing procedures, and tests must be conducted using good laboratory practices. Practice D6792 is suggested as a guide. Some locations may be familiar with ISO 9000 and use that as a guide.

10.2 For on-line analyzers, the associated sample system and sample conditioning system shall provide a representative sample to the analyzer. Practice D7453 is suggested as a guide.

10.3 For on-line analyzers, the line sample must be representative of the material being analyzed by the online analyzer. Sampling and handling shall follow specific practices that maintain the integrity of the sample and the properties of interest in order to allow for proper assessment of analyzer performance.

11. User Requirements

11.1 The user is expected to maintain documentation and carry out testing to measure properties of petroleum products and meet with the following requirements.