



Designation: ~~D8321–21~~ D8321 – 22

Standard Practice for Development and Validation of Multivariate Analyses for Use in Predicting Properties of Petroleum Products, Liquid Fuels, and Lubricants based on Spectroscopic Measurements¹

This standard is issued under the fixed designation D8321; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This practice covers a guide for the multivariate calibration of infrared (IR) spectrophotometers and Raman spectrometers used in determining the physical, chemical, and performance properties of petroleum products, liquid fuels including biofuels, and lubricants. This practice is applicable to analyses conducted in the near infrared (NIR) spectral region (roughly 780 nm to 2500 nm) through the mid infrared (MIR) spectral region (roughly 4000 cm^{-1} to 400 cm^{-1}). For Raman analyses, this practice is generally applied to Stokes shifted bands that occur roughly 400 cm^{-1} to 4000 cm^{-1} below the frequency of the excitation.

NOTE 1—While the practice described herein deals specifically with mid-infrared, near-infrared, and Raman analysis, much of the mathematical and procedural detail contained herein is also applicable for multivariate quantitative analysis done using other forms of spectroscopy. The user is cautioned that typical and best practices for multivariate quantitative analysis using other forms of spectroscopy may differ from the practice described herein for mid-infrared, near-infrared, and Raman spectroscopies.

1.2 Procedures for collecting and treating data for developing IR and Raman calibrations are outlined. Definitions, terms, and calibration techniques are described. The calibration establishes a multivariate correlation between the spectral features and the properties to be predicted. This correlation is herein referred to as the multivariate model. Criteria for validating the performance of the multivariate model are described. The properties against which a multivariate model is calibrated and validated are measured by Primary Test Methods (PTMs) and the results of the PTM measurement are herein referred to as Primary Test Method Results (PTMR). The analysis of the spectra using the multivariate model produces a Predicted Primary Test Method Result (PPTMR).

1.3 The implementation of this practice requires that the IR spectrophotometer or Raman spectrometer has been installed in compliance with the manufacturer's specifications. In addition, it assumes that, at the time of calibration, validation, and analysis, the analyzer is operating at the conditions specified by the manufacturer. The practice includes instrument performance tests which define the instrument performance at the time of calibration, and which qualify the instrument by demonstrating comparable performance during validation and analysis.

1.4 This practice covers techniques that are routinely applied for online, at-line, and laboratory quantitative analysis. The practice outlined covers the general cases for liquids and solids that are single phase homogeneous samples when presented to the analyzers. Online application is limited by sample viscosity and the ability to introduce sample to the analyzer. All techniques covered require the use of a computer for data collection and analysis.

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

1.5 This practice is most typically applied when the spectra and the PTMR against which the analysis is calibrated are measured on the same sample. However, for some applications, spectra may be measured on a basestock and the PTMR may be measured on the same basestock after constant level additivation.

1.5.1 Biofuel applications will typically fall into three categories.

1.5.1.1 The spectra and the PTM both measure the finished biofuel blend.

1.5.1.2 The spectra are measured on a petroleum derived blendstock, and the PTM measures the same blendstock after a constant level additivation with the biocomponent.

1.5.1.3 The spectra and PTM both measured the petroleum derived blendstock, and the PPTMRs from the multivariate model are used as inputs into a second model which predicts the results obtained when the PTM is applied to the analysis of the finished blended product. The practice described herein only applies to the first of these two models.

1.6 This practice includes a checklist in **Annex A2** against which multivariate calibrations can be examined to determine if they conform to the requirements defined herein.

1.7 For some multivariate spectroscopic analyses, interferences and matrix effects are sufficiently small that it is possible to calibrate using mixtures that contain substantially fewer chemical components than the samples that will ultimately be analyzed. While these surrogate methods generally make use of the multivariate mathematics described herein, they do not conform to procedures described herein, specifically with respect to the handling of outliers. Surrogate methods may indicate that they make use of the mathematics described herein, but they should not claim to follow the procedures described herein. Test Methods **D5845** and **D6277** are examples of surrogate methods.

1.8 *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.

1.9 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.10 *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.*

1.11 *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

[D1265 Practice for Sampling Liquefied Petroleum \(LP\) Gases, Manual Method](#)

[D1319 Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption](#)

[D2699 Test Method for Research 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](#)

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

[D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards](#)

[D5769 Test Method for Determination of Benzene, Toluene, and Total Aromatics in Finished Gasolines by Gas Chromatography/Mass Spectrometry](#)

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.

- D5842 Practice for Sampling and Handling of Fuels for Volatility Measurement
- D5845 Test Method for Determination of MTBE, ETBE, TAME, DIPE, Methanol, Ethanol and *tert*-Butanol in Gasoline by Infrared Spectroscopy
- D6122 Practice for Validation of the Performance of Multivariate Online, At-Line, Field and Laboratory Infrared Spectrophotometer, and Raman Spectrometer Based Analyzer Systems
- D6277 Test Method for Determination of Benzene in Spark-Ignition Engine Fuels Using Mid Infrared Spectroscopy
- D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
- D6792 Practice for Quality Management Systems in Petroleum Products, Liquid Fuels, and Lubricants Testing Laboratories
- D7278 Guide for Prediction of Analyzer Sample System Lag Times
- D7453 Practice for Sampling of Petroleum Products for Analysis by Process Stream Analyzers and for Process Stream Analyzer System Validation
- D7717 Practice for Preparing Volumetric Blends of Denatured Fuel Ethanol and Gasoline Blendstocks for Laboratory Analysis
- D7915 Practice for Application of Generalized Extreme Studentized Deviate (GESD) Technique to Simultaneously Identify Multiple Outliers in a Data Set
- D8009 Practice for Manual Piston Cylinder Sampling for Volatile Crude Oils, Condensates, and Liquid Petroleum Products
- D8340 Practice for Performance-Based Qualification of Spectroscopic Analyzer Systems
- E131 Terminology Relating to Molecular Spectroscopy
- E456 Terminology Relating to Quality and Statistics
- E1655 Practices for Infrared Multivariate Quantitative Analysis
- E1866 Guide for Establishing Spectrophotometer Performance Tests
- E2056 Practice for Qualifying Spectrometers and Spectrophotometers for Use in Multivariate Analyses, Calibrated Using Surrogate Mixtures

3. Terminology

3.1 For terminology related to molecular spectroscopic methods, refer to Terminology **E131**. For terminology relating to quality and statistics, refer to Terminology **E456**. For terminology relating to petroleum products, liquid fuels and lubricants, refer to Terminology **D4175**.

3.2 Definitions:

3.2.1 *absorptivity, n*—the absorbance divided by the product of the concentration of the substance and the sample pathlength, $a = A/(bc)$. The units of *b* and *c* shall be specified. [ASTM D8321-22](https://standards.iteh.ai/catalog/standards/sist/89fda23d-a997-47fc-be8c-a93a32fd5eec/astm-d8321-22) **E131**

<https://standards.iteh.ai/catalog/standards/sist/89fda23d-a997-47fc-be8c-a93a32fd5eec/astm-d8321-22>

3.2.2 *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).*

3.2.3 *analyzer, n—see analyzer system.*

3.2.4 *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**

3.2.4.1 Discussion—

Online analyzers that utilize extractive sampling include sample loop, sample conditioning system and excess sample return system (see Fig. 1 in **D3764** for example). Online analyzers that utilize insertion probes include fiber optics and sample probes.

3.2.4.2 Discussion—

At-line, field and laboratory analyzers include the instrument and all associated sample introduction apparatuses.

3.2.5 *anti-Stokes line (band), n—a Raman line (band) that has a frequency higher than that of the incident monochromatic beam.* **E131**

3.2.6 *attenuated total reflection (ATR), n—reflection that occurs when an absorbing coupling mechanism acts in the process of total internal reflection to make the reflectance less than unity.*

3.2.6.1 Discussion—

In this process, if an absorbing sample is placed in contact with the reflecting surface, the reflectance for total internal reflection

will be attenuated to some value between zero and unity ($0 < R < 1$) in regions of the spectrum where absorption of the radiant power can take place. **E131**

3.2.7 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.

3.2.8 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.

3.2.9 calibration transfer, *n*—a method of applying a multivariate calibration developed using spectra from one analyzer for analysis of spectra collected on a second analyzer by mathematically modifying the multivariate model or by instrument standardization. **D6122**

3.2.10 chemical property, *n*—a property of a material associated with its elemental or molecular composition.

3.2.10.1 Discussion—

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

3.2.11 fluorescence, *n*—the emission of radiant energy from an atom, molecule, or ion resulting from absorption of a photon and a subsequent transition to the ground state without a change in total spin quantum number.

3.2.11.1 Discussion—

The initial and final states of the transition are usually both singlet states. The average time interval between absorption and fluorescence is usually less than 10^{-6} s. **E131**

3.2.12 inlier, *n*—see nearest neighbor distance inlier. **D6122**

3.2.13 inlier detection methods, *n*—statistical tests which are conducted to determine if a spectrum resides within a region of the multivariate calibration space which is sparsely populated. **D6122**

3.2.14 instrument, *n*—for multivariate spectroscopic analyzers used in used in the analysis of liquid petroleum products and fuels, the spectrometer or spectrophotometer, associated electronics and computer, spectrometer, or spectrophotometer cell, and if utilized, transfer optics. **D6122**

<https://standards.iteh.ai/catalog/standards/sist/89fda23d-a997-47fc-be8c-a93a32fd5ecc/astm-d8321-22>

3.2.15 instrument performance verification sample, *n*—for multivariate spectroscopic analyzers used in the analysis of liquid petroleum products and fuels, a material representative of the product being analyzed which is adequately stored in sufficient quantity to be used as a check on instrument performance; instrument performance verification samples are used in instrument performance tests and as checks on calibration transfer, but the samples and their spectra are generally not reproducible long term. **D6122**

3.2.15.1 Discussion—

In **E1866** and previous versions of **D6122** and this practice, an instrument performance verification samples were referred to as test samples.

3.2.16 instrument qualification sample, *n*—for multivariate spectroscopic analyzers used in the analysis of liquid petroleum products and fuels, a single pure compound, or a known, reproducible mixture of compounds whose spectra is constant over time such that it can be used in an instrument performance test. **D6122**

3.2.16.1 Discussion—

In **E1866** and previous versions of **D6122** and this practice, an instrument qualification sample was referred to as a check sample.

3.2.17 instrument standardization, *n*—a procedure for standardizing the response of multiple instruments such that a common multivariate model is applicable for measurements conducted by these instruments, the standardization being accomplished by way of adjustment of the spectrophotometer hardware or by way of mathematical treatment of the collected spectra. **D6122**

3.2.18 liquid petroleum products and fuels, *n*—in relation to 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. **D8340**

3.2.19 model degrees of freedom, (dof), n —the dimension of the multivariate space defined by the number of calibration sample spectra, the number of model variables, and the number of variables used in defining the property level dependence of the Standard Error of Calibration (SEC). **D6122**

3.2.19.1 Discussion—

For a multivariate model that is not mean-centered, $dof = n - k - c$, where n is the number of calibration samples, k is the number of model variables, and c is 0, 1 or 2 depending on whether SEC is level independent, has a linear dependence on property level, or has a power dependence. For a mean-centered model, $dof = n - k - c - 1$.

3.2.20 model variables, n —the independent variables derived from the calibration spectra which are regressed against the calibration sample properties to produce the multivariate model. **D6122**

3.2.20.1 Discussion—

For MLR, the model variables would be the absorbance at the selected wavelengths or frequencies; for PCR or PLS, the model variables are the Principal Components or latent variables.

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

3.2.22 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.

3.2.22.1 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.

3.2.23 nearest neighbor distance inlier, n —the spectrum of a sample not used in the calibration which, when analyzed, resides within a gap in the multivariate calibration space, and for which the result is subject to possible interpolation error. **D6122**

3.2.24 outlier detection limits, n —the limiting value for application of an outlier detection method to a spectrum, beyond which the spectrum represents an extrapolation of the multivariate model. **D6122**

3.2.25 outlier spectrum, n —a spectrum whose analysis by a multivariate model represents an extrapolation of the model. **D6122**

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

3.2.26.1 Discussion—

Examples of performance properties include research and motor octane numbers.

3.2.27 photometer, n —a device so designed that it furnishes the ratio or a function of the ratio, of the radiant power of two electromagnetic beams. The two beams may be separated in time, space, or both. **E131**

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

3.2.28.1 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.

3.2.29 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**

3.2.30 preprocessing, v —performing mathematical operations on raw spectral data prior to multivariate analysis or model development, such as selecting spectral regions, correcting for baseline, smoothing, differentiation, data transformation, mean centering, and assigning weights to certain spectral positions.

3.2.31 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**

3.2.32 primary analyzer, *n*—the analyzer(s) on which calibration spectra are collected for the purpose of building a multivariate model.

3.2.33 primary test method (PTM), *n*—the analytical procedure used to generate the reference values against which the analyzer is both calibrated and validated. **D3764**

3.2.34 primary test method result(s) (PTMR), *n*—test result(s) produced from an ASTM or other established standard test method that is accepted as the reference measure of a property. **D3764**

3.2.35 secondary analyzer, *n*—an analyzer not used in the development of the multivariate model, but which will be used for analysis of new materials.

3.2.36 site precision (*R'*), *n*—the value below which the absolute difference between two individual test results obtained under site precision conditions may be expected to occur with a probability of approximately 0.95 (95 %). It is defined as 2.77 times the standard deviation of results obtained under site precision conditions. exceed about 5 % of the time (one case in 20 in the long run) in the normal and correct operation of the test method.

3.2.36.1 Discussion—

It is defined as 2.77 times σ_R , the standard deviation of results obtained under site precision conditions. **D6299**

3.2.37 site precision conditions, *n*—conditions under which test results are obtained by one or more operators in a single site location practicing the same test method on a single measurement system which may comprise multiple instruments, using test specimens taken at random from the same sample of material over an extended period of time spanning at least a 15 day interval.

3.2.37.1 Discussion—

Site precision conditions should include all sources of variation that are typically encountered during normal, long term operation of the measurement system. Thus, all operators who are involved in the routine use of the measurement system should contribute results to the site precision determination. In situations of high usage of a test method where multiple QC results are obtained within a 24 h period, then only results separated by at least 4 h to 8 h, depending on the absence of auto-correlation in the data, the nature of the test method/instrument, site requirements, or regulations, should be used in site precision calculations to reflect the longer term variation in the system. **D6299**

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3.2.38 spectral intensity, *n*—a generic term referring to either infrared absorbance or Raman scattering intensity. **321-22**

3.2.39 spectral position, *n*—a generic term referring to either wavelength or frequency position in spectrum.

3.2.40 spectrometer, *n*—an instrument for measuring some function of power, or other physical quantity, with respect to spectral position within a spectral range. **E131**

3.2.41 spectrophotometer, *n*—a spectrometer with associated equipment, so designed that it furnishes the ratio, or a function of the ratio, of the radiant power of two beams as a function of spectral position. The two beams may be separated in time, space, or both. **E131**

3.2.42 standard error of calibration (SEC), *n*—a measure of the agreement between PPTMR and PTMR for the samples used in developing a multivariate model.

3.2.42.1 Discussion—

If the model error is level independent, then $SEC = \sqrt{\frac{1}{dof} \sum_{i=1}^n (PPTMR_i - PTMR_i)^2}$, where *dof* is the model degrees of freedom and *n* is the number of calibration samples.

3.2.42.2 Discussion—

If the model error is level dependent, then *SEC* is expressed as a function of *m* which is the average of PPTMR and PTMR, and *SEC(m)* is calculated using a procedure described in Practice **D6122** Annex A4 and in Practice **D8321** Annex A2. **D6122**

3.2.43 Stokes line (band), *n*—a Raman line (band) that has a frequency lower than that of the incident monochromatic beam. **E131**

3.2.44 *test performance index, n*—an approximate measure of a laboratory’s testing capability, defined as the ratio of test method reproducibility (R) to site precision (R’). **D6792**

3.3 *Definitions of Terms Specific to This Standard:*

~~3.3.1 *analysis, n*—in the context of this practice, 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).~~

~~3.3.1 *basestock, n*—in the preparation of a biofuel, the petroleum derived blendstock to which a biocomponent is added.~~

~~3.3.3 *calibration, n*—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.~~

~~3.3.4 *calibration samples, n*—the set of samples with known (measured by the PTM) component concentrations or property values that are used for creating a multivariate model.~~

~~3.3.5 *calibration transfer, n*—a method of applying a multivariate calibration developed using spectra from one analyzer for analysis of spectra collected on a second analyzer by mathematically modifying the multivariate model or by instrument standardization.~~

~~3.3.6 *check sample, n*—in the context of this practice, a check sample is a material that is representative of the product being analyzed which is adequately stored in sufficient quantity to be used as a long-term check on analyzer performance; check samples are used for Level B instrument performance tests, and as checks on calibration transfer.~~

~~3.3.7 *chemical property, n*—a property of a material associated with its elemental or molecular composition.~~

~~3.3.7.1 *Discussion*—~~

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

~~3.3.2 *combination band, n*—in vibrational spectroscopy, a spectral band that are observed in the vibrational spectrum of a molecule when two or more fundamental vibrations are excited, or multiply excited simultaneously.~~

~~3.3.3 *cross-validation, n*—an exploratory data analysis tool which provides an assessment the optimal number of variables to use in a multivariate model and estimates the model’s ability to predict new data not used in development of the model.~~

~~3.3.3.1 *Discussion*—~~

~~Cross-validation involves a repetitive procedure in which a calibration sample set is partitioned into two subsets, a training set which is used to develop a multivariate model, and a testing set which is analyzed using this model. The procedure repeats using different partitions and the results are combined to estimate the model’s predictive performance.~~

~~3.3.3.2 *Discussion*—~~

~~Cross-validation is a useful tool in guiding the development of the multivariate model, but it is not a substitute for validation of the model with an independent set of validation samples.~~

~~3.3.4 *fundamental band, n*—in vibrational spectroscopy, a spectral band that occurs in the spectrum of a molecule when that molecule makes a transition from the ground ($v = 0$) to first excited state ($v = 1$), where v is the vibrational quantum number.~~

~~3.3.5 *homoscedastic, n*—a condition where all the model errors have the same finite variance.~~

~~3.3.12 *inlier, n*—see *nearest neighbor distance inlier*. **D6122**~~

~~3.3.13 *inlier detection methods, n*—statistical tests which are conducted to determine if a spectrum resides within a region of the multivariate calibration space, which is sparsely populated. **D6122**~~

~~3.3.14 instrument, *n*—for the purpose of this practice, the word instrument will be used describe all parts of the analyzer system that are associated with the spectral measurement but will exclude all parts of the analyzer associated with sampling and sample conditioning.~~

~~3.3.15 instrument standardization, *n*—a procedure for standardizing the response of multiple instruments such that a common multivariate model is applicable for measurements conducted by these instruments, the standardization being accomplished by way of adjustment of the spectrophotometer hardware or by way of mathematical treatment of the collected spectra. **D6122**~~

3.3.6 mean center, *v*—to scale a set of data by subtracting the mean value of the set.

3.3.6.1 Discussion—

To mean center spectra, calculate the average spectrum, and then subtract this average from each individual spectrum.

~~3.3.17 model degrees of freedom, (*dof*), *n*—the number of calibration samples minus the number of model variables where the mean counts as a variable for mean centered models.~~

~~3.3.18 model variables, *n*—the independent variables upon which a multivariate model is based.~~

~~3.3.18.1 Discussion—~~

~~The model variables may be spectral intensity at individual spectral positions for MLR, principle components for PCR, or latent variables for PLS. **D6122**~~

3.3.7 model validation, *n*—the process of testing a multivariate model with validation samples to determine accuracy and precision of the PPTMR produced by the model relative to the PTMR.

3.3.8 model validation samples, *n*—a set of samples used in validating the model which are not part of the set of calibration samples, and for which PTMRs are compared to PPTMRs.

3.3.8.1 Discussion—

This practice uses the phrase model validation samples to distinguish these from the validation samples defined in Practice **D6122** used in validating analyzer performance.

~~3.3.21 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.~~

~~3.3.21.1 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.~~

~~3.3.22 nearest neighbor distance inlier, *n*—a spectrum residing within a gap in the multivariate calibration space, the result for which is subject to possible interpolation error. **D6122**~~

~~3.3.23 outlier detection limits, *n*—the limiting value for application of an outlier detection method to a spectrum, beyond which the spectrum represents an extrapolation of the multivariate model. **D6122**~~

~~3.3.24 outlier spectrum, *n*—a spectrum whose analysis by a multivariate model represents an extrapolation of the model. **D6122**~~

3.3.9 overtone band, *n*—in vibrational spectroscopy, a spectral band that occurs in the vibrational spectrum of a molecule when the molecule makes a transition from the ground state ($v = 0$) to an excited state higher than the first excited state ($v > 1$), where v is the vibrational quantum number.

3.3.9.1 Discussion—

Because of anharmonicity, the frequency at which an overtone occurs will typically be less than $v-1$ times the frequency of the fundamental vibration.

3.3.9.2 Discussion—

The intensity of overtones (absorbance or Raman scattering) decreases significantly as the vibrational quantum number increases.

~~3.3.26 performance property, *n*—a property of a material which measures how well the material functions in its intended use.~~

~~3.3.26.1 Discussion—~~

~~Examples of performance properties include research and motor octane numbers.~~

3.3.10 *physical correction, n*—a type of post-processing where the correction made to the numerical value produced by the multivariate model is based on a separate physical measurement of, for example, sample density, sample path length, or particulate scattering. **D6122**

~~3.3.28 physical property, n—~~a property of matter not involving in its manifestation a chemical change.

~~3.3.28.1 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.~~

~~3.3.29 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, differentiation, data transformation, mean centering, and assigning weights to certain spectral positions. **D6122**

~~3.3.30 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**

~~3.3.31 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**

~~3.3.32 primary instrument, n—~~the instrument(s) on which calibration spectra are collected for the purpose of building a multivariate model.

~~3.3.33 primary test method (PTM), n—~~the analytical procedure used to generate the reference values against which the analyzer is both calibrated and validated. **D6122**

~~3.3.34 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**

~~3.3.35 secondary instrument, n—~~an instrument not used in the development of the multivariate model, but which will be used for analysis of new materials.

~~3.3.36 spectral intensity, n—~~a generic term referring to either infrared absorbance or Raman scattering intensity.

~~3.3.37 spectral position, n—~~a generic term referring to either wavelength or frequency position in spectrum.

~~3.3.38 standard error of calibration (SEC), n—~~a measure of the agreement between PPTMR and PTMR for the samples used in developing a multivariate model,

$$SEC = \sqrt{\frac{1}{dof} \sum_{i=1}^n (PPTMR_i - PTMR_i)^2}, \text{ where } dof \text{ is the model degrees of freedom and } n \text{ is the number of calibration samples. } \mathbf{D6122}$$

~~3.3.11 standard error of cross-validation, n—~~an estimate of the performance of a multivariate model obtained using cross-validation.

3.3.12 *standard error of validation (SEV), n*—a measure of the performance of a multivariate model obtained by analyzing a set of model validation samples and comparing the PPTMR to PTMR measured on these samples.

3.3.12.1 *Discussion—*

$$SEV = \sqrt{\frac{1}{v} \sum_{i=1}^v (PPTMR_i - PTMR_i)^2} \text{ where } v \text{ is the number of model validation samples.}$$

3.3.13 *surrogate calibration, n*—a multivariate calibration that is developed using a calibration set which consists of mixtures which contain substantially fewer chemical components than the samples which will ultimately be analyzed.

3.3.14 *surrogate method, n*—a standard test method that is based on a surrogate calibration.

3.3.15 *vibrational spectroscopy, n*—infrared and Raman spectroscopies which involve the measurement of vibrational transitions in molecules.

3.3.16 *X-block, n*—the spectral data matrix used in the calibration or validation of a multivariate model.

3.3.17 *Y-block, n*—the component concentration or property data matrix using in the calibration or validation of a multivariate model.

3.4 Symbols:

3.4.1 Scalars are represented by italicized normal face letters. Vectors are represented by boldface italicized lowercase letters. Matrices are represented by boldface italicized uppercase letters. Lower case *i* and *j* as subscripts are indices indicating specific samples, spectral positions, or model variables.

3.4.2 ⁻¹— a minus 1 as a superscript indicates a matrix inverse.

3.4.3 $a(\lambda)$ —sample absorbance at wavelength λ .

3.4.4 $a(\lambda)$ —the absorptivity of the absorbing species at wavelength λ .

3.4.5 a —an absorbance spectrum.

3.4.6 \underline{A} —a c by f matrix with component spectra as rows, used in the matrix form of the Beer-Lambert Law.

3.4.7 b —the pathlength (sample thickness).

3.4.8 b —a single beam background spectrum.

3.4.9 \underline{B} —an n by n diagonal matrix of pathlengths for the matrix form of the Beer-Lambert Law.

3.4.10 c —the number of absorbing or scattering components in a sample.

3.4.11 \underline{c} —concentration of absorbing or scattering species.

3.4.12 \underline{C} —an n by c matrix of component concentrations in the matrix form of the Beer-Lambert Law.

3.4.13 \underline{e} —an n by 1 vector of property prediction errors.

3.4.14 \underline{e}_{cv} —an n times l by 1 vector of property prediction errors produced during cross-validation when only one property is modeled.

3.4.15 \underline{E} —an n by p matrix of property prediction errors.

3.4.16 \underline{E}_{cv} —an n times l by p vector of property prediction errors produced during crossvalidation when multiple properties are modeled.

3.4.17 f —the number of spectral positions in the spectral data used in a model.

- 3.4.18 I_o —in a Raman measurement, the power of the incident laser.
- 3.4.19 I_R —in a Raman measurement, the intensity of the scattered light.
- 3.4.20 l —during cross-validation, the number of times each sample is left out of the model construction and analyzed.
- 3.4.21 n —the number of calibration samples.
- 3.4.22 k —the number of variables used in a model, where variables may be, for example selected spectral data points for MLR, Principal Components for PCR, or latent variables for PLS.
- 3.4.23 K —a term in the Raman scattering equation that includes the solid angle visible to the Raman collection optics, and the volume of the sample that is illuminated by the laser and visible to the collection optics.
- 3.4.24 p —the number of properties being modeled.
- 3.4.25 \underline{p} —the f by 1 prediction vector.
- 3.4.26 \underline{P} —the f by p prediction matrix with \underline{p} for individual properties as columns.
- 3.4.27 $PRESS$ —the Predicted Residual Error Sum of Squares from cross-validation.
- 3.4.28 r —number of replicate PTM measurements.
- 3.4.29 s —a single beam sample spectrum.
- 3.4.30 $t(\lambda)$ —the transmittance of a sample at wavelength λ .
- 3.4.31 t —a transmittance spectrum equal to the ratio of s to b .
- 3.4.32 $'$ —as a superscript, indicates a vector or matrix transpose.
- 3.4.33 σ_R —the Raman scattering cross section for the scattering species.
- 3.4.34 ν —a vibrational energy level quantum number.
- 3.4.35 x_i —a 1 by f row vector containing the spectrum of the i^{th} sample.
- 3.4.36 x_{unk} —a 1 by f row vector containing the spectrum of the unknown sample being analyzed.
- 3.4.37 X —the spectral data matrix which contains the n spectra as rows of length f , also referred to as the model X-Block.
- 3.4.38 \bar{x} —the average spectrum; the average down the columns of X .
- 3.4.39 \hat{x} —the estimate of a spectrum based on the multivariate model.
- 3.4.40 X^- —an n by f matrix where each of the n rows contain \bar{x} used in mean centering X .
- 3.4.41 y_i —the PTMR value for a single property for the i^{th} sample.
- 3.4.42 \hat{y}_i —the PPTMR value for a single property for the i^{th} sample.

3.4.43 y —an n by 1 vector of PTMR values, also referred to as the model Y-Block; y contains the PTMR values for a single property for all the samples defined in the X-Block.

3.4.44 y^- —The average of the values in y .

3.4.45 \hat{y} —an n by 1 vector of PPTMR values; \hat{y} contains the PPTMR values for a single property for all the samples defined in the X-Block.

3.4.46 \hat{y}_{cv} —an n times l by 1 vector of estimated PPTMR values produced during cross validation when a single property is modeled.

3.4.47 Y —an n by p matrix of PTMR values, each column of which correspond to a y vector for a different property.

3.4.48 \hat{Y} —an n by p matrix of PPTMR values, each column of which correspond to a \hat{y} vector for a different property.

3.4.49 \hat{Y}_{cv} —an n time l by p matrix of estimated PPTMR values produced during cross validation when multiple properties are modeled; each column of which correspond to a \hat{y}_{cv} vector for a different property.

3.4.50 z_i —the transform of m_i ; $z_i = \max(m_i) - m_i$.

3.4.51 z^-_j —the transform of m^-_j ; $z^-_j = \max(m^-_j) - m^-_j$.

4. Summary of Practice

4.1 Multivariate mathematics is applied to correlate the spectra measured for a set of calibration samples to component concentrations or property values for the set of samples. The resultant multivariate model is applied to the analysis of spectra of unknown samples to predict the component concentration or property values for the unknown sample.

4.1.1 This practice applies to both infrared and Raman spectra. The infrared spectra are collected in the mid-infrared spectral region, the near-infrared spectral region or, in some cases, in an extended region that covers part of both the mid- and near-infrared.

4.1.2 The component concentrations and property values which are used in establishing and validating the multivariate model are measured by a Primary Test Method (PTM), typically an ASTM standard test method. The values are herein referred to as Primary Test Method Results (PTMR).

4.1.3 The predicted results produced by application of the model for the analysis of a spectrum are referred to as Predicted Primary Test Method Results (PPTMR).

4.2 Multilinear regression (MLR), principal components regression (PCR), partial least squares (PLS) and locally weighted regression (LWR) are examples of multivariate mathematical techniques that are commonly used for the development of the multivariate model. Other mathematical techniques are also used, but may not detect outliers, and may not be validated by the procedure described in this practice. It is the user's responsibility to verify that the mathematics employed satisfy the requirements of this practice.

4.3 Statistical tests are applied to detect outliers during the development of the multivariate model. Outliers include high leverage samples (samples whose spectra contribute a statistically significant fraction of one or more of the spectral variables used in the model), samples with high spectral residuals (suggestive of unmodeled components) and samples whose PTMR values are inconsistent with the model.

4.4 Validation of the multivariate model is performed by using the model to analyze a set of model validation samples and statistically comparing the PPTMR values for the model validation samples to PTMR values measured for these samples, to test for bias in the model and for the degree of agreement of the model with the PTM.

4.5 Statistical tests are applied to detect when PPTMR produced by application of the model represent extrapolation of the

calibration. A spectrum is labeled an outlier if its leverage exceeds that of the calibration samples, or if the spectrum produces high spectral residuals suggesting the presence of components which were not in the calibration samples. Optionally, a nearest neighbor outlier test may be employed to determine if the spectrum being analyzed falls in a void in the multivariate space defined by the calibration spectra.

4.6 Statistical expressions for calculating the repeatability of the spectroscopic analysis and the expected agreement between the spectroscopic analysis and the PTM are given.

5. Significance and Use

5.1 This practice can be used to establish the validity of the results obtained by an infrared (IR) spectrophotometer or Raman spectrometer at the time the calibration is developed. The ongoing validation of PPTMRs produced by analysis of unknown samples using the multivariate model is covered separately (see for example, Practice [D6122](#)).

5.2 The multivariate calibration procedures define the range over which measurements are valid and demonstrate whether the accuracy and precision of the analysis outputs meet user requirements.

5.3 This practice describes sampling procedures that must be followed to ensure that the sample which is analyzed by the spectrophotometer or spectrometer is the same as the sample analyzed by the PTM. The sampling procedures apply to analyses done on lab analyzers, at-line analyzers, and online analyzers.

6. Vibrational Spectroscopies

6.1 Both infrared and Raman spectroscopies measure signals associated with molecular vibrations. Various groups of bonded atoms in molecules give rise to vibrations that occur at characteristic frequencies. These groups of bonded atoms are referred to as functional groups, and the characteristic frequencies as functional group frequencies. While each compound will have a unique spectrum, in complex mixtures such as petroleum samples, the overlap of these spectra often precludes identification of individual molecular components.

6.1.1 Infrared spectroscopy measures the absorption of infrared light by molecules. Light from a broad band source is incident on the sample being measured. As the light passes through the sample, the intensity of the light at the functional group frequencies is reduced, the amount of the reduction being proportional to the concentration of the functional group. The absorption of the light induces vibrational excitation of the bonded atoms in the functional group.

6.1.1.1 Since the light incident on the sample cannot be directly measured, an infrared spectrum typically involves the collection of two separate single-beam spectra, a background, b , and a sample spectrum, s . The background is measured when there is no sample present in the infrared beam. The single-beam spectrum of the sample is ratioed (divided by) the single-beam background to produce a transmission spectrum, t . The transmission spectrum is converted to an absorbance spectrum, a , using a negative logarithm base 10.

$$t = sb \tag{1}$$

$$a = -\log_{10} t \tag{2}$$

6.1.2 Raman spectroscopy measures the inelastic scattering of light by molecules. Raman uses a monochromatic light source, typically a laser. The light interacts with molecular vibrations resulting in the frequency of the scattered light being shifted up or down by an amount corresponding to molecular vibration frequencies.

6.1.2.1 The interaction may transfer energy from the light to the molecule, thereby reducing the frequency of the scattered light relative to the laser frequency (Stokes scattering), or it may transfer energy from a molecule in an excited vibrational state to the scattered light, thereby increasing the frequency of the scattered light relative to the laser frequency (anti-Stokes scattering). Since the number of molecules in an excited vibrational state is always lower than the number in the ground vibrational state, anti-Stokes Raman is always weaker in intensity than Stokes Raman, the difference getting bigger as the frequency of the vibration increases. For this reason, Raman analyzer applications typically use Stokes Raman scattering.

6.1.2.2 Raman scattering is an inherently weak process. Only about 1 in 10 million of the scattered photons are scattered inelastically, most being scattered elastically with no frequency change (Rayleigh scattering). Therefore, Raman analysis is typically limited to materials that do not fluoresce significantly when exposed to the monochromatic light.

6.2 Molecules exhibit a manifold of vibrational energy levels.

6.2.1 Fundamental vibrations occur when molecules are excited from the vibrational ground state ($v=0$) to the first excited vibrational state ($v=1$), where v is the vibrational quantum number. Raman spectroscopy typically deals with vibrational fundamentals. Vibrational fundamentals occur in the mid-infrared region. Bands due to aliphatic C-H vibrations in petroleum are typically too strong to measure in transmission with cell pathlengths suitable for process analyzers but can be measured using attenuated total reflection (ATR). ATR is not commonly used for process measurements.

6.2.2 Overtone bands occur when a single vibration is excited from the vibrational ground state ($v=0$) to a higher vibrational level ($v>1$). The first overtone corresponds to a transition from $v=0$ to $v=2$. The n^{th} overtone corresponds to a transition from $v=0$ to $v=n+1$. The frequencies of the overtones will be less than $n+1$ times the fundamental frequency, the difference becoming larger as n increases.

6.2.3 Combination bands occur when two or more vibrations are excited simultaneously. Combination bands may involve multiple excitation of one or more of the combined vibrations.

6.3 Most fundamental bands occur in the mid-infrared region. All bands in the near-infrared region are overtones or combination bands, but some overtones and combination bands also occur in the mid-infrared region.

6.3.1 For example, the 910 cm^{-1} to 670 cm^{-1} region of the mid-infrared contain many fundamental vibrations associated with out-of-plane bending vibrations of aromatic C-H bonds. These bands are often too intense to measure in transmission with cell pathlengths suitable for process analysis, and this region is blocked by the absorption of some transmission cell window materials. Some overtones and combination bands of these aromatic C-H vibrations occur between 2000 cm^{-1} and 1667 cm^{-1} and can be measured using 0.25 mm to 0.5 mm transmission cells

6.4 For overtones and combinations, as the excitation level increases, the strength of the infrared absorbance (the absorptivity) decreases significantly. Thus, the pathlength necessary to measure the spectrum as one moves out to higher and higher overtone/combination band levels increases significantly. Table 1 shows some example pathlengths for mid-infrared and near-infrared measurements of petroleum products, liquid fuels and lubricants. The pathlengths listed typically produce C-H aliphatic stretching vibration peaks with absorbance less than 1.0. Pathlengths used for specific applications may vary. Pathlengths should be selected to maximize the absorbance and thus spectral signal-to-noise within the linear response range of the instrument.

7. Instrumentation

7.1 A complete description of all applicable types of infrared and Raman analyzers is beyond the scope of this practice. Only a general outline is given here. Instrumental performance criteria which are critical to successful multivariate application are discussed.

7.2 The analyzers fall into two categories, including systems that acquire continuous spectral data over wavelength or frequency ranges (spectrophotometers and spectrometers), and those that only examine one or several discrete wavelengths or frequencies (photometers).

7.2.1 Photometers may have one or a series of wavelength filters and a single detector. These filters are mounted on a turret wheel so that the individual wavelengths are presented to a single detector sequentially. Continuously variable filters may also be used

TABLE 1 Example Pathlengths for MIR and NIR Measurements

Region	Nominal Pathlength	Measures	Frequency / Wavelength
Mid-IR	<10 microns	Hydrocarbon Fundamentals	4000 cm^{-1} to 400 cm^{-1}
Mid- and Near-IR	0.25 mm to 0.5 mm	Hydrocarbon Overtones & Combination Bands, heteroatom fundamentals	2.5 microns to 25 microns 5000 cm^{-1} to 1000 cm^{-1}
Near-IR	2 mm	Hydrocarbon 1 st Overtones	2 microns to 10 microns 6400 cm^{-1} to 5000 cm^{-1}
Near-IR	1 cm	Hydrocarbon 2 nd Overtones and Combination Bands	1562.5 nm to 2000 nm 9200 cm^{-1} to 6400 cm^{-1}
Near-IR	10 cm	Hydrocarbon 3 rd Overtones and Combination Bands	1087 nm to 1562.5 nm 12000 cm^{-1} to 9200 cm^{-1} 833.3 nm to 1087 nm

in this fashion. These filters, either linear or circular, are moved past a slit to scan the wavelength being measured. Alternatively, photometers may have several monochromatic light sources, such as light-emitting diodes, that sequentially turn on and off.

7.2.1.1 For spectral data collected using photometers, the number of data points per spectrum is typically limited, and models are typically built using MLR. Such models do not produce spectral residual outlier statistics and are thus less capable of detecting new components in unknowns which were not in the calibration samples.

7.2.2 Spectrophotometers and spectrometers can be classified based upon the procedure by which light is separated into component wavelengths. Dispersive instruments generally use a diffraction grating to spatially disperse light into a continuum of wavelengths. Dispersion can occur before the sample (pre-dispersed) or after the sample (post-dispersed).

7.2.2.1 In scanning-grating systems, the grating is rotated so that only a narrow band of wavelengths is transmitted to a single detector at any given time.

7.2.2.2 Spectrophotometers and spectrometers are also available where the wavelength selection is accomplished without moving parts, using an array detector. Post-dispersion is utilized. A grating can provide this function, although other methods, such as a linear variable filter (LVF) accomplish the same purpose (an LVF is a multilayer filter that has variable thickness along its length, such that different wavelengths are transmitted at different positions). The array detector is used to acquire a continuous spectrum over wavelength without mechanical motion. The array detector is a compact aggregate of up to several thousand individual photodiode detectors. Each photodiode is in a different spectral region of the dispersed light beam and detects a unique range of wavelengths.

7.2.2.3 An additional category of spectrophotometers and spectrometers use mathematical transformations to convert modulated light signals into spectral data. The most well-known example is the Fourier transform, that when applied to infrared (IR) is known as FT-IR. In an interferometer, light is divided into two beams whose relative paths are varied by use of a moving optical element (for example, either a moving mirror, or a moving wedge of a high refractive index material). The beams are recombined to produce an interference pattern that contains all the wavelengths of interest. The interference pattern is mathematically converted into spectral data using the Fourier transform. The FT method can operate in the mid-IR and near-IR spectral regions. FT instruments use a single detector. In FT-Raman, the laser excited sample serves as the source for scattered light entering the interferometer.

7.3 Analyzers used in developing and applying multivariate models should be installed and operated in accordance with the instructions of the analyzer manufacturer. The performance of the instrument should be tested at the time the calibration is conducted using appropriate instrument performance tests (see Guide E1866). The performance of the analyzer should be monitored on a periodic basis using the same procedures. The monitoring procedure should detect changes in the performance of the instrument (relative to that seen during collection of the calibration spectra) that would affect the prediction made with the multivariate model.

7.4 Spectral axis reproducibility is critical for successful multivariate spectroscopic analyses. Multivariate modeling procedures assume that a change in intensity at a certain spectral position is always due to the same set of sample molecular components. If the collected spectra move across the spectral axis, then model performance is degraded.

7.4.1 If the spectral axis shifts during calibration sample spectra collection, then the resultant model will generally have lower precision than one that would be obtained with a reproducible spectral axis.

7.4.2 If the spectral axis shifts between the time the calibration was developed and the time unknowns are being analyzed, then the PPTMR values will typically be biased relative to the PTMR, and samples within the calibration range may be flagged as outliers.

7.4.3 If calibrations are to be used on more than one analyzer, then either the model must be adapted to compensate for spectral axis differences among the analyzers (calibration transfer), or the analyzers must be standardized to have common spectral axes to within the spectral axis precision of the calibration analyzer (instrument standardization). The spectral axes among analyzers may be adjusted in hardware or software to obtain adequate reproducibility.

7.4.4 Instrument performance tests should include a check of spectral axis registration.

7.5 Spectral absorbance or scattering intensity reproducibility is also critical for successful multivariate spectroscopic analysis.