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.

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Standard Practice for Development and Validation of Multivariate Analyses for Use in Predicting Properties of Petroleum Products, Liquid Fuels, and Lubricants based on Spectroscopic Measurements[1]

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 40 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.

1.5 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] 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

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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

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:*

[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.

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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. **E131**

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 (O < 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**

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

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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, $dof = n\text{-}k\text{-}c$, 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, $dof = n\text{-}k\text{-}c\text{-}1$.

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 is expected to 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 $\sigma_{R'}$, 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**

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

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

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.

3.3.6 *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.

3.3.7 *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.

3.3.9 *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.

3.3.10 *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**

3.3.11 *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*—$SEV = \sqrt{\frac{1}{v}\sum_{i=1}^{v}(PPTMR_i - PTMR_i)^2}$ where *v* 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.

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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 $\underline{a}(\lambda)$—sample absorbance at wavelength λ.

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

3.4.5 $\boldsymbol{a}$—an absorbance spectrum.

3.4.6 $\underline{\boldsymbol{A}}$—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 $\boldsymbol{b}$—a single beam background spectrum.

3.4.9 $\boldsymbol{B}$—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 $\boldsymbol{C}$—an *n* by *c* matrix of component concentrations in the matrix form of the Beer-Lambert Law.

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

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

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

3.4.16 $\boldsymbol{E}_{cv}$—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 volumn 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 $\underline{\boldsymbol{p}}$—the *f* by 1 prediction vector.

3.4.26 $\underline{\boldsymbol{P}}$—the *f* by *p* prediction matrix with $\underline{\boldsymbol{p}}$ 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 $\boldsymbol{s}$—a single beam sample spectrum.

3.4.30 $t(\lambda)$—the transmittance of a sample at wavelength λ.

3.4.31 $\boldsymbol{t}$—a transmittance spectrum equal to the ratio of $\boldsymbol{s}$ to $\boldsymbol{b}$.

3.4.32 ^{t}—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 *v*—a vibrational energy level quantum number.

3.4.35 $\boldsymbol{x}_i$—a 1 by *f* row vector containing the spectrum of the ith sample.

3.4.36 $\boldsymbol{x}_{unk}$—a 1 by *f* row vector containing the spectrum of the unknown sample being analyzed.

3.4.37 $\boldsymbol{X}$—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 $\bar{\boldsymbol{x}}$—the average spectrum; the average down the columns of $\boldsymbol{X}$.

3.4.39 $\hat{\boldsymbol{x}}$—the estimate of a spectrum based on the multivariate model.

3.4.40 $\bar{\boldsymbol{X}}$—an *n* by *f* matrix where each of the *n* rows contain $\bar{\boldsymbol{x}}$ used in mean centering $\boldsymbol{X}$.

3.4.41 y_i—the PTMR value for a single property for the ith sample.

3.4.42 $\hat{y}_i$—the PPTMR value for a single property for the ith sample.

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

3.4.44 $\bar{y}$—The average of the values in $\boldsymbol{y}$.

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

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

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

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

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3.4.49 $\hat{\boldsymbol{Y}}_{cv}$—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 $\bar{z}_j$—the transform of $\bar{m}_j$; $\bar{z}_j = \max(\bar{m}_j) - m$.

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, $\boldsymbol{b}$, and a sample spectrum, $\boldsymbol{s}$. 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, $\boldsymbol{t}$. The transmission spectrum is converted to an absorbance spectrum, $\boldsymbol{a}$, using a negative logarithm base 10.

$$\boldsymbol{t} = \boldsymbol{s}/\boldsymbol{b} \tag{1}$$

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

6.1.2 Raman spectroscopy measures the inelastic scattering of light by molecules. Raman uses a monochromatic light

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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 a 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 nth 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 in this fashion. These filters, either linear or circular, are moved past a slit to scan the wavelength being

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} 2.5 microns to 25 microns
Mid- and Near-IR	0.25 mm to 0.5 mm	Hydrocarbon Overtones & Combination Bands, heteroatom fundamentals	5000 cm^{-1} to 1000 cm^{-1} 2 microns to 10 microns
Near-IR	2 mm	Hydrocarbon 1st Overtones	6400 cm^{-1} to 5000 cm^{-1} 1562.5 nm to 2000 nm
Near-IR	1 cm	Hydrocarbon 2nd Overtones and Combination Bands	9200 cm^{-1} to 6400 cm^{-1} 1087 nm to 1562.5 nm
Near-IR	10 cm	Hydrocarbon 3rd Overtones and Combination Bands	12000 cm^{-1} to 9200 cm^{-1} 833.3 nm to 1087 nm

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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. The assumption inherent to the multivariate model is that if the same sample is presented twice to the analyzer, the spectrum, suitably preprocessed to remove correctable artifacts will be the same to within the spectral measurement noise.

7.5.1 For some analyzers, it may be necessary to limit the intensity range used in models to ensure that the signals fall within the linear response range of the analyzer. Mathematics used in developing multivariate models generally assumes a linear relationship between signal (absorbance or scattering intensity) and concentration (see X1.2). Nonlinear response will cause changes in spectral band shapes that lead to additional variables (PCs or latent variables) being required to account for the spectral variance. While inclusion of these additional variables may produce adequate models, these models may be unstable relative to analyzer maintenance and for calibration transfer to a second analyzer.

7.5.2 Infrared absorbance and Raman scattering intensity are dependent on the pathlength and scattering volume (see Section 8). Transfer of models from one analyzer to another (or to the same analyzer after maintenance), must account for any change in pathlength or scattering volume.

7.6 Infrared and Raman spectra are temperature dependent.

7.6.1 To first order, over a narrow temperature range, the largest effect of temperature is to change in sample density which results in a change in the amount of sample that fits in the measurement volume (infrared cell beam path volume or Raman scattering volume). Hydrocarbons will typically expand when heated. This will result in less material fitting in the infrared cell beam path or Raman scattering volume, and thus a decrease in spectral intensity.

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7.6.2 Temperature change can have additional effects on spectra depending on the compositions of the samples being measured.

7.6.2.1 For samples containing functional groups which hydrogen bond, changes in temperature can cause changes in band frequency and intensity.

7.6.2.2 For molecules which exist in different conformations, spectra are sensitive to temperature due to Boltzmann distribution and degeneracy. Changing temperature changes conformational equilibrium and hence the vibrational spectra which is the weighted sum of the contribution from each conformation.

7.6.3 Multivariate models assume each spectrum represents the same amount of material, the amount that fits in the measurement volume at a fixed measurement temperature. If the temperatures at which different spectra are collected differ, this assumption may be violated. Failure to compensate for temperature differences among calibration spectra may reduce model precision and accuracy.

7.6.4 Alternatively, preprocessing and modeling techniques may be used to adjust spectra to represent a constant volume of sample (see X2.2.3).

7.6.5 Over a large temperature range, changes in spectral bandwidth will be observed. These changes limit the temperature range over which a temperature compensated multivariate model can adequately perform.

8. Basis for Quantitative, Multivariate Spectral Measurements

8.1 Multivariate models can be subdivided into three types based on the relationship between the spectra, and the property being modeled.

8.2 Hard models are based on a direct and distinct chemical relationship between features in the spectra and the component or functional group concentration being modeled. Peaks in an infrared or Raman spectra are due to the molecular components in the sample being measured. Hard models' only assumption is that the component of interest exhibits one or more spectral bands which are resolved and differentiable from bands of other components, and whose intensity varies as a function of concentration. There are no peaks that relate directly to any physical or performance property, so models for physical and performance properties are not hard models.

8.2.1 For infrared, hard models are based on the Beer-Lambert Law. The absorbance at wavelength, λ, $\underline{a}(\lambda)$ of a homogeneous sample containing an absorb substance is linearly proportional to the concentration of the absorbing species, $\underline{c}$, and the pathlength (sample thickness), b.

$$\underline{a}(\lambda) = a(\lambda)b\underline{c} \tag{3}$$

The $\underline{a}(\lambda)$ is defined as the logarithm to the base ten of the reciprocal of the transmittance, ($t(\lambda)$), at the same wavelength. $t(\lambda)$ is defined as the ratio of radiant power transmitted by the sample to the radiant power incident on the sample. The proportionality constant, $a(\lambda)$, is referred to as the absorptivity. The absorptivity is a characteristic of the absorbing species and is wavelength dependent.

8.2.1.1 The above equation, which only deals with a single wavelength (or frequency) can be expressed in a multivariate form.

$$\boldsymbol{X} = \boldsymbol{B}\boldsymbol{C}\underline{\boldsymbol{A}} \tag{4}$$

$\boldsymbol{X}$ is an n by f matrix of the sample spectra, $\underline{\boldsymbol{A}}$ is a c by f matrix of the spectra of the s components in the samples, $\boldsymbol{C}$ is an n by c matrix of the concentrations of the c components in the n samples, and $\boldsymbol{B}$ is an n by n diagonal matrix of the pathlengths. See X1.2 for a discussion of the use of this multivariate form of Beer-Lambert Law in Classical Least Squares analysis.

8.2.2 For Raman scattering, an equation analogous to the Beer-Lambert Law applies. The measured Raman scattering intensity, I_R, is proportional to the incident laser power, I_o, and to the concentration of the scattering species, c.

$$I_R = I_o \sigma_R K c \tag{5}$$

8.2.3 The proportionality constants are σ_R, the Raman cross-section of the scattering species and K a function of numerous factors including 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 (**1**).[3] A similar multivariate version of this equation can be derived.

8.2.4 Hard models are generally limited to quantitation of individual chemical species which possess unique spectral features, to groups of such chemical species, or to function group concentrations.

8.2.4.1 An example of a hard model is Test Method D6277 where benzene volume % is measured based on a unique feature at 675 cm^{-1}. Multivariate techniques are used to compensate for baseline level interferences from other aromatics.

8.2.4.2 For samples with a maximum carbon number of C8, it is possible by mid-IR or Raman to differentiate all possible aromatic species, and thus build hard models for individual species and for total aromatics. The ability to do this in the NIR is highly dependent on resolution. For samples with higher carbon number, the overlap among aromatic species generally precludes quantitation of all individual aromatic species, and total aromatics models are no longer hard models, because the spectral variables used in the model typically represent the average carbon number and isomer distributions represented by the calibration samples. Such soft models provide accurate prediction as long as the samples being analyzed contain similar distributions but can be biased when used to analyze samples where the distributions are different.

8.2.4.3 For individual oxygenates (Ethanol, MTBE), hard models can generally be built based on the unique spectra features of the oxygenate. For FAME, hard models can be built for the ester content of a diesel fuel, but models that predict volume % FAME are not hard, since they include assumptions about the carbon number of the FAME molecule fatty acid chain and will give biased predictions if the sample being analyzed contains a FAME with a different carbon number fatty acid.

[3] The boldface numbers in parentheses refer to a list of references at the end of this standard.

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8.2.5 Both the Beer-Lambert Law and the Raman scattering equation assume that component concentrations are volumetric in nature, that is, that they are either volume fraction, volume percent, grams per unit volume, or moles per unit volume. Both the infrared and Raman measurements are done on a fixed volume of sample. For infrared, this volume is the product of the pathlength times the infrared beam cross-section. For Raman, the volume is the volume of the sample that is illuminated by the laser and visible to the collection optics. For multivariate models built on PTMR values expressed in weight %, there is a built-in assumption that the weight of sample in the fixed volume is a constant, that is, that the density of the samples is a constant. Thus, models that predict weight % are inherently soft due to this constant density assumption.

8.2.6 The amount of sample that fit in the fixed volume is temperature dependent. Failure to account for temperature effects in hardware or modeling may decrease the accuracy and precision of models.

8.3 Soft models also depend directly on the Beer-Lambert law or the Raman scattering equation, but do not assume a distinct relationship between the spectral features and the property being modeled. Soft models are also referred to as inferential models since they infer a relationship between the composition expressed by the spectrum and the property being modeled. Soft models may depend upon properties of the calibration set which are not reflected in the spectra.

8.3.1 For example, infrared and Raman spectra contain features corresponding to aromatic ring vibrations. However, aside from light sample containing C8 aromatics or less, the spectroscopies do not distinguish among aromatics based on length of aliphatic side chains or number of aliphatic ring substituents. Models for total volume percent aromatics incorporate information as to the average carbon number of the aromatic moieties in the calibration samples and assume that this average number applies to samples being analyzed. If this assumption applies, the PPTMR may be accurate and precise. If this assumption is violated, the PPTMR may be inaccurate and imprecise.

8.3.2 For physical and performance properties, the calibration essentially involves calculation of blending values for each of the mathematically derived components (principal components or latent variables) derived from the calibration sample spectra. The application of the model assumes that these blending values can be applied linearly over the range of the model. If the property does not blend linearly over the range of the calibration sample PTMRs, then the model performance may suffer.

8.3.3 Transforming a property such that it is volumetrically based can improve the likelihood that it can be adequately modeled.

8.3.3.1 For example, API does not blend linearly based on volume, so models predicting API will likely show nonlinearity over a large enough range. A superior model will typically be achieved by converting API to specific gravity, modeling specific gravity, and converting the PPTMR back to API.

8.3.3.2 The petrochemical industry has developed a number of blending indices that are used to calculate the property of a blend based on the properties of the blend components. In some cases, modeling the blending index instead of the property may produce superior results.

8.4 Circumstantial models do not have any direct relationship to the Beer-Lambert law or the Raman scattering equation. Circumstantial models are strictly based on a statistically identifiable relationship between the calibration spectra and the property being modeled, but they do not have any underlying scientific explanation. Circumstantial models may depend on other, potentially unknown relationships among the calibration samples.

8.4.1 Vibrational spectroscopies measure molecules, not elements. Thus, any model that predicts sulfur or nitrogen content may be circumstantial. For a limited set of feeds, there may, for instance, be a relationship between a spectrally detectable level of product sample hydrotreating and sulfur or nitrogen content, allowing a model to be developed. The model may work well for the limit set of feeds but fail for more compositionally diverse feeds.

8.4.2 Vibrational spectroscopies are used to predict distillation properties of petroleum feeds, products and liquid fuels. Models that predict the volume fraction of a sample that distills at a fixed temperature are soft models because they assume that a volume fraction for each spectral variable can be inferred from the calibration set. However, models that predict the temperature at which a fixed percentage of a sample distills are by definition circumstantial because there is no definable linear relationship between these temperatures and composition.

8.4.3 Circumstantial models may produce results comparable to hard and soft models, but they may be less robust to changes in process operation.

9. Sampling

9.1 Proper sampling is critical to successful spectroscopic analyzer applications. The objectives are to ensure that the sample is representative of the process stream from which it is taken, and that the sample whose spectra is collected is identical to the sample measured by the PTM.

9.2 If calibration sample spectra are collected on a laboratory or at-line analyzer, follow Practice D7453 for proper procedures in collecting line and composite samples, and Practice D1265, D4057, D5842, or D8009 for procedures for collecting tank samples. Line samples will typically offer a larger range of variation in composition and properties which is desirable for modeling.

9.3 If calibration spectra are collected on an online analyzer, follow Practices D7278 and D7453 to account for lag times to ensure that the line sample taken for PTM analysis corresponds to the sample whose spectrum was collected.

9.3.1 If calibration spectra are collected on a flowing or static (stop-flow) sample, and if more than one spectrum is collected during the time period over which a sample is taken, then after accounting for lag time, the spectra collected over the sampling period should be averaged, and either the average spectrum, or the individual spectrum closest to the average should be used as the calibration spectrum.

9.3.2 If calibration spectra are collected on flowing or static (stop-flow) samples, and the spectral collection time exceeds

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the time required to collect a line sample, then considering lag times, the sample collection should be timed to correspond as closely as possible to the middle of the spectral collection period.

9.4 Samples should be stored in containers that are at least 70 % to 85 % full to minimize partitioning of lighter components into the headspace. For spark ignition fuels, chill containers to the temperature recommended by the PTM before opening for analysis by PTM and before open transfer from one sample holder to another before use in lab, at-line, or field spectral analyzers (that is, analyzers not attached to the process). If necessary, split the chilled sample into separate containers of appropriate size for the volumes required by the PTM and spectral measurement. If the same sample is being measured using more than one PTM, use the most stringent sampling requirements for transfer from one sample holder to another.

9.5 If the calibration samples are Blendstocks for Oxygenate Blending (BOBs), but the PTM measures a final fuel containing ethanol, follow Practice D7717 in preparing the blends for the PTM measurement.

9.6 Handblends (preferably prepared in accordance with Practice D4307) may be used to extend the variability of available calibration samples.

9.7 Process spectroscopic analyzers use either in situ or extractive sampling.

9.7.1 Analyzers that use in situ sampling generally employ fiber optics to take the light from the analyzer to the sample and back. A sample probe is inserted into the process to allow the light to interact with the sample.

9.7.2 In extractive sampling, the sample is removed from the process and introduced into the analyzer system. Typically, a small fraction of the process material is diverted into a fast sample loop from which it may be sampled by the analyzer. Sample conditioning may be employed prior to the spectral measurement.

9.7.3 Detailed discussion of in situ and extractive sampling are beyond the scope of this practice. However, if transferring calibrations among analyzers, users should be aware that differences in sample condition and presentation can affect analysis results unless they are corrected for in spectral preprocessing or modeling.

10. Overview of Multivariate Calibration

10.1 Before starting the multivariate calibration process, several prerequisites shall be satisfied.

10.1.1 Determine what type of instrument performance testing will be done both while the calibration spectral data is being collected, and later when the multivariate model is applied for the analysis of product. It is critical to establish the level of performance achieved during the collection of the calibration spectra so that this level can be maintained when the model is used for analysis.

10.1.2 Determine what type of instrument standardization or calibration transfer approach will be used. Some approaches require that spectra of one or more reference material be collected on the initial calibration instrument, and again on the instrument to be used for analysis. These reference spectra should be collected at the start of the calibration process.

10.2 The practice of spectroscopic multivariate quantitative analysis involves the following steps:

10.2.1 *Selecting the Calibration Set*—The calibration set is intended to represent all the chemical and physical variation which would normally be encountered during routine analysis for the desired application. Selection of the calibration set is discussed in Section 21, after the statistical terms necessary to define the selection criteria have been defined.

10.2.2 *Determination of Concentrations or Properties, or Both, for Calibration Samples*—The chemical, physical or performance properties, or both, of samples in the calibration set must be accurately and precisely measured by the PTM in order to accurately calibrate the multivariate model for prediction of the unknown samples. PTM measurements are discussed in Section 11.

10.2.3 *The Collection of Spectra*—The collection of spectral data must be performed with care to present calibration samples, validation samples, and prediction (unknown) samples for analysis in an alike manner. Variation in sample presentation technique among calibration, validation, and prediction samples will introduce variation and error which has not been modeled within the calibration. Instrumentation is discussed in Section 7 and spectral measurements in Section 8.

10.2.4 *Calculating the Multivariate Model*—The calculation of multivariate (calibration) models may involve a variety of data treatments and algorithms. The more common linear techniques are discussed in Section 14 and Appendix X1. A variety of statistical techniques are used to evaluate and optimize the model. These techniques are described in Section 17 and Appendix X3. Statistics used to detect outliers in the calibration set are covered in 18.1.

10.2.5 *Establishing Criteria for Identifying Outliers During Analysis*—Based on the outlier statistics for the calibration spectra, limits are set for each statistic. If, during analysis of an unknown, the value for an outlier statistic exceeds the limit, the spectrum is considered an outlier and the PPTMR is considered invalid.

10.2.6 *Validation of the Multivariate Model*—Validation of the efficacy of a specific multivariate model requires that the model be applied for the analysis of a separate set of model validation samples, and that the PPTMR values for these samples be statistically compared to PTMR values obtained by application of the PMT to these same samples. The statistical tests to be applied for validation of the model are discussed in Section 22.

10.2.7 *Application of the Model for the Analysis of Unknowns*—The multivariate model is applied to the spectra of unknown samples to produce the PPTMR. (see Section 15 and X1.8). Outlier statistics are used to detect when the analysis involves extrapolation of the model (see Section 20).

10.2.8 *Routine Analysis and Monitoring*—Once the efficacy of one or more multivariate model is established, the equations must be monitored for continued accuracy and precision. Simultaneously, the instrument performance must be monitored to trace any deterioration in performance to either the multivariate model itself or to a failure in the instrument.

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Procedures for verifying the performance of the analysis are covered in detail in Practice D6122. The use of Practice D6122 requires that an instrument performance test procedure be established at the time the model is developed. Instrument performance test results collected during the time the calibration spectra are collected can be used to establish suitable performance levels. Analyzer vendors may recommend instrument performance tests and provide expected levels of performance against which future test results are compared.

10.2.9 *Calibration Transfer and Instrument Standardization*—A model built using calibration spectra from one analyzer may be used to analyze unknown samples on additional analyzers, or on the first analyzer after major maintenance has been performed. It may be necessary to adjust the model or the analyzers in order to achieve acceptable PPTMR and outlier statistics. In this practice, the term calibration transfer is used to refer to procedures that are used to adapt the model from the first analyzer to perform correctly on the other analyzers. Instrument standardization is used to refer to procedures that are used to adapt the other analyzers to adequately match the first analyzer such that no change to the model is required to achieve correct performance. Calibration transfer and instrument standardization are discussed in Section 26.

11. Primary Test Method (PTM) and Primary Test Method Result (PTMR)

11.1 Infrared and Raman spectroscopies require calibration to determine the proportionality relationship between the signals measured and the component concentrations or properties that are to be predicted. During the calibration, spectra are measured for samples for which these PTMRs are known, and the multivariate relationship between the sample spectral signals and the PTMRs is determined. The relationship, the multivariate model, is then applied to the spectrum of an unknown sample to predict the PPTMR for that sample.

11.2 For simple mixtures containing only a few chemical components, it is generally possible to prepare mixtures that can serve as standards for the multivariate calibration of an infrared and Raman analyses. Because of potential interferences among the spectral signals of the components, it is not sufficient to vary the concentration of only some of the mixture components, even when analyses for only one component are being developed. Instead, all components should be varied over a range representative of that expected for future unknown samples that are to be analyzed. Since infrared measurements are conducted on a fixed volume of sample (for example, a fixed cell pathlength), and Raman measurements are conducted on a fixed scattering volume, it is preferable that concentration PTMR values be expressed in volumetric terms, for example, in volume percentage, grams per milliliter, moles per cubic centimeter, and so forth. Developing multivariate calibrations for concentrations expressed in other terms (for example, weight percentage) can lead to models that are linear approximations to what is really a nonlinear relationship and can lead to less accurate estimates of the concentrations.

11.3 For complex mixtures, such as those obtained from petrochemical processes, preparation of calibration standards is generally impractical, and the multivariate calibration of a spectroscopic analysis must typically be performed on actual process samples. In this case, the PTMRs used to calibrate the analysis are obtained by application of the PTM. The accuracy of a PPTMR value produced by a multivariate spectral analysis is highly dependent on the accuracy and precision of the PTMRs used in the calibration. The expected agreement between the infrared or Raman PPTMRs and those obtained from a single PTM measurement can never exceed the site precision of the PTM, since, even if the PPTMR is the true value, the measurement of agreement is limited by the precision of the PTMR. Knowledge of the site precision of the PTM is critical in the development of a multivariate calibration. The precision of the PTMR data used in developing a model, and the accuracy of the model can be improved by averaging repeated PTM measurements.

NOTE 2—If the PTMR values used to calibrate a multivariate infrared analysis are generated in a single laboratory, it is essential that the measurement process used to generate these values be monitored for bias and precision using suitable quality assurance procedures as outlined in Practice D6299. If primary standards are not available to allow the bias of the PTM to be established, it is recommended that the laboratory participate in an interlaboratory crosscheck program as a means of demonstrating accuracy.

NOTE 3—Samples like hydrocarbons from petrochemical process streams can degrade with time unless careful sampling and sample storage procedures are followed. It is critical that the composition of samples taken for laboratory or at-line spectroscopic analysis, or for PTM measurement be representative of the process at the time the samples are taken, and that composition is maintained during storage and transport of the samples either to the analyzer or to the laboratory. Sampling should be done in accordance with methods like Practices D1265, D4057, D4177, or D7453 whichever are applicable. Whenever possible, sample storage for extended time periods is not recommended because of the likelihood of samples degrading with time despite sampling precautions taken. Degradation of samples can cause changes in the spectra measured by the analyzer and thus in the values estimated, and in the property or quality measured by the PTM. If necessary, store samples in containers that are at least 70 % to 85 % full and avoid exposure to light and extreme temperatures. For spark ignition fuels, refrigerated storage is recommended.

11.4 If the PTM is an established ASTM method, then repeatability and reproducibility of the PTM are documented in the method. In this case, the user should use procedures described in Practice D6299 to establish the site precision for the PTM, calculate the PTM's Test Performance Index (TPI), and demonstrate that the TPI is within an acceptable range as discussed in Practice D6792. If the reproducibility of the PTM is level dependent, then at least three QC samples should be used to estimate the level dependence of the site precision. These samples should be chosen to span the range of values over which the calibration is to be developed, one sample having a PTMR in the bottom third of the range, one sample having a PTMR in the middle third of the range, and one sample having a PTMR in the upper third of the range. Practice D6299 control charts should be maintained for each of the QC samples and used to estimate the site precision at the QC samples.

11.5 PTMs that are not ASTM methods can be used for the multivariate calibration of infrared analyses, but in this case, it is the responsibility of the user to establish the site precision of the PTM using procedures in Practice D6299. Since the level

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dependence of the PTM may not be known, three QC samples should be used as described in 11.4 above. The TPI of the PTM will not be known.

11.6 Most multivariate models are built using a single spectrum and a single PTMR for each calibration sample. Multivariate modeling methods generally assume that the errors in the PTMRs are normally distributed and homoscedastic, that is that the errors have a common variance.

11.6.1 If multiple PTM measurements are done on a calibration sample, then the average PTMR value will be more precise than the individual PTMR values by $\sqrt{r}$, where r is the number of replicate measurements. If multiple PTM measurements are done on calibration samples, then it is likely that similar numbers of PTM measurements will be required on validation samples for herein, for model validation, and for Practice D6122 analyzer validation.

11.6.2 If the PTM precision is not level dependent, and if all the calibration samples are measured r times using the PTM, then the averaged PTMR values should be homoscedastic, and normal modeling methods can be employed. However, the statistics produced by the modeling software will reflect r PTM measurements. If analyzer performance is to be validated against a single PTM measurement, then the statistics must be adjusted to account for the variance removed by the PTM averaging. See 17.2.3.1 for details.

11.6.3 If the PTM precision is not level dependent, and if differing numbers of PTM measurements are done for different calibration samples, the mixed replicate level PTMR values will not be homoscedastic. A weighted regression approach can be employed in this case (see X1.10). The committee is unaware of any commercial software package that is typically used in spectroscopic multivariate modeling that provides for this weighted regression approach.

11.6.4 For many ASTM PTMs, the precision of the method is level dependent. In this case, the errors in the PTMRs may not be homoscedastic. Normal modeling methods do not account for the heteroscedasticity. In this case, the model SEC should be tested for level dependence (see Annex A2), and any detected level dependence should be used in validation of the model (see Section 22).

11.7 When multiple PTM measurements are made on an individual calibration or validation sample, an Extreme Studentized Deviate technique (see Practice D7915) may be applied to the values to determine if all of the PTMR values came from the same population, or if one or more of the values is suspect and should be rejected.

12. Simple Procedure to Develop a Feasibility Model

12.1 For new applications, it is generally not known whether an adequate spectroscopic multivariate model can be developed. In this case, feasibility studies can be performed to determine if there is a relationship between the IR spectra and the component/property of interest, and whether a model of adequate precision could possibly be built. If the feasibility calibration is successful, then it can be expanded and validated. A feasibility calibration involves the following steps:

12.1.1 Approximately 30 to 50 samples are collected covering the entire range for the PTMRs of interest. Care should be exercised to avoid intercorrelations among major constituents unless such intercorrelations always exist in the materials being analyzed. The standard deviation in the PTMRs should be preferably five times, but not less than three times, the standard deviation of the site precision (site precision/2.77) of the PTM. If the site precision of the PTM has not been established prior to the feasibility study, substitute the PTM reproducibility.

12.1.2 When collecting spectral data on these samples, variations in sample presentation, and process conditions which are expected during analysis must be reproduced.

12.1.3 Analyses on these samples are conducted using the PTM. If the standard deviation for the PTMRs is not at least five times the standard deviation of the reproducibility for the PTM, then r replicate analyses should be conducted on each sample such that the $\sqrt{r}$ times the PTMR standard deviation is preferably five times, but at least three times, the standard deviation of the PTM analyses. The SEC calculated for the model should be adjusted using the procedure described in 17.2.3.1 to account for the variance removed by averaging the individual PTMRs to provide a better estimate of what model performance can be expected for a model built using one PTMR per sample.

12.1.4 A multivariate model is developed using one or more of the mathematical techniques described in Section 14 and Appendix X1. The multivariate model is preferably tested using cross-validation methods to produce statistics such as SECV or PRESS (see 17.3.9). Other statistics can also be used to judge the overall quality of the calibration.

12.1.5 If the SECV value obtained from the cross-validation suggests that a model of adequate precision can be built, then additional samples are collected to round out the calibration set, and to serve as a validation set, spectra of these samples are collected, a final model is developed and validated as described in Sections 14 and 22 respectively.

13. Data Processing

13.1 Various types of data preprocessing algorithms can be applied to the spectral data prior to the development of a multivariate model. Most preprocessing is designed to either remove unwanted signals from the spectral data, to remove unwanted variations in spectral intensity, or for spectral registration. For example, numerical derivatives of the spectra may be calculated using digital filtering algorithms to remove varying baselines. Such filtering generally causes a significant decrease in the spectral signal-to-noise. Digital filters may also be employed to smooth data, improving signal to noise at the expense of resolution. A complete description of all possible preprocessing methods is beyond the scope of this practice, but more commonly used types of preprocessing are described in Appendix X2. For the purpose of this practice, preprocessing of the spectral data can be used if it produces a model which has acceptable precision, and which passes the validation test described in Section 22. In addition, any spectral preprocessing method must be automated to provide an exactly reproducible result, and must be applied consistently to all calibration spectra, validation spectra, and to spectra of unknowns which are to be analyzed.

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13.1.1 Autoscaling of the X-Block is not recommended for spectral data since it amplifies the baseline noise relative to the absorbance or scattering signal.

13.1.2 If multiple preprocessing steps are used, the proper order of operations should be established and used throughout calibration and analysis. Generally, treatments that adjust spectral registration should be done first, treatments that remove unwanted signals in the spectral data should be done second, and treatments that remove unwanted variations in spectral intensity should be done last.

13.2 The Y-Block may also be preprocessed. Transformations may be used to convert property data into a form that is more linearly dependent on concentration and thus potentially easier to model. Such transformations are often used in process models for estimating the property of a blend from component properties. An example would be converting API Gravity to specific gravity.

13.3 One type of preprocessing requires special mention. Mean-centering refers to a procedure in which the average of the calibration spectra (average spectral intensity over the calibration spectra as a function of spectral position) is calculated and subtracted from the spectra of the individual calibration samples prior to the development of the model. The average PTMR value among the calibration samples is also calculated and subtracted from the individual PTMR values for the calibration samples. The model is then built on the mean-centered data. If the spectral and PTMR data are mean-centered prior to the development of the model, then:

13.3.1 When an unknown sample is analyzed, the average spectrum for the calibration set must be subtracted from the spectrum of the unknown prior to applying the mean-centered model, and the average PTMR value for the calibration set must be added to the estimate from the mean-centered model to obtain the final estimate; and

13.3.2 The degrees of freedom used in calculating the standard error of calibration must be diminished by one to account for the degree of freedom used in calculating the average (see 17.2.2).

13.3.3 Mean centering will typically be done either before or after all other types of preprocessing are started or completed.

14. Calibration – Creating the Multivariate Model

14.1 Multivariate mathematical techniques are used to relate the spectra measured for a set of calibration samples to the PTMRs obtained by applying the PTM to the same set of samples. The object is to establish a multivariate model that can be applied to the spectra of future, unknown, samples to predict property or concentration values (PPTMRs) for these samples. Linear multivariate techniques are described in this practice, that is, it is assumed that the PTMRs can be modeled as a linear function of the sample spectra. Various nonlinear multivariate techniques have been developed but have generally not been as widely used as the linear techniques discussed herein. This practice is not intended to compare or contrast among techniques. For this practice, the suitability of any specific mathematical technique should be judged only on the following two criteria:

14.1.1 The technique should be capable of producing a multivariate model that can be validated as described in Section 22; and

14.1.2 The technique should be capable of providing statistics suitable for identifying if samples being analyzed are outside the range for which the model was developed; that is, when the estimated values represent extrapolation of the model (see Sections 18, 19, and 20).

NOTE 4—In the following derivations, matrices are indicated using boldface capital letters, vectors are indicated using boldface lowercase letters, and scalars are indicated using lowercase letters. Vectors are column vectors, and their transposes are row vectors. Italicized lowercase letters indicate matrix or vector dimensions.

14.1.3 All linear, multivariate techniques are designed to solve the same generic problem. If n calibration spectra are measured at f discrete spectral positions, then $\boldsymbol{X}$, the spectral data matrix, is defined as an n by f matrix containing the spectra (or some function of the spectra produced by preprocessing, as described in Section 11) as columns. Similarly, $\boldsymbol{y}$ is a vector of dimension n by 1 containing the PTMRs for the calibration samples.

14.1.3.1 *Discussion*—The selection of whether the calibration spectra are stored in rows or columns of $\boldsymbol{X}$ is arbitrary. Rows are used here to be more consistent with various references that describe PCR and PLS algorithms (**2-12**). This choice is the opposite of that used in Practice E1655 where spectra are stored in columns of $\boldsymbol{X}$.

14.1.3.2 The object of the linear, multivariate modeling is to calculate a prediction vector $\underline{\boldsymbol{p}}$ of dimension f by 1 that solves Eq 6 :

$$\boldsymbol{y} = \boldsymbol{X}\underline{\boldsymbol{p}} + \boldsymbol{e} \tag{6}$$

The error vector, $\boldsymbol{e}$ is a vector of dimension n by 1, that is the difference between the PTMR values $\boldsymbol{y}$ and their predictions, $\hat{\boldsymbol{y}}$ (the PPTMRs), where:

$$\hat{\boldsymbol{y}} = \boldsymbol{X}\underline{\boldsymbol{p}} \tag{7}$$

14.1.3.3 Some multivariate techniques allow more than one property to be modeled simultaneously. In this case, the equation being solved becomes

$$\boldsymbol{Y} = \boldsymbol{X}\underline{\boldsymbol{P}} + \boldsymbol{E} \tag{8}$$

$\boldsymbol{Y}$ is an n by p matrix whose columns are the PTMRs for the p different properties being modeled, and $\underline{\boldsymbol{P}}$ is an f by p matrix containing the prediction vectors for the p properties as columns.

14.1.4 For some applications, it may be useful to combine the spectral data with other measured variables (for example, sample temperature, density, or viscosity). These additional heterogeneous variables may simply be appended to the spectrum of each sample as if they were spectral intensities measured at additional spectral positions. When heterogeneous data is used, it is important to consider the possibility that it may be appropriate to apply weighting factors to the heterogeneous variables to appropriately balance their influence on the calibration with respect to the influence of the spectral variables. Incorporation of additional heterogeneous variables in a model requires that these variables be measured for all future samples being analyzed using the model.

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14.1.5 The estimation of the prediction vector $\underline{\boldsymbol{p}}$ is generally calculated to minimize the sum of squares of the errors,

$$\boldsymbol{e}^t\boldsymbol{e} = \sum_{i=1}^{n} e_i^2 = (\boldsymbol{y} - \boldsymbol{X}\,\underline{\boldsymbol{p}})^t(\boldsymbol{y} - \boldsymbol{X}\,\underline{\boldsymbol{p}}) \tag{9}$$

Since $\boldsymbol{X}$ is generally not a square matrix, it cannot be directly inverted to solve Eq 1. Instead, the pseudo or generalized inverse of $\boldsymbol{X}$, $\boldsymbol{X}^+$ is calculated as:

$$\boldsymbol{X}^+\boldsymbol{y} = (\boldsymbol{X}^t\,\boldsymbol{X})^{-1}\boldsymbol{X}^t\boldsymbol{y} = \underline{\hat{\boldsymbol{p}}} \tag{10}$$

where $\underline{\hat{\boldsymbol{p}}}$ is the least square estimate of the prediction vector $\underline{\boldsymbol{p}}$. It should be noted that, in applying Eq 6-10, it is assumed that the errors in the spectral data in $\boldsymbol{X}$ are negligible compared to the errors in the reference data, and that there is a linear relationship between the PTMR and the spectral data. If either of these assumptions is incorrect, then the linear models derived here will not yield an optimal estimate of $\underline{\boldsymbol{p}}$.

14.1.6 All the linear regression modeling methods, MLR, PCR, and PLS, are different ways of estimating $\underline{p}$.

14.1.7 In calculating the least squares solution in Eq 10, it is assumed that the individual error values in $\boldsymbol{e}$ (see Eq 6) are normally distributed with common variance. This is more likely to be true if each of the individual PTMR values in $\boldsymbol{y}$ represents the result of the same number of PTM measurements, and if the site precision of the PTM is constant over the range of values in $\boldsymbol{y}$. If the values in $\boldsymbol{y}$ represent averages of different numbers of PTM determination, then the least square expression in Eq 10 is not applicable. In this case, a weighted regression (see X1.10) must be used. If the PTM has a level dependent precision, then the least squares solutions may be applied, but the SEC for the resultant model must be evaluated for level dependence using procedures described in Annex A2, and any level dependence identified shall be used in validating the model and analyzer results.

14.1.8 Typically, when the model is used for analysis of new materials, the PPTMR value produced by an analyzer will be compared to a single PTMR value produced by the PTM. If a weighted regression is used in developing the model, the SEC shall be corrected for the variance removed by averaging PTMR results (see 17.2.3).

14.1.9 For some cases, if the calibration spectra are collected over an extended wavelength (or frequency) range, the number of individual spectral intensity values per spectrum, f, will exceed the number of calibration spectra, n. In this case, the matrix ($\boldsymbol{X}^t\boldsymbol{X}$) is rank deficient and cannot be directly inverted. Even in cases where $f < n$, collinearity among the calibration spectra can cause ($\boldsymbol{X}^t\boldsymbol{X}$) to be nearly singular (to have a determinant that is near zero), and the direct use of Eq 10 can produce an unstable model, that is, a model for which changes on the order of the spectral noise level produce significant changes in the predicted values. To solve Eq 10, it is therefore necessary to reduce the dimensionality of **X** so that a stable inverse can be calculated. The various linear, mathematical techniques used for multivariate calibration are different means of reducing the dimensionality of $\boldsymbol{X}$ to be able to calculate stable inverses of ($\boldsymbol{X}^t\boldsymbol{X}$) and the estimate p.

14.2 *Multilinear Regression Analysis:*

14.2.1 In multilinear regression (MLR), a specific number, k, of individual wavelengths (or frequencies), or analytical regions, or both, are chosen such that $k \leq n/6$. Depending on the application, the individual wavelength, or analytical regions may be individual wavelengths with or without baseline correction, or they may be a linear combination of several wavelengths (for example, ratios or integrated peak areas) with or without baseline correction. The MLR algorithm is discussed in more detail in Appendix X1.

14.2.2 The choice of the number of wavelengths (or frequencies), k, to use in multilinear regression is a critical step in the model development. If too few wavelengths are used, a less precise model will be developed. If too many wavelengths are used, collinearity among the absorption values at these wavelengths may lead to an unstable model. The optimum number of wavelengths (or frequencies) for a model is related to the number of spectrally distinguishable components in the calibration spectra (see 17.3) and can generally only be determined by trial and error. As a rule, the number of wavelengths (or frequencies) used must be large enough to produce a model with the desired precision, but small enough to produce a stable model that passes validation.

14.2.3 The choice of specific wavelengths (or frequencies) to include in a multilinear regression model is also a critical factor in the model development. Several mathematical algorithms have been suggested for making this selection **(13-16)**. Alternatively, selection may be based on prior knowledge of a relationship between the spectral intensities measured and the property or component being modeled. It is beyond the scope of this practice to compare alternative selection methods. An adequate set of wavelengths (or frequencies) will, for this practice, be defined as a set that produces a model with the desired precision that passes the validation test procedure described in Section 22.

14.3 *Principal Components Regression (PCR):*

14.3.1 Principal Components Regression is a two-step process.

14.3.1.1 In the first step, a Principal Components Analysis (PCA) is conducted on the X-Block. PCA is a dimensionality reduction technique that represents the n spectra in the X-Block as linear combinations of k loading vectors, where $k < n$, and typically $k << n$. The loadings are axes in the reduced dimension multivariate space, and scores are the location of the spectra on these new axes. The variables calculated by PCA only describe the X-Block variance and are in decreasing order of the variance accounted for.

14.3.1.2 In the second step, the Y-Block values are regressed against the scores to produce the PCR model.

14.3.2 The PCR algorithms are discussed in more detail in Appendix X1.

14.3.3 The choice of the number of principal components, k, to use in the regression is a critical step in the model development. If too few principal components are used, a less precise model will be developed. If too many principal components are used, noise characteristics of the calibration samples will be incorporated into the model leading to unstable predictions. The optimum number of principal components for a model is related to the number of spectrally distinguishable

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components in the calibration spectra (see 17.3) and can generally only be determined by trial and error. As a rule, the number of principal components used must be large enough to produce a model with the desired precision, but small enough to produce a stable model that passes validation.

14.4 *Partial Least Squares (PLS):*

14.4.1 Like PCR, PLS involves the decomposition of the spectral data matrix, $\boldsymbol{X}$, into the product of loading and scores matrices. Unlike PCR where $\boldsymbol{X}$ is first decomposed, and then regressed versus the reference values, in PLS, the **y** vector is used in obtaining the decomposition of $\boldsymbol{X}$. PLS derives a set of latent variables to simultaneously decompose both the X- and Y-Blocks to explain as much as possible the covariance between $\boldsymbol{X}$ and $\boldsymbol{Y}$. PLS can be implemented in several different ways, as is discussed in Appendix X1.

14.5 *Frequency/Wavelength Selection in PCR/PLS Models:*

14.5.1 An important step in the development of PCR and PLS models is the selection of which frequencies/wavelengths to include in the model. The multivariate model will not necessarily include data in the entire spectral range measured by the spectrometer/spectrophotometer. When analyzing specific analytes, spectral regions can be chosen based on knowledge as to where the analyte signals occur. When modeling physical or performance properties however, it may be advisable to include as much of the spectral range and information as practical. Spectral regions may be excluded from multivariate models for a variety of reasons including high spectral noise, nonlinear spectrometer response and spectral interferences due to optical or environmental sources.

14.5.1.1 Spectrometers/spectrophotometers typically have limited range over which they will respond linearly. For example, for dispersive spectrophotometers, stray light may limit the linear response range. Similarly, for FTIR spectrophotometers, phase errors can limit the linear response range. If spectral regions exhibiting nonlinear response are included in multivariate models, the number of variables needed to model the calibration data will increase. The nonlinearity in the X-Block may limit the transferability of the model between spectrometers (see Section 26), as well as the robustness of the model to spectrometer maintenance. Regions where samples are optically opaque should always be excluded from models.

14.5.1.2 Spectra can contain signals that are due to the spectrometer, sampling optics or the environment. For instance, for mid-IR, spectra often contain contributions from water vapor and carbon dioxide due to purge variations. The robustness of models can sometimes be improved by excluding spectral regions where such interferences occur. If regions with variable interference are included, it is important to either account for the variation or to take measures to remove the interference physically, for example, use a dry air purge to remove water vapor.

14.5.2 In selecting frequencies/wavelengths for inclusion in a model, it may be useful to calculate the average, $\bar{\boldsymbol{x}}$, and standard deviation, $\boldsymbol{\sigma}_X$, of the calibration spectra. If **1** is a *1* by *n* vector of ones, then:

$$\bar{\boldsymbol{x}} = \frac{1\boldsymbol{X}}{n} \tag{11}$$

$$\sigma_x = diag\left(\sqrt{\frac{(X - 1^t\,\bar{x})^t(X - 1^t\,\bar{x})}{n-1}}\right) \tag{12}$$

14.5.3 *r* replicate spectra ($\boldsymbol{X}_r$) of one or more calibration samples should be collected, and similar average ($\bar{\boldsymbol{x}}_r$) and standard deviations ($\boldsymbol{\sigma}_r$) values should be calculated.

$$\bar{\boldsymbol{x}}_r = \frac{\mathbf{1}\boldsymbol{X}_r}{r} \tag{13}$$

$$\sigma_r = diag\left(\sqrt{\frac{(\boldsymbol{X}_r - \mathbf{1}^t\,\bar{\boldsymbol{x}}_r)^t(\boldsymbol{X}_r - \mathbf{1}^t\,\bar{\boldsymbol{x}}_r)}{r-1}}\right) \tag{14}$$

The ratio of $\boldsymbol{\sigma}_r$ to $\boldsymbol{\sigma}_x$ is useful in selecting frequencies/wavelengths for inclusion/exclusion from the model.

14.5.3.1 If, for a given frequency/wavelength, the ratio of $\boldsymbol{\sigma}_r$ to $\boldsymbol{\sigma}_x$ is less than 0.3, then the variation in the calibration set is significantly above the spectral noise level, and the frequency/wavelength should typically be included in the model.

14.5.3.2 If, for a given frequency/wavelength, the ratio of $\boldsymbol{\sigma}_r$ to $\boldsymbol{\sigma}_x$ is close to unity, then the variation in the calibration set is comparable to the spectral noise level, and the frequency/wavelength is a candidate for exclusion from the model.

14.5.4 During analyses, spectral residuals are useful in detecting species that are not represented in the calibration samples. Exclusion of frequencies/wavelengths may reduce outlier detection capabilities of the model.

15. Prediction of Values from Spectra

15.1 If $\boldsymbol{x}$ (a 1 by *f* vector) is the spectrum of a sample, then $\hat{y}$ (a scalar), the predicted component concentration or property value, *PPTMR*, is given by Eq 7, above which is repeated here.

$$\hat{y} = \boldsymbol{x}\underline{p}$$

If multiple properties were modeled, the prediction becomes

$$\hat{\boldsymbol{y}} = \mathbf{x}\underline{P} \tag{15}$$

$\hat{\boldsymbol{y}}$ is the 1 by *p* vector of *PPTMR* values. The prediction vector $\underline{p}$ or matrix $\underline{P}$ is obtained from the multivariate calibration. The expression in Eq 7 involves only the dot product of two vectors to obtain the estimated value; it has the advantage of being computationally simple. However, alternative computations are often employed in obtaining $\hat{y}$ and $\hat{\boldsymbol{y}}$, since they provide additional parameters required to calculate the uncertainty in the estimation and whether the estimation is being made by interpolation or extrapolation of the multivariate model. For more detail, see Appendix X1.

16. Post Processing

16.1 Several multivariate methods involve some post processing of the predictions from the multivariate model. The most common example is for mean-centered models (see 13.3 and X2.3), where the average reference value for the calibration set must be added to the initial predictions from the model to obtain the final prediction. A model can be developed to predict changes in the pathlength of the cell used to contain the sample for analysis, and the initially predicted concentrations or property values can be scaled based on the results of the pathlength prediction.

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