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Designation: E1655 − 17

Standard Practices for Infrared Multivariate Quantitative Analysis[1]

This standard is issued under the fixed designation E1655; 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 These practices cover a guide for the multivariate calibration of infrared spectrometers used in determining the physical or chemical characteristics of materials. These practices are applicable to analyses conducted in the near infrared (NIR) spectral region (roughly 780 to 2500 nm) through the mid infrared (MIR) spectral region (roughly 4000 to 400 cm^{-1}).

NOTE 1—While the practices described herein deal specifically with mid- and near-infrared 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 practices described herein for mid- and near-infrared spectroscopies.

1.2 Procedures for collecting and treating data for developing IR calibrations are outlined. Definitions, terms, and calibration techniques are described. Criteria for validating the performance of the calibration model are described.

1.3 The implementation of these practices require that the IR spectrometer has been installed in compliance with the manufacturer's specifications. In addition, it assumes that, at the times of calibration and of validation, the analyzer is operating at the conditions specified by the manufacturer.

1.4 These practices cover techniques that are routinely applied in the near and mid infrared spectral regions for quantitative analysis. The practices outlined cover the general cases for coarse solids, fine ground solids, and liquids. All techniques covered require the use of a computer for data collection and analysis.

1.5 These practices provide a questionnaire against which multivariate calibrations can be examined to determine if they conform to the requirements defined herein.

1.6 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.

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

1.8 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.9 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1265 Practice for Sampling Liquefied Petroleum (LP) Gases, Manual Method

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D4855 Practice for Comparing Test Methods (Withdrawn 2008)[3]

D6122 Practice for Validation of the Performance of Multivariate Online, At-Line, and Laboratory Infrared Spectrophotometer Based Analyzer Systems

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical

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[1] These practices are under the jurisdiction of ASTM Committee E13 on Molecular Spectroscopy and Separation Science and are the direct responsibility of Subcommittee E13.11 on Multivariate Analysis.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The last approved version of this historical standard is referenced on www.astm.org.

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Measurement System Performance
D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants
E131 Terminology Relating to Molecular Spectroscopy
E168 Practices for General Techniques of Infrared Quantitative Analysis
E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers
E334 Practice for General Techniques of Infrared Microanalysis
E456 Terminology Relating to Quality and Statistics
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
E932 Practice for Describing and Measuring Performance of Dispersive Infrared Spectrometers
E1421 Practice for Describing and Measuring Performance of Fourier Transform Mid-Infrared (FT-MIR) Spectrometers: Level Zero and Level One Tests
E1866 Guide for Establishing Spectrophotometer Performance Tests
E1944 Practice for Describing and Measuring Performance of Laboratory Fourier Transform Near-Infrared (FT-NIR) Spectrometers: Level Zero and Level One Tests

3. Terminology

3.1 *Definitions*—For terminology related to molecular spectroscopic methods, refer to Terminology E131. For terminology relating to quality and statistics, refer to Terminology E456.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *analysis, n—in the context of this practice*, the process of applying the calibration model to a spectrum, preprocessed as required, so as to estimate a component concentration value or property.

3.2.2 *calibration, n*—a process used to create a model relating two types of measured data. In the context of this practice, a process for creating a model that relates component concentrations or properties to spectra for a set of known reference samples.

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

3.2.4 *calibration samples, n*—the set of reference samples used for creating a calibration model. Reference component concentration or property values are known (measured by reference method) for the calibration samples and a calibration model is found which relates these values to the spectra during the calibration.

3.2.5 *estimate, n*—the value for a component concentration or property obtained by applying the calibration model for the analysis of an absorption spectrum.

3.2.6 *model validation, n*—the process of testing a calibration model with validation samples to determine bias between the estimates from the model and the reference method, and to test the agreement between estimates made with the model and the reference method.

3.2.7 *multivariate calibration, n*—a process for creating a model that relates component concentrations or properties to the absorbances of a set of known reference samples at more than one wavelength or frequency.

3.2.8 *reference method, n*—the analytical method that is used to estimate the reference component concentration or property value which is used in the calibration and validation procedures.

3.2.9 *reference values, n*—the component concentrations or property values for the calibration or validation samples which are measured by the reference analytical method.

3.2.10 *spectrometer/spectrophotometer qualification, n*—the procedures by which a user demonstrates that the performance of a specific spectrometer/spectrophotometer is adequate to conduct a multivariate analysis so as to obtain precision consistent with that specified in the method.

3.2.11 *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.

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

3.2.13 *validation samples*—a set of samples used in validating the model. Validation samples are not part of the set of calibration samples. Reference component concentration or property values are known (measured by reference method), and are compared to those estimated using the model.

4. Summary of Practices

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

4.2 Multilinear regression (MLR), principal components regression (PCR), and partial least squares (PLS) are examples of multivariate mathematical techniques that are commonly used for the development of the calibration model. Other mathematical techniques are also used, but may not detect outliers, and may not be validated by the procedure described in these practices.

4.3 Statistical tests are applied to detect outliers during the development of the calibration 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), and samples whose reference values are inconsistent with the model.

4.4 Validation of the calibration model is performed by using the model to analyze a set of validation samples and statistically comparing the estimates for the validation samples

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to reference values measured for these samples, so as to test for bias in the model and for agreement of the model with the reference method.

4.5 Statistical tests are applied to detect when values estimated using the model represent extrapolation of the calibration.

4.6 Statistical expressions for calculating the repeatability of the infrared analysis and the expected agreement between the infrared analysis and the reference method are given.

5. Significance and Use

5.1 These practices can be used to establish the validity of the results obtained by an infrared (IR) spectrometer at the time the calibration is developed. The ongoing validation of estimates produced by analysis of unknown samples using the calibration model should be covered separately (see for example, Practice D6122).

5.2 These practices are intended for all users of infrared spectroscopy. Near-infrared spectroscopy is widely used for quantitative analysis. Many of the general principles described in these practices relate to the common modern practices of near-infrared spectroscopic analysis. While sampling methods and instrumentation may differ, the general calibration methodologies are equally applicable to mid-infrared spectroscopy. New techniques are under study that may enhance those discussed within these practices. Users will find these practices to be applicable to basic aspects of the technique, to include sample selection and preparation, instrument operation, and data interpretation.

5.3 The calibration procedures define the range over which measurements are valid and demonstrate whether or not the sensitivity and linearity of the analysis outputs are adequate for providing meaningful estimates of the specific physical or chemical characteristics of the types of materials for which the calibration is developed.

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6. Overview of Multivariate Calibration

6.1 The practice of infrared multivariate quantitative analysis involves the following steps:

6.1.1 *Selecting the Calibration Set*—This set is also termed the training set or spectral library set. This set is to represent all of the chemical and physical variation normally encountered for routine analysis for the desired application. Selection of the calibration set is discussed in Section 17, after the statistical terms necessary to define the selection criteria have been defined.

6.1.2 *Determination of Concentrations or Properties, or Both, for Calibration Samples*—The chemical or physical properties, or both, of samples in the calibration set must be accurately and precisely measured by the reference method in order to accurately calibrate the infrared model for prediction of the unknown samples. Reference measurements are discussed in Section 9.

6.1.3 *The Collection of Infrared Spectra*—The collection of optical data must be performed with care so as 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. Infrared instrumentation is discussed in Section 7 and infrared spectral measurements in Section 8.

6.1.4 *Calculating the Mathematical Model*—The calculation of mathematical (calibration) models may involve a variety of data treatments and calibration algorithms. The more common linear techniques are discussed in Section 12. A variety of statistical techniques are used to evaluate and optimize the model. These techniques are described in Section 15. Statistics used to detect outliers in the calibration set are covered in Section 16.

6.1.5 *Validation of the Calibration Model*—Validation of the efficacy of a specific calibration model (equation) requires that the model be applied for the analysis of a separate set of test (validation) samples, and that the values predicted for these test samples be statistically compared to values obtained by the reference method. The statistical tests to be applied for validation of the model are discussed in Section 18.

6.1.6 *Application of the Model for the Analysis of Unknowns*—The mathematical model is applied to the spectra of unknown samples to estimate component concentrations or property values, or both, (see Section 13). Outlier statistics are used to detect when the analysis involves extrapolation of the model (see Section 16).

6.1.7 *Routine Analysis and Monitoring*—Once the efficacy of one or more calibration equations is established, the equations must be monitored for continued accuracy and precision. Simultaneously, the instrument performance must be monitored so as to trace any deterioration in performance to either the calibration model itself or to a failure in the instrumentation performance. Procedures for verifying the performance of the analysis are only outlined in Section 22. For petrochemicals, these procedures are covered in detail in Practice D6122. The use of Practice D6122 requires that a quality control procedure be established at the time the model is developed. The QC check sample is discussed in Section 22. For practices to compare reference methods and analyzer methods, refer to Practice D4855.

6.1.8 *Transfer of Calibrations*—Transferable calibrations are equations that can be transferred from the original instrument, where calibration data were collected, to other instruments where the calibrations are to be used to predict samples for routine analysis. In order for a calibration to be transferable it must perform prediction after transfer without a significant decrease in performance, as indicated by established statistical tests. In addition, statistical tests that are used to detect extrapolation of the model must be preserved during the transfer. Bias or slope adjustments, or both, are to be made after transfer only when statistically warranted. Calibration transfer, that is sometimes referred to as instrument standardization, is discussed in Section 21.

7. Infrared Instrumentation

7.1 A complete description of all applicable types of infrared instrumentation is beyond the scope of these practices. Only a general outline is given here.

7.2 The IR instrumentation is comprised of two categories, including instruments that acquire continuous spectral data over wavelength or frequency ranges (spectrophotometers), 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 measured. Alternatively, photometers may have several monochromatic light sources, such as light-emitting diodes, that sequentially turn on and off.

7.3 Spectrophotometers 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. 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. Dispersion can occur before the sample (pre-dispersed) or after the sample (post-dispersed).

7.3.1 Spectrophotometers are also available where the wavelength selection is accomplished without moving parts, using a photodiode array detector. Post-dispersion is utilized. A grating can again provide this function, although other methods, such as a linear variable filter (LVF) accomplish the same purpose (a LVF is a multilayer filter that has variable thickness along its length, such that different wavelengths are transmitted at different positions). The photodiode 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 located in a different spectral region of the dispersed light beam and detects a unique range of wavelengths.

7.3.2 The acousto-optical tunable filter is a continuous variant of the fixed filter photometer with no moving optical parts for wavelength selection. A birefrigent crystal (for example, tellurium oxide) is used, in which acoustic waves at a selected frequency are applied to select the wavelength band of light transmitted through the crystal. Variations in the acoustic frequency cause the crystal lattice spacing to change, that in turn, causes the crystal to act as a variable transmission diffraction grating for one wavelength (that is, a Bragg diffractor). A single detector is used to analyze the signal.

7.3.3 An additional category of spectrophotometers uses 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. 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 of 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. The FT instruments use a single detector.

7.3.4 A second type of transformation spectrophotometer uses the Hadamard transformation. Light is initially dispersed with a grating. Light then passes through a mask mounted on or adjacent to a single detector. The mask generates a series of patterns. For example, these patterns may be formed by electronically opening and shutting various locations, such as in a liquid crystal display, or by moving an aperture or slit through the beam. These modulations alter the energy distribution incident upon the detector. A mathematical transformation is then used to convert the signal into spectral information.

7.4 Infrared instruments used in multivariate calibrations should be installed and operated in accordance with the instructions of the instrument manufacturer. Where applicable, the performance of the instrument should be tested at the time the calibration is conducted using procedures defined in the appropriate ASTM practice (see 2.1). The performance of the instrument 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 estimation made with the calibration model.

7.5 For most infrared quantitative applications involving complex matrices, it is a general consensus that scanning-type instruments (either dispersive or interferometer based) provide the greatest performance, due to the stability and reproducibility of modern instrumentation and to the greater amount of spectral data provided for computer interpretation. These data allow for greater calibration flexibility and additional options for selections of spectral areas less sensitive to band shifts and extraneous noise within the spectral signal. Scanning/interferometer-based systems also allow greater wavelength/frequency precision between instruments due to internal wavelength/frequency standardization techniques, and the possibilities of computer-generated spectral corrections. For example, scanning instruments have received approval for complex matrices, such as animal feed and forages (**1, 2**).[4]

7.6 Descriptions of instrumentation designs related to Refs (**1**) and (**2**) are found in Refs (**3**) and (**4**). Other instrumentation similar in performance to that described in these references is acceptable for all near-infrared techniques described in these practices.

7.7 For information describing the measurement of performance of ultraviolet, visible, and near infrared spectrophotometers, refer to Practice E275. For information describing the measurement of performance of dispersive infrared spectrophotometers, refer to Practice E932. For information describing the measurement performance of Fourier Transform mid-infrared spectrophotometers, refer to Practice E1421. For information describing the measurement performance of Fourier Transform near-infrared spectrophotometers, refer to Practice E1944. For spectrophotometers to which these practice do not apply, refer to Guide E1866.

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

8. Infrared Spectral Measurements

8.1 Multivariate calibrations are based on Beer's Law, namely, the absorbance of a homogeneous sample containing an absorbing substance is linearly proportional to the concentration of the absorbing species. The absorbance of a sample is defined as the logarithm to the base ten of the reciprocal of the transmittance, (*T*).

$$A = \log_{10}(1/T)$$

The transmittance, *T*, is defined as the ratio of radiant power transmitted by the sample to the radiant power incident on the sample.

8.1.1 For measurements conducted by reflectance, the reflectance, *R*, is sometimes substituted for the transmittance *T*. The reflectance is defined as the ratio of the radiant power reflected by the sample to the radiant power incident on the sample.

NOTE 2—The relationship $A = \log_{10}(1/R)$ is not a definition, but rather an approximation designed to linearize the relationship between the measured reflectance, *R*, and the concentration of the absorbing species. For some applications, other linearization functions (for example, Kubelka-Munk) may be more appropriate (**5**).

8.1.2 For most types of instrumentation, the radiant power incident on the sample cannot be measured directly. Instead, a reference (background) measurement of the radiant power is made without the sample being present in the light beam.

NOTE 3—To avoid confusion, the reference measurement of the radiant power will be referred to as a background measurement, and the word reference will only be used to refer to measurements made by the reference method against which the infrared is to be calibrated. (See Section 9.)

8.1.3 A measurement is then conducted with the sample present, and the ratio, *T*, is calculated. The background measurement may be conducted in a variety of ways depending on the application and the instrumentation. The sample and its holder may be physically removed from the light beam and a background measurement made on the "empty beam". The sample holder (cell) may be emptied, and a background measurement may be taken through the "empty cell."

NOTE 4—For optically thin cells, care may be necessary to avoid optical interferences resulting from multiple internal reflections within the cell. For very thick cells, differences in the refractive index between the sample and the empty cell may change properties of the optical system, for example, shift focal points.

8.1.4 The sample holder (cell) may be filled with a liquid that has minimal absorption in the spectral range of interest, and the background measurement may be taken through the "background liquid." Alternatively, the light beam may be split or alternately passed through the sample and through an "empty beam," an "empty cell," or a "background liquid." For reflectance measurements, the reflectance of a material having minimal absorbance in the region of interest is generally used as the background measurement.

8.1.5 The particular background referencing scheme that is used may vary among instruments, and among applications. The same background referencing scheme must be employed for the measurement of all spectra of calibration samples, validation samples, and unknown samples to be analyzed.

8.2 Traditionally, a sample is manually brought to the instrument and placed in a cell or cuvette with windows that transmit in the region of interest. Alternatively, transfer pipes can be used to allow liquid to flow through an optical cell in the instrument for continuous analysis. With optical fibers, the sample can be analyzed remotely from the instrument. Radiation is sent to the sample through an optical fiber or bundle of fibers and returned to the instrument by means of another fiber or bundle of fibers. Instruments have been developed that use single fibers to transmit and receive the radiation, as well as those using bundles of fibers for this purpose. Detectors and radiation sources external to the instrument can also be used, in which case only one fiber or bundle is needed. For spectral regions where transmitting fibers do not exist, the same function can be performed over limited distances using appropriate transfer optics.

NOTE 5—If the instrument uses predispersion of the light, some caution must be exercised to avoid introducing ambient light into the system at the sample position, since such light may be detected, giving rise to erroneous absorbance measurements.

8.3 Although most multivariate calibrations for liquids involve the direct measurement of transmitted light, alternative sampling technologies (for example, attenuated total reflectance) can also be employed. Transmittance measurements can be employed for some types of solids (for example, polymer films), whereas other solids (for example, powdered solids) are more commonly measured by diffuse reflectance techniques.

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8.4 For most infrared instrumentation, a variety of adjustable parameters are available to control the collection and computation of the spectral data. These parameters control, for instance, the optical and digital resolution, and the rate of data acquisition (scan speed). A detailed description of the spectral acquisition parameters and their effect on multivariate calibrations is beyond the scope of these practices. However, it is essential that all adjustable parameters that control the collection and computation of spectral data be maintained constant for the collection of spectra of calibration samples, validation samples, and unknown samples for which estimates are to be made.

8.5 For definitions and further description of general infrared quantitative measurement techniques, refer to Practices E168. For a description of general techniques of infrared microanalysis, refer to Practice E334.

9. Reference Method and Reference Values

9.1 Infrared spectroscopy requires calibration to determine the proportionality relationship between the signals measured and the component concentrations or properties that are to be estimated. During the calibration, spectra are measured for samples for which these reference values are known, and the relationship between the sample absorbances and the reference values is determined. The proportionality relationship is then applied to the spectra of unknown samples to estimate the concentration or property values for the sample.

9.2 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 analysis. Because of potential interferences among the absorbances 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), it is preferable that concentration reference values be expressed in volumetric terms, for example, in volume percentage, grams per millilitre, moles per cubic centimetre, and so forth. Developing multivariate calibrations for reference 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.

9.3 For complex mixtures, such as those obtained from petrochemical processes, preparation of reference standards is generally impractical, and the multivariate calibration of an infrared analysis must typically be performed on actual process samples. In this case, the reference values used to calibrate the infrared analysis are obtained by a reference analytical method. The accuracy of a component concentration or property value estimated by a multivariate infrared analysis is highly dependent on the accuracy and precision of the reference values used in the calibration. The expected agreement between the infrared estimated values and those obtained from a single reference measurement can never exceed the repeatability of the reference method, since, even if the infrared estimated the true value, the measurement of agreement is limited by the precision of the reference values. Knowledge of the precision (repeatability) of the reference method is critical in the development of an infrared multivariate calibration. The precision of the reference data used in developing a model, and the accuracy of the model can be improved by averaging repeated reference measurements.

NOTE 6—If the reference 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 (see for example, Practice D6299. If primary standards are not available to allow the bias of the reference measurement process to be established, it is recommended that the laboratory participate in an interlaboratory cross-check program as a means of demonstrating accuracy.

NOTE 7—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 infrared analysis, or for laboratory measurement of the reference data 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 and D4057, or Practice D4177, whichever are applicable. Whenever possible, sample storage for extended time periods is not recommended because of the likelihood of samples degrading with time in spite of 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 reference method.

9.4 If the reference method used to obtain reference values for the multivariate calibration is an established ASTM method, then repeatability and reproducibility data are included in the method. In this case, it is only necessary to demonstrate that the reference measurement is being practiced in accordance with the procedure described in the method, and that the repeatability obtained is statistically comparable to that published in the method. Data from established quality control procedures can be used to demonstrate that the repeatability of the reference method is within ASTM specifications. If such data is not available, then repeatability data should be collected on at least three of the samples that are to be used in the calibration. These samples should be chosen to span the range of values over which the calibration is to be developed, one sample having a reference value in the bottom third of the range, one sample having a value in the middle third of the range, and one sample having a value in the upper third of the range. At least six reference measurements should be made on each sample. The standard deviation among the measurements should be calculated and compared to that expected based on the published repeatability.[5]

9.5 If the reference method to be used for the multivariate calibration is an established ASTM method, and the samples to be used in the calibration have been analyzed by a cooperative testing program (for example, octane values obtained from recognized exchange groups), then the reference values obtained by the cooperative testing program can be used directly, and the standard deviations established by the cooperative testing program can be used as the estimate of the precision of the reference data.

9.6 Reference methods 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 method developer to establish the precision of the reference method using procedures similar to those detailed in Practice E691, in the *Manual for Determining Precision for ASTM Methods on Petroleum Products and Lubricants*[5] and in Practice D6300.

9.7 When multiple reference measurements are made on an individual calibration or validation sample, a Dixon's Test (see A1.1) should be applied to the values to determine if all of the reference values came from the same population, or if one or more of the values is suspect and should be rejected.

10. Simple Procedure to Develop a Feasibility Calibration

10.1 For new applications, it is generally not known whether an adequate IR 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:

10.1.1 Approximately 30 to 50 samples are collected covering the entire range for the constituent/property of interest. Care should be exercised to avoid intercorrelations among

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[5] *Manual on Determining Precision Data for ASTM Methods on Petroleum Products and Lubricants*, which has been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1007.

major constituents unless such intercorrelations always exist in the materials being analyzed. The range in the concentration/property should be preferably five times, but not less than three times, the standard deviation of the reproducibility (reproducibility/2.77) of the reference analysis.

10.1.2 When collecting spectral data on these samples, variations in particle size, sample presentation, and process conditions which are expected during analysis must be reproduced. Multiple spectra of the same sample under different conditions can be employed if such variations in conditions are anticipated during analysis.

10.1.3 Reference analyses on these samples are conducted using the accepted reference method. If the range for the component/property is not at least five times the standard deviation of the reproducibility for the reference analysis, then r replicate analyses should be conducted on each sample such that the $\sqrt{r}$ times the range is preferably five times, but at least three times, the standard deviation of the reference analysis.

10.1.4 A calibration model is developed using one or more of the mathematical techniques described in Sections 11 and 12. The calibration model is preferably tested using cross-validation methods such as SECV or PRESS (see 15.3.6). Other statistics can also be used to judge the overall quality of the calibration.

10.1.5 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 13, 14, and 15.

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11. Data Preprocessing

11.1 Various types of data preprocessing algorithms can be applied to the spectral data prior to the development of a multivariate calibration model. 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 these practices. For the purpose of these practices, 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 21. In addition, any spectral preprocessing method must be automated so as 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.

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

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

11.2.2 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 15.2).

12. Multivariate Calibration Mathematics

12.1 Multivariate mathematical techniques are used to relate the spectra measured for a set of *calibration samples* to the reference values (property or component concentration values) obtained for this set of samples from a reference test. The object is to establish a multivariate *calibration model* that can be applied to the spectra of future, unknown, samples to estimate values (property or component concentration values). Only linear multivariate techniques are described in these practices; that is, it is assumed that the property or component concentration values 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 following linear techniques. These practices are not intended to compare or contrast among these techniques. For the purpose of these practices, the suitability of any specific mathematical technique should be judged only on the following two criteria:

12.1.1 The technique should be capable of producing a calibration model that can be validated as described in Section 18; and

12.1.2 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 16.3).

NOTE 8—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.

12.1.3 All linear, multivariate techniques are designed to solve the same generic problem. If n calibration spectra are measured at f discrete wavelengths (or frequencies), then $\mathbf{X}$, the spectral data matrix, is defined as an f by n matrix containing the spectra (or some function of the spectra produced by preprocessing, as described in Section 9) as columns. Similarly $\mathbf{y}$ is a vector of dimension n by 1 containing the reference values for the calibration samples. The object of the linear, multivariate modeling is to calculate a prediction vector $\mathbf{p}$ of dimension f by 1 that solves Eq 1:

$$\mathbf{y} = \mathbf{X}^t\mathbf{p} + \mathbf{e} \tag{1}$$

where $\mathbf{X}^t$ is the transpose of the matrix **X** obtained by interchanging the rows and columns of **X**. The error vector, **e**, is a vector of dimension *n* by 1, that is the difference between the reference values **y** and their estimates, $\hat{\mathbf{y}}$, where:

$$\hat{\mathbf{y}} = \mathbf{X}^t\mathbf{p} \qquad (2)$$

12.1.4 For some applications, it may be useful to combine the spectral data with other measured variables (for example, sample temperature, pH, mixing rates, etc.). These additional heterogeneous variable may simply be appended to the spectrum of each sample as if they were additional measured wavelengths. 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 in order 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.

12.1.5 The estimation of the prediction vector **p** is generally calculated so as to minimize the sum of squares of the errors,

$$\mathbf{e}^t\mathbf{e} = ||\,\mathbf{e}^2\,|| = (\mathbf{y} - \mathbf{X}^t\,\mathbf{p})^t(\mathbf{y} - \mathbf{X}^t\mathbf{p}) \qquad (3)$$

Since **X** is generally not a square matrix, it cannot be directly inverted to solve Eq 3. Instead, the pseudo or generalized inverse of **X, X⁺**, is calculated as:

$$\mathbf{X}^+\mathbf{y} = (\mathbf{X}\mathbf{X}^t)^{-1}\mathbf{X}\mathbf{y} = \mathbf{p} \qquad (4)$$

where **p** is the least square estimate of the prediction vector **p**. It should be noted that, in applying Eq 1-4, it is assumed that the errors in the spectral data in **X** are negligible compared to the errors in the reference data, and that there is a linear relationship between the component concentration or property and the spectral data. If either of these assumptions is incorrect, then the linear models derived here will not yield an optimal estimate of **p**.

12.1.6 In calculating the least square solution in Eq 4, it is assumed that the individual error values in **e** (see Eq 1) are normally distributed with common variance. This will be true if each of the individual reference values in **y** represents the result of a single reference measurement, and if the repeatability of the reference method is constant over the range of values in **y**. If the values in **y** represent averages of more than one reference method determination, then the least square expression in Eq 4 is not applicable. If r_i reference values y_{i1}, y_{i2}, y_{i3}, . . . y_{ir} are measured for calibration sample *i*, then a weighted regression can be employed. If **R** is a diagonal matrix of dimension *n* by *n* containing the r_i values for each of the calibration samples, then the weighted regression is given by:

$$\sqrt{\mathbf{R}}\,\bar{\mathbf{y}} = \sqrt{\mathbf{R}}\mathbf{X}^t\mathbf{p} + \mathbf{e} \qquad (5)$$

$$(\mathbf{X}\mathbf{R}\mathbf{X}^t)^{-1}\mathbf{X}\mathbf{R}\bar{\mathbf{y}} = \mathbf{p} \qquad (6)$$

where $\sqrt{\mathbf{R}}$ indicates the diagonal matrix containing the square roots of the r_i values, and $\bar{\mathbf{y}}$ is the vector containing the averages of the r_i reference values for each sample. If averages of multiple reference values are used in **y** and a weighted regression is used, special care must be taken to add back the variance removed by calculating the average reference values (see Section 11) so that the statistics for the model can be compared to those for a single reference value determination. The specific method in which the weighting is applied depends on the specific multivariate mathematics that are employed.

12.1.7 For most cases, if the calibration spectra are collected over an extended wavelength (or frequency) range, the number of individual absorption values per spectrum, *f*, will exceed the number of calibration spectra, *n*. In this case, the matrices $(\mathbf{X}\mathbf{X}^t)$ and $(\mathbf{X}\mathbf{R}\mathbf{X}^t)$ are rank deficient and cannot be directly inverted. Even in cases where $f < n$, colinearity among the calibration spectra can cause $(\mathbf{X}\mathbf{X}^t)$ and $(\mathbf{X}\mathbf{R}\mathbf{X}^t)$ to be nearly singular (to have a determinant that is near zero), and the direct use of Eq 4 and Eq 6 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 estimated values. In order to solve Eq 4 and Eq 6, 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 **X** so as to be able to calculate stable inverses of $(\mathbf{X}\mathbf{X}^t)$ and $(\mathbf{X}\mathbf{R}\mathbf{X}^t)$ and the estimate **p**.

12.2 *Multilinear Regression Analysis:*

12.2.1 In multilinear regression (MLR), a specific number, *k*, of individual wavelengths (or frequencies), or analytical regions, or both, are chosen such that *k* <= *n*/6. Depending on the particular 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. A new matrix **M** of dimension *k* by *n* is obtained from **X** by extracting the rows from **X** that correspond to the selected wavelengths (or frequencies). The calibration equation then becomes:

$$\mathbf{y} = \mathbf{M}^t\mathbf{b} + \mathbf{e} \qquad (7)$$

where **b** is a vector of dimension *k* by 1 containing the set of regression coefficients defined at each of the chosen wavelengths (or frequencies). The solution for the regression coefficients is obtained as:

$$(\mathbf{M}\mathbf{M}^t)^{-1}\mathbf{M}\mathbf{y} = \mathbf{b} \qquad (8)$$

If M comprises exclusively a subset of the wavelengths in X, the estimate of the full prediction vector, **p**, is obtained from **b** by substituting the values from **b** into the corresponding positions in **p** (corresponding to the selected wavelengths or frequencies), and setting all other elements of **p** (corresponding to the wavelengths or frequencies that were eliminated in going from **X** to **M**) to zero. If M comprises any integrated peak areas, then the value of *b* which is substituted into the corresponding positions of **p** must be adjusted by dividing by the number of wavelengths incorporated into the integrated peak area. If baseline correction was applied to any wavelengths or integrated peak areas, then the same baseline correction must be applied to the spectrum measured for the unknown sample before applying the regression vector, **p**.

12.2.2 If a weighted regression is used, the corresponding form for Eq 8 becomes:

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$$(\mathbf{MRM}^t)^{-1}\mathbf{MRy} = \mathbf{b} \tag{9}$$

12.2.3 Not all commercial software packages that implement MLR include options for weighted regressions. If MLR models are developed with such packages, averages of multiple reference values should still be included in the **y** vector if they are available. The use of the average values will lead to better estimates of the regression coefficients, but the model produced will not be the least squares minimum. Standard errors of calibration calculated by the software will generally not be meaningful in these cases since they are not expressed relative to a single reference measurement. Standard errors of calibration should be recalculated using the procedure described in Section 11.

12.2.4 The choice of the number of wavelengths (or frequencies), *k*, to use in multilinear regression is a critical factor in the model development. If too few wavelengths are used, a less precise model will be developed. If too many wavelengths are used, colinearity 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 Section 15) 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.

12.2.5 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 (**6, 7, 8, 9**). Alternatively, selection may be based on prior knowledge of a relationship between the absorptions measured and the property or component being modeled. It is beyond the scope of these practices to compare alternative selection methods. An adequate set of wavelengths (or frequencies) will, for the purpose of these practices, be defined as a set that produces a model with the desired precision that passes the validation test procedure described in Section 18.

12.3 *Principal Components Regression (PCR):*

12.3.1 Principal components regression (PCR) is based on the singular value decomposition of the spectral data matrix. The singular value decomposition takes the form:

$$\mathbf{X} = \mathbf{L}\sum\mathbf{S}^t \tag{10}$$

12.3.1.1 The scores matrix, **S**, is a *n* by *n* matrix that satisfies the relationship:

$$\mathbf{S}^t\mathbf{S} = \mathbf{I} \tag{11}$$

$$\mathbf{S}^t(\mathbf{X}^t\mathbf{X})\mathbf{S} = \Lambda \tag{12}$$

where **I** is a *n* by *n* identity matrix, and Λ is the matrix of eigenvalues of $\mathbf{X}^t\mathbf{X}$. The *n* by *n* matrix ∑ is the matrix of singular values, that are the square roots of the eigenvalues, that is:

$$\sum{}^2 = \Lambda \tag{13}$$

12.3.1.2 The loadings matrix, **L**, is a *f* by *n* matrix that satisfies the relationships:

$$\mathbf{L}^t\mathbf{L} = \mathbf{I} \tag{14}$$

$$\mathbf{L}^t(\mathbf{XX}^t)\mathbf{L} = \Lambda \tag{15}$$

12.3.1.3 The row vectors that make up the matrices **S** and **L** are orthonormal, that is, the dot product of the vector with itself is 1, and the dot product with any other vector in the matrix is 0.

NOTE 9—In some implementations of PCR, the data matrix **X** may be decomposed as the product of only two matrices, **S** and **L**. Either **S** or **L** is then orthogonal but not orthonormal, and either $\mathbf{S}^t\mathbf{S} = \Lambda$ or $\mathbf{L}^t\mathbf{L} = \Lambda$.

12.3.1.4 Using the singular value decomposition, the pseudo inverse of the matrix **X** can be calculated as:

$$\mathbf{X}^+ = \mathbf{S}\sum{}^{-1}\mathbf{L}^t \tag{16}$$

12.3.1.5 Using the pseudo inverse relationship in Eq 16, it is then possible to solve for the prediction vector **p**. In practice, however, the full inverse of **X** as given in Eq 16 is not used, since it contains information relating to the spectral noise in the calibration spectra.

12.3.2 When a principal components analysis is conducted on a matrix **X** containing the calibration spectra, the signals arising from the calibration sample components generally account for the majority of the variance in **X**, and are concentrated into the first *k* loading vectors, that correspond to the larger eigenvalues. While the separation of signal and noise is seldom perfect, it is preferable to use only the first *k* vectors in building a model. The singular value decomposition of **X** is then written as:

$$\mathbf{X} = \mathbf{L}_a\sum{}_a\mathbf{S}_a^t + \mathbf{L}_n\sum{}_n\mathbf{S}_n^t \tag{17}$$

where $\mathbf{S_a}$ is a *n* by *k* matrix containing the first *k* columns of **S,** $\mathbf{L_a}$ is a *f* by *k* matrix containing the first *k* columns of **L,** $\mathbf{\Sigma_a}$ is a *k* by *k* diagonal matrix containing the first *k* singular values, and $\mathbf{S_n}$, $\mathbf{L_n}$ and $\mathbf{\Sigma_n}$ are the corresponding matrices containing the last *n-k* elements of **S, L** and **Σ**. The pseudo inverse of **X** is then approximated as:

$$\mathbf{X}^+ = \mathbf{S}_a\sum{}_a^{-1}\mathbf{L}_a^t \tag{18}$$

12.3.2.1 The estimate for the prediction vector, **p**, is then given as:

$$\mathbf{p} = \mathbf{L}_a\sum{}_a^{-1}\mathbf{S}_a^t\mathbf{y} \tag{19}$$

12.3.2.2 Alternatively, the scores, **S**, may be regressed against the reference values, **y**, to obtain a set of regression coefficients, **b**:

$$\mathbf{y} = \mathbf{S}_a\mathbf{b} + \mathbf{e} \tag{20}$$

$$\mathbf{b} = (\mathbf{S}_a^t\,\mathbf{S}_a)^{-1}\mathbf{S}_a^t\mathbf{y} = \mathbf{S}_a^t\mathbf{y} \tag{21}$$

12.3.2.3 Various stepwise regression algorithms (**10, 11, 12**) may be used to test which of the principal components (which columns in the scores matrix, **S**) show a statistically significant correlation to the reference values in **y**. Coefficients (elements of **b**) for principal components that do not show a statistically significant correlation may be set to zero. The estimate for the prediction vector then becomes:

$$\mathbf{p} = \mathbf{L}_a\Sigma_a^{-1}\,\mathbf{b} \tag{22}$$

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12.3.3 If the average of multiple reference measurements is used in the **y** vector, then a weighted regression should be used in calculating the prediction vector. The weighting is preferably applied to the scores in Eq 20 and Eq 21, and the spectra in **X** are not weighted prior to the singular value decomposition.

12.3.3.1 If r_i individual reference values are measured for the ith calibration sample, then entering r_i copies of the spectrum x_i into the **X** matrix, or weighting the spectrum x_i by $\sqrt{r_i}$ will alter the loadings that are calculated. If the spectrum x_i is only measured once, the uncertainty in the spectral variables contributed by x_i is no different from that for the other $n - 1$ spectra. Weighting the spectrum x_i prior to the singular value decomposition will tend to force noise characteristics of x_i into the loadings, adversely affecting the model. Weighting the scores during the calculation of the regression coefficients will properly account for the differences in the variance among the components of the $\bar{\mathbf{y}}$ vector. The weighted regression equations become:

$$\sqrt{\mathbf{R}}\,\bar{\mathbf{y}} = \sqrt{\mathbf{R}}\mathbf{S}_a\mathbf{b}+\mathbf{e} \tag{23}$$

$$\mathbf{b} = (\mathbf{S}_a^t\,\mathbf{R}\mathbf{S}_a)^{-1}\mathbf{R}\mathbf{S}_a^t\,\bar{\mathbf{y}} \tag{24}$$

12.3.4 Not all commercial software packages that implement PCR include options for weighted regressions. If PCR models are developed with such packages, averages of multiple reference values should still be included in the **y** vector if they are available. The use of the average values will lead to better estimates of the regression coefficients, but the model produced will not be the least squares minimum. Standard errors of calibration calculated by the software will generally not be meaningful in these cases since they are not expressed relative to a single reference measurement. Standard errors of calibration should be recalculated using the procedure described in 15.1.

12.3.5 As with wavelengths in multilinear regression, the choice of the number of principal components, k, to use in the regression is a critical factor 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 estimations. The optimum number of principal components for a model is related to the number of spectrally distinguishable components in the calibration spectra (see Section 15), 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.

12.4 *Partial Least Squares (PLS):*

NOTE 10—The term PLS has been used to describe various mathematical algorithms. The version described here is a specific representation of the PLS-1 algorithm, and deals with only one set of reference values at a time. PLS-2 or multiblock PLS algorithms exist that can be used for the simultaneous calibration of multiple components or concentrations, or both. Except in special cases, PLS-2 generally produces calibrations which do not perform as well as those produced by PLS-1, and multiblock PLS involves complexities beyond the scope of these practices. Therefore, these practices do not address PLS-2 nor multiblock PLS algorithms. Various descriptions of the PLS-1 algorithm have been published (**13**, **14**, **15**, **16**, **17**, **18**, **19**, **20**) many of which differ slightly in the actual computational steps. In implementing the PLS-1 algorithm, a choice must be made as to which, if either, of the scores or loadings vectors are to be normalized. In the following derivation, the scores vectors were normalized. If neither vector is normalized, or if the loadings vector is normalized instead of the scores vector, a different expression will be obtained for the prediction vector. Differences in the derivations should not result in significant differences in the numerical values obtained for the prediction vector, nor in estimates based on it.

12.4.1 Like PCR, PLS involves the decomposition of the spectral data matrix, **X**, into the product of matrices. Unlike PCR where **X** is first decomposed, and then regressed versus the reference values, in PLS, the **y** vector is used in obtaining the decomposition of **X**. The PLS proceeds by means of a series of steps, which are repeated in a loop. Each time the steps are repeated, a weighting vector $\mathbf{w_i}$ (of dimension f by 1), a scores vector $\mathbf{s_i}$ (of dimension n by 1), a regression coefficient b_i (a scalar), and a loadings vector $\mathbf{l_i}$ (of dimension f by 1) are calculated. The subscript $_i$ indicates the number of times the entire loop has been executed, and is initially 1.

12.4.1.1 *Step 1*—Calculation of a weighting vector of dimension f by 1, $\mathbf{w}_i$:

$$\mathbf{X}^t = \mathbf{y}\mathbf{w}_i^t+\mathbf{Z} \tag{25}$$

$$\hat{w}_i = \mathbf{X}\mathbf{y} \tag{26}$$

12.4.1.2 *Step 2*—Scaling the weight vector $\hat{w}_i$ and calculation of a normalized scores vector, $\mathbf{s}_i$, of dimension n by 1:

$$\mathbf{X}^t = \mathbf{s}_i\,\widehat{\mathbf{w}}_i^t+\mathbf{Z} \tag{27}$$

$$\hat{\mathbf{s}} = \mathbf{X}^t\,\widehat{\mathbf{w}}_i \tag{28}$$

$$\widehat{\mathbf{w}}_i = \widehat{\mathbf{w}}_i(\hat{\mathbf{s}}^t\,\hat{\mathbf{s}})^{1/2} \tag{29}$$

$$\hat{\mathbf{s}}_i = \frac{\hat{\mathbf{s}}_\mathbf{i}}{(\hat{\mathbf{s}}^t\,\hat{\mathbf{s}})^{1/2}} \tag{30}$$

12.4.1.3 *Step 3*—Regressing the scores vector against the reference values to obtain a regression coefficient, b_i:

$$\mathbf{y} = \hat{\mathbf{s}}_i b_i+\mathbf{e} \tag{31}$$

$$b_i = \hat{\mathbf{s}}_i^t\mathbf{y} \tag{32}$$

12.4.1.4 *Step 4*—Calculation of a loading vector, $\mathbf{l}_i$ of dimension f by 1:

$$\mathbf{X} = \mathbf{l}_i\,\hat{\mathbf{s}}_i{}^t+\mathbf{Z} \tag{33}$$

$$\mathbf{l}_i = \mathbf{X}\hat{\mathbf{s}}_i \tag{34}$$

12.4.1.5 *Step 5*—Calculation of the residuals:

$$\mathbf{Z_i} = \mathbf{X} - \mathbf{l}_i\hat{\mathbf{s}}_i{}^t \tag{35}$$

$$\mathbf{e}_i = \mathbf{y} - b_i\hat{\mathbf{s}}_i \tag{36}$$

12.4.1.6 For subsequent times through the loop, the matrix **X** is replaced with the residuals matrix $\mathbf{Z}_{i-1}$ from the previous loop, and the **y** vector is replaced with the residuals vector $\mathbf{e}_{i-1}$. The loop is repeated k times to obtain k weighting, scores, and loading vectors, and k regression coefficients. The overall expression for the results is then:

$$\mathbf{X} = \mathbf{L}\mathbf{S}^t+\mathbf{Z} \tag{37}$$

$$\mathbf{y} = \mathbf{S}\mathbf{b}+\mathbf{e} \tag{38}$$

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where **S** is the n by k matrix containing the $\hat{\mathbf{s}}_i$ as rows, **L** is the f by k matrix containing the $\mathbf{l_i}$ as individual rows, **Z** is the residual from the spectral data matrix, and **e** is the residual from the estimation of the reference values. The estimate of the prediction vector is then given by:

$$p = W(L^t\, W)^{-1}\mathbf{b} \tag{39}$$

12.4.2 If the values in the vector $\bar{\mathbf{y}}$ contain the average of multiple reference measurements, then a weighted regression should be employed in developing the model. Unfortunately, for PLS, development of an appropriate weighting scheme is complicated by the use of **y** in the decomposition of **X**. If the spectrum x_i corresponds to a sample for which x_i reference values are measured, then weighting both **X** and **y** by $\sqrt{\mathbf{R}}$ in Step 1 of the PLS algorithm will over emphasize the spectral variables contributed by x_i. Preferably, weighting is done only in the calculation of the regression coefficients in Step 3. Eq 31and Eq 32 then become:

$$\sqrt{\mathbf{R}}\,\bar{\mathbf{y}} = \sqrt{\mathbf{R}}\hat{\mathbf{s}}_i b_i + \mathbf{e} \tag{40}$$

$$b_i = (\hat{\mathbf{s}}_i{}^{\mathbf{t}}\mathbf{R}\hat{\mathbf{s}}_i)^{-1}\hat{\mathbf{s}}_i{}^{\mathbf{t}}R\,\bar{\mathbf{y}} \tag{41}$$

12.4.2.1 The other steps in the algorithm proceed unchanged.

12.4.3 Not all commercial software packages that implement PLS include options for weighted regressions. If PLS models are developed with such packages, averages of multiple reference values should still be included in the $\bar{\mathbf{y}}$ vector if they are available. The use of the average values will lead to better estimates of the regression coefficients, but the model produced will not be the least squares minimum. Standard errors of calibration calculated by the software will generally not be meaningful in these cases since they are not expressed relative to a single reference measurement. Standard errors of calibration should be recalculated using the procedure described in 15.2.

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

12.5.1 An important step in the development of PCR and PLS models is the selection of which frequencies/wavelengths to include in the model. The calibration model will not necessarily include data in the entire spectral range measured by the spectrometer. 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 calibration models for a variety of reasons including high spectral noise, nonlinear spectrometer response and spectral interferences due to optical or environmental sources.

12.5.1.1 Spectrometers typically have limited range over which they will respond linearly. For dispersive spectrometers, stray light may limit the linear response range. Similarly, for FTIR spectrometers, 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 22), as well as the robustness of the model to spectrometer maintenance. Regions where samples are optically opaque should always be excluded from models.

12.5.1.2 Spectra can contain signals that are due to the spectrometer, sampling optics for 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.

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

$$\bar{\mathbf{x}} = \frac{\mathbf{X1}}{n} \tag{42}$$

$$\sigma_{\mathbf{x}} = diag\left(\sqrt{\frac{(\mathbf{X} - \bar{\mathbf{x}}\mathbf{1}^t)*(\mathbf{X} - \bar{\mathbf{x}}\mathbf{1}^t)^t}{n-1}}\right) \tag{43}$$

r replicate spectra ($\mathbf{X_r}$) of one or more calibration samples should be collected, and similar average ($\bar{\mathbf{x}}_r$) and standard deviations (σ_r) values should be calculated.

$$\bar{\mathbf{x}}_r = \frac{\mathbf{X}_r\mathbf{1}}{r} \tag{44}$$

$$\sigma_r = diag\left(\sqrt{\frac{(\mathbf{X}_r - \bar{\mathbf{x}}_r\mathbf{1}^t)*(\mathbf{X}_r - \bar{\mathbf{x}}_r\mathbf{1}^t)^t}{r-1}}\right) \tag{45}$$

The ratio of σ_r to σ_x is useful in selecting frequencies/wavelengths for inclusion/exclusion from the model.

12.5.2.1 If, for a given frequency/wavelength, the ratio of σ_r to σ_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.

12.5.2.2 If, for a given frequency/wavelength, the ratio of σ_r to σ_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.

12.5.3 During analyses, 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.

13. Estimation of Values from Spectra

13.1 If **x** (an f by 1 vector) is the spectrum of a sample, then $\hat{y}$ (a scalar), the estimated component concentration or property value, is given by:

$$\hat{y} = \mathbf{x}^{\mathbf{t}}\mathbf{p} \tag{46}$$

where p is the prediction vector obtained from the multivariate calibration. The expression in Eq 46 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 $\hat{y}$, since they provide additional parameters required to calculate the uncertainty in the estimation as well