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Standard Practice for Qualifying Spectrometers and Spectrophotometers for Use in Multivariate Analyses, Calibrated Using Surrogate Mixtures[1]

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1. Scope

1.1 This practice relates to the multivariate calibration of spectrometers and spectrophotometers used in determining the physical and chemical characteristics of materials. A detailed description of general multivariate analysis is given in Practice E 1655. This standard refers only to those instances where surrogate mixtures can be used to establish a suitable calibration matrix. This practice specifies calibration and qualification data set requirements for interlaboratory studies (ILSs), that is, round robins, of standard test methods employing surrogate calibration techniques that do not conform exactly to Practices E 1655.

NOTE 1—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 in Practices E 1655, they do not conform to procedures described therein, specifically with respect to the handling of outliers.

1.2 This practice specifies how the ILS data is treated to establish spectrometer/spectrophotometer performance qualification requirements to be incorporated into standard test methods.

NOTE 2—Spectrometer/spectrophotometer qualification procedures are intended to allow the user to determine if the performance of a specific spectrometer/spectrophotometer is adequate to conduct the analysis so as to obtain results consistent with the published test method precision.

1.2.1 The spectroscopies used in the surrogate test methods would include but not be limited to mid- and near-infrared, ultraviolet/visible, fluorescence and Raman spectroscopies.

1.2.2 The surrogate calibrations covered in this practice are: multilinear regression (MLR), principal components regression (PCR) or partial least squares (PLS) mathematics. These calibration procedures are described in detail in Practices E 1655.

1.3 For surrogate test methods, this practice recommends limitations that should be placed on calibration options that are allowed in the test method. Specifically, this practice recommends that the test method developer demonstrate that all calibrations that are allowed in the test method produce statistically indistinguishable results.

1.4 For surrogate test methods that reference spectrometer/spectrophotometer performance practices, such as Practices E 275, E 387, E 388, E 579, E 925, E 932, E 958, E 1421, E 1683, E 1866 or E 1944, this practice recommends that instrument performance data be collected as part of the ILS to establish the relationship between spectrometer/spectrophotometer performance and test method precision.

2. Referenced Documents

2.1 *ASTM Standards:*

D 6277 Test Method for Determination of Benzene in Spark-Ignition Engine Fuels by Mid Infrared Spectroscopy[2]

D 6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants[3]

E 131 Terminology Relating to Molecular Spectroscopy[3]

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers[3]

E 387 Test Method for Estimating Stray Radiant Power of Spectrophotometers by the Opaque Filter Method[3]

E 388 Test Method for Spectral Bandwidth and Wavelength Accuracy of Fluorescence Spectrophotometers[3]

E 579 Test Method for Limit of Detection of Fluorescence of Quinine Sulfate[3]

E 691 Practice for Conducting an Inter-Laboratory Study to Determine the Precision of a Test Method[4]

E 925 Practice for the Periodic Calibration of Narrow Band-Pass Spectrophotometers[3]

E 932 Practice for Describing and Measuring Performance of Dispersive Infrared Spectrometers[3]

[1] This practice is under the jurisdiction of ASTM Committee E13 on Molecular Spectroscopy and is the direct responsibility of Subcommittee E13.11 on Chemometrics.

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[2] *Annual Book of ASTM Standards*, Vol 05.03.

[3] *Annual Book of ASTM Standards*, Vol 03.06.

[4] *Annual Book of ASTM Standards*, Vol 14.02.

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E 958 Practice for Measuring Practical Spectral Bandwidth of Ultraviolet-Visible Spectrophotometers[3]

E 1421 Practice for Describing and Measuring Performance of Fourier Transform Infrared Spectrophotometers: Level Zero and Level One Tests[3]

E 1655 Practices for Infrared, Multivariate, Quantitative Analysis[3]

E 1683 Practice for Testing the Performance of Scanning Raman Spectrometers[3]

E 1866 Guide for Establishing Spectrophotometer Performance Tests[3]

E 1944 Practice for Describing and Measuring Performance of Fourier Transform Near-Infrared Spectrometers: Level Zero and Level One Tests[3]

3. Terminology

3.1 *Definitions*:

3.1.1 For definitions of terms and symbols relating to infrared, ultraviolet/visible and Raman spectroscopy, refer to Terminology E 131.

3.1.2 For definitions of terms and symbols relating to multivariate analysis, refer to Practices E 1655.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *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 test method.

3.2.2 *surrogate calibration*, *n*—a multivariate calibration that is developed using a calibration set which consists of mixtures with pre-specified and reproducible compositions that contain substantially fewer chemical components than the samples that will ultimately be analyzed.

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

4. Summary of Practice

4.1 A surrogate test method must specify the composition of two sets of samples. One set is used to calibrate the spectrometers/spectrophotometers. The second set of samples is used to qualify the spectrometer/spectrophotometer to perform the analysis. The compositions of both sets are expressed in terms of weight or volume fraction depending on whether the samples are prepared gravimetrically or volumetrically. The compositions of both sets should be specified in the surrogate test method. If the surrogate test method is being used to estimate a physical property, then the test method should indicate what value of the property is to be assigned to each of the calibration and qualification samples.

4.2 The surrogate test method should specify the minimum spectrometer/spectrophotometer requirements for instruments that can be used to perform the test method.

4.3 The spectrometer/spectrophotometer test method should specify the exact conditions that are to be used to collect and, where appropriate, to calculate the spectral data used in the calibration and analysis.

4.4 The test method should specify the exact mathematics that are to be used to develop the multivariate calibration. Allowable spectral preprocessing methods should be defined. The specific mathematics (MLR, PCR or PLS) should be specified, and the acceptable range for the numbers of variables should be given.

4.5 When the ILS is conducted to establish the precision of the surrogate test method, the calibration data for all of the participating laboratories should be collected and used to calculate a pooled standard error of calibration for the test method. The pooled standard error of calibration and its associated degrees of freedom should be reported in the test method.

4.5.1 When a user is calibrating a spectrometer/spectrophotometer, the standard error of calibration is calculated and compared to the pooled standard error of calibration from the ILS to determine if the performance of the calibrated spectrometer/spectrophotometer is adequate to produce analyses of the precision specified in the test method.

4.5.2 If a user is purchasing a precalibrated spectrometer/spectrophotometer, the instrument vendor should supply the standard error of calibration and its statistical comparison to the pooled standard error of calibration.

4.6 During the ILS, each participating laboratory analyzes a set of qualification samples and reports both the compositions of the qualification set and the estimates made using the multivariate analysis. A pooled error of qualification is calculated and reported as part of the test method along with its corresponding degrees of freedom.

4.6.1 Before a user may use the spectrometer/spectrophotometer, it must be qualified to perform the surrogate test method. The qualification set is analyzed, and a standard error of qualification is calculated. The standard error of qualification is statistically compared with the pooled standard error of qualification to determine if the performance of the calibrated spectrometer/spectrophotometer is adequate to produce analyses of the precision specified in the test method.

4.6.2 Spectrometer/spectrophotometer qualification is required regardless of whether the calibration is performed by the vendor or the user.

4.6.3 Spectrometer/spectrophotometer qualification should be repeated after major maintenance has been performed on the spectrometer/spectrophotometer so as to determine whether recalibration is required.

5. Significance and Use

5.1 This practice should be used by the developer of standard test methods that employ surrogate calibrations.

5.1.1 This practice assists the test method developer in setting and documenting requirements for the spectrometer/spectrophotometers that can perform the test method.

5.1.2 This practice assists the test method developer in setting and documenting spectral data collection and computation parameters for the test method.

5.1.3 This practice assists the test method developer in selecting among possible multivariate analysis procedures that could be used to establish the surrogate calibration. The practice describes statistical tests that should be performed to ensure that all multivariate analysis procedures that are allowed within the scope of the test method produce statistically indistinguishable results.

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5.1.4 This practice describes statistical calculations that the test method developer should perform on the calibration and qualification data that should be collected as part of the ILS that establishes the test method precision. These calculations establish the level of performance that spectrometers/spectrophotometers must meet in order to perform the test method.

5.2 This practice describes how the person who calibrates a spectrometer/spectrophotometer can test the performance of said spectrometer/spectrophotometer to determine if the performance is adequate to conduct the test method.

5.3 This practice describes how the user of a spectrometer/spectrophotometer can qualify the spectrometer/spectrophotometer to conduct the test method.

6. Surrogate Calibrations

6.1 Practices E 1655 assumes that the calibration set used to develop a multivariate model contains samples of the same type as those that are to eventually be analyzed using the model. Practices E 1655 requires use of outlier statistics to ensure that samples being analyzed are sufficiently similar to the calibration samples to produce meaningful results. For some spectroscopic analyses, however, it is possible to calibrate using gravimetrically or volumetrically prepared mixtures that contain significantly fewer components than the samples that will ultimately be analyzed. For these surrogate test methods, the outlier statistics described in Practices E 1655 are not appropriate since all samples are expected to be outliers relative to the simplified calibrations. Thus, surrogate test methods cannot fulfill the requirements of Practices E 1655. While surrogate test methods may make use of the mathematics described in Practices E 1655, they should not claim to follow the procedures described in that practice.

6.1.1 In developing surrogate test methods, it is necessary to thoroughly understand and account for potential spectral interferences. Typically, the spectral range used in surrogate calibrations will be limited so as to minimize interferences. For those interferences that cannot be eliminated through limiting the spectral range, representative components that mimic the interference should be included in the calibration mixtures.

6.1.2 Test Method D 6277 provides an example of a surrogate test method. The FT-MIR analysis of benzene in gasoline is calibrated using mixtures of benzene, isooctane, toluene and xylenes and PLS mathematics. The calibration mixtures contain far fewer components than gasoline, but the spectral range used in the analysis is limited to a narrow range about a relatively interference-free benzene peak. Toluene and xylenes are used in the calibration mixtures to adequately mimic the interferences that are present in gasolines.

6.2 *Calibration Sets*:

6.2.1 The sets of surrogate samples that are used to calibrate the spectrometers/spectrophotometers should satisfy the requirements of Practices E 1655. If k is the number of variables (MLR wavelengths or frequencies, PCR principal components or PLS latent variables) used in the model, then the minimum number of calibration samples should be the greater of 24 or $6k$.

6.2.2 When calibrating for a single component, the calibration set should uniformly span the range over which the analysis of that component is to be conducted. Additional components that are present in the calibration set to simulate interferences should be independently and uniformly varied over a range at least as large as is likely to be encountered during actual application of the test method.

6.2.3 When calibrating for a property that depends on more than one chemical component, the calibration set should uniformly span the range over which the property analysis is to be conducted, and all components that contribute to the property should be varied independently.

6.2.4 The test method should specify the compositions of the calibration samples, including components and target concentrations. The purity of materials to be used in preparing the calibration samples should also be specified in the test method.

6.3 *Qualification Sets*:

6.3.1 The sets of surrogate samples that are used to qualify the spectrometers/spectrophotometers should satisfy the validation requirements of Practices E 1655. If k is the number of variables (MLR wavelengths or frequencies, PCR principal components or PLS latent variables) used in the model, then the minimum number of qualification samples should be the greater of 20 or $5k$.

6.3.2 The compositions of the qualification samples should span the same ranges as did the calibration samples.

6.3.3 The test method should specify the compositions of the qualification samples, including components and target concentrations. The purity of materials to be used in preparing the qualification samples should also be specified in the test method.

6.4 *Precision of Surrogate Calibration Test Methods*:

6.4.1 An ILS determines the precision of a surrogate test method. The interlaboratory study must conform to the requirements of Practice E 691, and to any other relevant practices. For example, a test method applicable to petroleum products should conform to Practice D 6300.

6.4.2 The standard error of calibration ($SEC_{surrogate}$) and the standard error of qualification ($SEQ_{surrogate}$) for a surrogate test method cannot be used reliably to infer the precision that can be expected for the analysis of actual samples. However, $SEC_{surrogate}$ and $SEQ_{surrogate}$ are representative of the necessary spectrometer/spectrophotometer performance that must be achieved in order to obtain precision comparable to that established by the ILS.

7. Requirements for Test Methods Using Surrogate Calibrations

7.1 *Surrogate Calibrations of Individual Spectrometers/Spectrophotometers*:

7.1.1 The multivariate spectroscopic analysis is calibrated using a set of surrogate mixtures. These mixtures are prepared volumetrically or gravimetrically to compositions defined by the test method. Spectra of the mixtures are collected under conditions defined by the test method. The spectral data is pretreated as prescribed in the test method, and a multivariate calibration model is developed as prescribed in the test method.

7.1.1.1 The y values that are used in the development of the model can be the concentrations of individual components in

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