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

This standard is issued under the fixed designation E2056; 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 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 E1655. 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 E1655.

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 E1655, 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 E1655.

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 E275, E925, E932, E958, E1421, E1683, or E1944; Test Methods E387, E388, or E579; or Guide E1866, 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:*[2]

D6277 Test Method for Determination of Benzene in Spark-Ignition Engine Fuels Using Mid Infrared Spectroscopy

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

E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers

E387 Test Method for Estimating Stray Radiant Power Ratio of Dispersive Spectrophotometers by the Opaque Filter Method

E388 Test Method for Wavelength Accuracy and Spectral Bandwidth of Fluorescence Spectrometers

E579 Test Method for Limit of Detection of Fluorescence of Quinine Sulfate in Solution

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

E925 Practice for Monitoring the Calibration of Ultraviolet-Visible Spectrophotometers whose Spectral Bandwidth

[1] This practice is under the jurisdiction of ASTM Committee E13 on Molecular Spectroscopy and Separation Science and is 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.

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does not Exceed 2 nm
E932 Practice for Describing and Measuring Performance of Dispersive Infrared Spectrometers
E958 Practice for Measuring Practical Spectral Bandwidth of Ultraviolet-Visible Spectrophotometers
E1421 Practice for Describing and Measuring Performance of Fourier Transform Mid-Infrared (FT-MIR) Spectrometers: Level Zero and Level One Tests
E1655 Practices for Infrared Multivariate Quantitative Analysis
E1683 Practice for Testing the Performance of Scanning Raman Spectrometers
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:*

3.1.1 For definitions of terms and symbols relating to infrared, ultraviolet/visible and Raman spectroscopy, refer to Terminology E131.

3.1.2 For definitions of terms and symbols relating to multivariate analysis, refer to Practices E1655.

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.

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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.

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 E1655 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 E1655 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 E1655 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 E1655. While surrogate test methods may make use of the mathematics described in Practices E1655, 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 D6277 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 E1655. 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 $6k$. If the calibration set is derived from an experimental design, and if the spectra have been shown to be linear functions of the component concentrations, then fewer calibration samples can be used, but in all cases the minimum number of calibration samples should be the greater of 24 or $4k$. The experimental design must independently vary all components over the desired analysis range.

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 E1655. 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 $5k$. If the qualification set is derived from an experimental design, and if the spectra have been shown to be linear functions of the component concentrations, then fewer qualification samples can be used, but in all cases the minimum number of qualification samples should be the greater of 20 or $3k$. The experimental design must independently vary all components over the entire calibration range.

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 E691, and to any other relevant practices. For example, a test method applicable to petroleum products should conform to Practice D6300.

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