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Standard Guide for Establishing Spectrophotometer Performance Tests[1]

This standard is issued under the fixed designation E1866; 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 guide covers basic procedures that can be used to develop spectrophotometer performance tests. The guide is intended to be applicable to spectrophotometers operating in the ultraviolet, visible, near-infrared and mid-infrared regions.

1.2 This guide is not intended as a replacement for specific practices such as Practices E275, E925, E932, E958, E1421, or E1683 that exist for measuring performance of specific types of spectrophotometers. Instead, this guide is intended to provide guidelines in how similar practices should be developed when specific practices do not exist for a particular spectrophotometer type, or when specific practices are not applicable due to sampling or safety concerns. This guide can be used to develop performance tests for on-line process spectrophotometers.

1.3 This guide describes univariate level zero and level one tests, and multivariate level A and level B tests which can be implemented to measure spectrophotometer performance. These tests are designed to be used as rapid, routine checks of spectrophotometer performance. They are designed to uncover malfunctions or other changes in instrument operation, but do not specifically diagnose or quantitatively assess the malfunction or change. The tests are not intended for the comparison of spectrophotometers of different manufacture.

1.4 *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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E131 Terminology Relating to Molecular Spectroscopy
E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers
E925 Practice for Monitoring the Calibration of Ultraviolet-Visible Spectrophotometers whose Spectral Bandwidth 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

3. Terminology

3.1 *Definitions*—For terminology relating to molecular spectroscopic methods, refer to Terminology E131.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *action limit, n*—the limiting value from an instrument performance test, beyond which the spectrophotometer is expected to produce potentially invalid results.

3.2.2 *check sample, n*—a single pure compound, or a known, reproducible mixture of compounds whose spectrum is constant over time such that it can be used in a performance test.

3.2.3 *level A test, n*—a pass/fail spectrophotometer performance test in which the spectrum of a check or test sample is compared against historical spectra of the same sample via a multivariate analysis.

3.2.4 *level B test, n*—a pass/fail spectrophotometer performance test in which the spectrum of a check or test sample is analyzed using a multivariate model, and the results of the analysis are compared to historical results for prior analyses of the same sample.

3.2.5 *level one (1) test, n*—a simple series of measurements designed to provide quantitative data on various aspects of spectrophotometer performance and information on which to base the diagnosis of problems.

3.2.6 *level zero (0) test, n*—a routine check of spectrophotometer performance, which can be done in a few minutes, designed to visually detect significant changes in instrument

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[1] This guide is under the jurisdiction of ASTM Committee E13 on Molecular Spectroscopy and Separation Science and is the direct responsibility of Subcommittee E13.03 on Infrared and Near Infrared Spectroscopy.

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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.

performance and provide a database to determine instrument performance over time.

3.2.7 *optical reference filter, n*—an optical filter or other device which can be inserted into the optical path in the spectrophotometer or probe producing an absorption spectrum which is known to be constant over time such that it can be used in place of a check or test sample in a performance test.

3.2.8 *test sample, n*—a process or product sample, or a mixture of process or product samples which has a constant spectrum for a finite time period and which can be used in a performance test. Test samples and their spectra are generally not reproducible in the long term.

4. Significance and Use

4.1 If ASTM Committee E13 has not specified an appropriate test procedure for a specific type of spectrophotometer, or if the sample specified by a Committee E13 procedure is incompatible with the intended spectrophotometer operation, then this guide can be used to develop practical performance tests.

4.1.1 For spectrophotometers which are equipped with permanent or semi-permanent sampling accessories, the test sample specified in a Committee E13 practice may not be compatible with the spectrophotometer configuration. For example, for FT-MIR instruments equipped with transmittance or IRS flow cells, tests based on polystyrene films are impractical. In such cases, these guidelines suggest means by which the recommended test procedures can be modified so as to be performed on a compatible test material.

4.1.2 For spectrophotometers used in process measurements, the choice of test materials may be limited due to process contamination and safety considerations. These guidelines suggest means of developing performance tests based on materials which are compatible with the intended use of the spectrophotometer.

4.2 Tests developed using these guidelines are intended to allow the user to compare the performance of a spectrophotometer on any given day with prior performance. The tests are intended to uncover malfunctions or other changes in instrument operation, but they are not designed to diagnose or quantitatively assess the malfunction or change. The tests are not intended for the comparison of spectrophotometers of different manufacture.

5. Test Conditions

5.1 When conducting the performance tests, the spectrophotometer should be operated under the same conditions as will be in effect during its intended use. Sufficient warm-up time should be allowed before the commencement of any measurements.

5.1.1 If possible, the optical configuration used for measurements of test and check samples should be identical to that used for normal operations. If identical optical configurations are not possible, the user should recognize that the performance tests may not measure the performance of the entire instrument.

5.1.2 Data collection and computation conditions should generally be identical to those used in normal operation. Spectral data used in performance tests should be date and time stamped, and the results of the tests should be stored in a historical database.

6. Samples Used for Performance Testing

6.1 The sample used for performance testing is chosen to be compatible with the spectrophotometer configuration, and to provide spectral features which are adequate for the tests being performed.

6.1.1 The sample used for performance testing should generally be in the same physical state (gas, liquid, or solid) as the samples to be analyzed during normal operation of the spectrophotometer.

6.1.2 The sample used for performance testing should be physically and chemically compatible with the samples analyzed during normal operation.

6.1.3 The sample used for performance is chosen such that its spectrum is similar to the spectra which will be collected during normal operation.

6.1.4 The sample used for performance testing should have several significant absorbances ($0.3 < \text{absorbance} < 1.0$) across the spectral range used for normal operation of the spectrophotometer.

6.1.5 In order to adequately determine the photometric linearity of the instrument, the peak absorbance for at least one absorption band of the sample should be similar to and preferably slightly greater than the largest absorbance expected for samples measured during normal operation.

6.2 *Check Samples*—Check samples are generally used for conducting performance tests. Check samples are single pure compounds or mixtures of compounds of definite composition.

6.2.1 If mixtures are utilized as check samples, they must be prepared in a repeatable manner and, if stored, stored such that the mixture is stable over long periods of time. In preparing mixtures, components should be accurately pipetted or weighed at ambient temperature. It is recommended that mixtures be independently verified for composition prior to use.

6.2.2 While mixtures can be used as check samples, their spectra may be adversely affected by temperature sensitive interactions that may manifest themselves by wavelength (frequency) and absorbance changes.

6.3 *Test Samples*—A test sample is a process or product sample or a mixture of process or product samples whose spectrum is expected to be constant for the time period it is used in performance testing. The test sample must be stored in bulk quantities in controlled conditions such that the material is stable over time.

6.3.1 Since test samples are often complex mixtures which cannot be synthetically reproduced, they can only be used for performance testing for limited time periods. If test samples are used for this purpose, collection of historical data on a new test sample should be initiated before previous test samples are depleted. It is recommended that new test samples be analyzed sequentially with old test samples at least 15 times before they are used to replace the old test sample. The 15 analyses must be performed over a time period that does not exceed one month in duration.

6.4 *Optical Filters*—An optical reference filter is an optical filter or other optical device located in the spectrophotometer or in a fiber optic sample probe which produces an absorption spectrum which is known to be constant over time. This filter may be automatically inserted into the optical path to allow instrument performance tests to be performed.

6.4.1 Optical filters are used principally with on-line process spectrophotometers equipped with fiber optic probes when removal of the probe is inconvenient, precluding the use of check or test samples for routine instrument performance testing.

6.4.2 If an optical filter is used routinely to check or correct the spectral data collection or computation, then the same filter is preferably not used for instrument performance testing. If the same filter is used, then the part of the filter spectrum used in the performance testing should preferably differ from that part used to check or correct the instrument. For example, polystyrene filters are used to standardize (continuously check and correct) the wavelength scale of some dispersive NIR spectrophotometers. For such systems, polystyrene filters are preferably not to be employed for wavelength stability performance testing. If polystyrene filters are used, then the peaks used for wavelength stability testing should be different from those used for standardizing the wavelength scale.

7. Univariate Measures of Spectrophotometer Performance

7.1 *Energy Level Tests*—Energy level tests are intended to detect changes in the radiant power in the spectrophotometer beam. Decreases in energy levels may be associated with deterioration of the spectrophotometer source, with contamination or misalignment of optical surfaces in the light path, or with malfunctions of the detector.

7.1.1 For single beam spectrophotometers where background and sample spectra are measured separately at different times, energy level tests are generally conducted on a background spectrum. For double beam spectrophotometers where the ratio of background and sample beam intensities is measured directly, energy levels can be measured if it is possible to block the sample beam.

7.1.2 Energy levels should be measured at at least three fixed frequencies (wavelengths), one each in the upper, middle and lower third of the spectral range. The frequencies (wavelengths) at which energy levels are measured should be chosen to avoid interferences due to atmospheric components (for example, absorptions of water vapor and carbon dioxide) and from interferences due to optical components (for example, OH absorptions in SiO_2 cells and fibers). Preferably, regions where the background spectrum is relatively flat and slowly varying should be used for this test.

7.1.3 To minimize the effects of photometric noise on the energy level measurement, it is preferable to average the energy over a narrow frequency (wavelength) window. Typically, the intensity at five points centered on the test frequency are averaged.

7.2 *Photometric Noise Tests*—Photometric noise is measured at the same frequencies (wavelengths) used for the energy level tests. Preferably, photometric noise tests are conducted on a 100 % line spectrum. Alternatively, photometric noise tests may be conducted on the spectrum of a check or test sample at regions where the spectrum is relatively flat and the sample absorbance is minimal (<0.1).

7.2.1 For single beam spectrophotometers where background and sample spectra are measured separately at different times, a 100 % line spectrum is obtained by ratioing two successive background measurements to obtain a transmittance spectrum. If, during normal operation of the spectrophotometer, backgrounds are collected with a reference material in the optical path, then this same configuration should be used for performance testing. Photometric noise calculations are preferably done directly on the transmittance spectrum. Alternatively, the transmittance spectrum may be converted to an absorption spectrum by taking the negative $\log_{10}$ before the photometric noise calculations.

7.2.2 For double beam spectrophotometers, a 100 % line spectrum is measured when the two beams are both empty, both contain empty matched cells, or both contain reference samples in matched cells.

7.2.3 Photometric noise is measured by fitting a line to the spectrum over a short spectral region centered on the test frequency (wavelength). The region should contain at least 11 data points, preferably contains 101 data points, and should not exceed 2 % of the spectral range. The line is subtracted from the spectral data, and the RMS noise is calculated as the square root of the mean square residual.

7.2.3.1 If T_i is the transmittance at the frequency v_i, then the slope, m, and intercept, b, of a line through the n data points centered at test frequency v_0 are given by the following:

$$m = \frac{n\sum iT_i - \sum T_i \sum i}{n\sum i^2 - \left(\sum i\right)^2} \tag{1}$$

$$b = \frac{\sum i^2 \sum T_i - \sum i \sum iT_i}{n\sum i^2 - \left(\sum i\right)^2} \tag{2}$$

The photometric noise is calculated as follows:

$$\text{Noise}_{\text{RMS}} = \sqrt{\frac{\sum\left(T_i - (mi+b)\right)^2}{n-2}} \tag{3}$$

The index i in Eq 1-3 runs from $-(n-1)/2$ to $(n-1)/2$ (n must be odd). The intercept represents the transmittance at test frequency v_0.

7.2.3.2 If photometric noise is calculated on absorbance spectra, the absorbance values, A_i, are used in place of the transmittance values, T_i, in Eq 1-3. If the abscissa for the spectral data is wavelength, then wavelength values, λ_i, are used in place of the frequency values, v_i, in Eq 1-3. Calculations should be consistently performed on the same data types.

7.2.4 Increases in the photometric noise can indicate a misalignment of optical components, a source malfunction, or a malfunction in the detector or electronics.

7.3 *Short Term Baseline Stability Test*—The transmittance is monitored at each of the test frequencies (wavelengths) used in the energy level and photometric noise tests. The intercept calculated in Eq 2 represents the transmittance averaged over the n points around test frequency v_0. Deviation from 100 %

transmittance is an indication of short term baseline instability and may indicate a malfunction of the spectrophotometer.

7.3.1 If the tests are conducted on absorbance spectra, deviations from zero absorbance is used as an indication of baseline instability.

7.3.2 If photometric noise tests are conducted on the spectrum of a check or test sample, then variations in the absorbance spectrum at the test frequencies are taken as an indication of short term baseline instability.

7.4 *Optical Contamination Tests*—The single beam background scan which was used for the energy tests is examined for absorptions which might indicate contamination of optical surfaces in the beam path.

7.4.1 Failure to clean cell or probe windows, IRS surfaces, etc., are the most common source of optical contamination. Frequencies (wavelengths) at which typical samples exhibit maximum absorbance should generally be examined. For example, for IR systems used in hydrocarbon analysis, the regions where the C-H stretching vibrations occur should be examined. Significant increases above a nominal background level may indicate contamination of windows and surfaces.

7.4.2 Spectrophotometer optical surfaces can be contaminated by impurities in purge gases. For systems equipped with flow cells or circulating liquid temperature control, leaks in connecting lines can expose an optical surface to contamination. Users should consider possible sources of contamination and determine appropriate frequencies at which absorptions would result.

7.5 *Purge Contamination Tests*—For spectrophotometers which are purged to minimize absorptions due to atmospheric components, the single beam spectrum used for energy tests should be checked for variations in purge quality. Frequencies (wavelengths) at which potential contaminants absorb should be identified, as should baseline points where contaminant absorption would be minimal. The absorbance for contaminants is calculated as the negative $\log_{10}$ of the ratio of the peak intensity to the baseline intensity.

7.6 *Frequency (Wavelength) Stability Tests*—Frequency (wavelength) stability tests are conducted by monitoring the peak positions of several peaks across the absorption spectrum of the check or test sample or optical filter. At least three peaks are used for the test. If possible, the peaks should be in the upper, middle and lower third of the spectral range.

7.6.1 The absorption for peaks used in this test are preferably in the range from 0.37 to 0.75. For peak absorptions outside this range, the wavelength stability measurement may show greater sensitivity to photometric noise.

7.6.2 Peaks used for the frequency stability test are preferably symmetric in shape and well resolved from neighboring peaks. If such peaks are not available in the spectrum of the check/test sample or optical filter, the user should be aware that changes in spectrophotometer resolution will affect the measured peak position.

7.6.3 It is recommended that the peak position be determined by the following steps:

7.6.3.1 Compute the first derivative of the spectrum by applying the appropriate digital filter to the spectrum. A commonly used filter has been defined by Savitzki and Golay (**1**)[3] with corrections by Steiner, Termonia, and Deltour (**2**), with application criteria discussed by Willson and Polo (**3**). The latter reference discusses optimum filter parameters based upon the relationship between spectral bandwidth and digitization interval. A cubic filter is recommended. The number of points used in the filter should be the quotient of the full-width-at-half-maximum of the peak being measured divided by the digital resolution, and rounded up to the nearest odd integer.

7.6.3.2 Identify the zero crossing associated with the peak absorbance and compute its location by linear interpolation between the two adjacent points straddling the zero crossing. The zero crossing is taken as a measure of the peak position.

NOTE 1—Other peak finding algorithms can be used provided that they accurately track peak position. The procedure described in Annex A1 should be used to test peak finding algorithms to determine if they are appropriate for this application. It is the users responsibility to demonstrate that the peak finding algorithm is appropriate for monitoring spectrophotometer frequency (wavelength) stability.

7.7 *Resolution Stability Tests*—The resolution stability of the spectrophotometer is monitored by measuring the bandwidths of several absorption peaks in the absorption spectrum of the check/test sample or optical filter. At least three peaks are used for the test. If possible, the peaks should be in the upper, middle and lower third of the spectral range. Variations in the measured bandwidths are taken as an indication that the optical resolution of the spectrophotometer is varying, suggesting a malfunction.

7.7.1 The absorption for peaks used in this test are preferably in the range from 0.37 to 0.75. For peak absorptions outside this range, the resolution stability measurement may show increased sensitivity to photometric noise.

7.7.2 Peaks used for the resolution stability test are preferably symmetric in shape and well resolved from neighboring peaks. If such peaks are not available in the spectrum of the check/test sample or optical filter, the results of the resolution stability test may be variable.

7.7.3 It is recommended that the peak bandwidth be determined by the following steps:

7.7.3.1 Compute the second derivative of the spectrum by applying the appropriate digital filter to the spectrum. A commonly used filter has been defined by Savitzki and Golay (**1**) with corrections by Steiner, Termonia, and Deltour (**2**), with application criteria discussed by Willson and Polo (**3**). The latter reference discusses optimum filter parameters based upon the relationship between spectral bandwidth and digitization interval. A cubic filter is recommended. The number of points used in the filter should be the quotient of the full-width-at-half-maximum of the peak being measured divided by the digital resolution, and rounded up to the nearest odd integer.

7.7.3.2 Identify the zero crossing on each side of the peak absorbance and compute their locations by linear interpolation between the two adjacent points straddling the zero crossings. The difference in the frequencies of the interpolated zero crossings is taken as a measure of the peak bandwidth.

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

7.8 *Photometric Linearity Tests*—Linearity of the spectrometer response is important for quantitative applications. Unfortunately, the absolute photometric linearity cannot be checked in a quick performance test. To do so would generally require the use of multiple standards of known absorbance. The test described here is intended only to measure changes in the photometric linearity of a spectrophotometer.

7.8.1 Photometric linearity is tested using the ratio of the absorbances of two or more peaks in the absorbance spectrum. One peak should have an absorbance at or near the maximum absorbance that will be used for normal operations. The other peaks are preferably less intense than this maximum. If only two peaks are used, the second peak should be approximately half the intensity of the first peak.

7.8.2 Linear baselines for each peak are calculated from points of minimal absorbance on opposite sides of the peaks. The maximum absorbance for each peak is corrected for the baseline, and the ratio of the absorbances for the two peaks is calculated. The ratio is used to track changes in the photometric linearity.

8. Multivariate Measures of Spectrophotometer Performance

8.1 *Level A Tests*—A Level A performance test is a pass/fail test that is sensitive to many of the univariate performance parameters discussed in Section 7. Level A tests do not identify specific failure modes, but merely indicate if the instrument performance is within historical bounds. In this test, the spectrum of a check sample, a test sample or an optical filter is compared to a historical spectra of the check sample, the test sample or the optical filter by multivariate methods (least squares fitting or a PCR/PLS model; see Practice E1655 for descriptions of PCR and PLS). This procedure can provide some information about specific instrument parameters, but essentially looks for deviations in the residual spectrum as compared to the historical residual spectra.

8.1.1 Level A tests are generally applied on spectrophotometers which are in use for multivariate, quantitative analysis. The spectral range used in Level A tests should be comparable to that used in the calibration model for the analysis being performed. If the spectrum of the check sample, the test sample or the optical filter used in the Level A test contains absorptions that are significantly higher than those of the typical samples being analyzed, then these peaks can be excluded from the Level A fit.

8.1.2 *Level A Tests Using a Least Squares Method:*

8.1.2.1 In this Level A test, a least squares fit of the current spectrum of the check sample, test sample or optical filter is conducted against a historical spectrum of the same material. Baseline terms may be included in the fit to compensate for variations in baseline, and scaling may be applied to compensate for pathlength variations. The types of compensations (baseline or pathlength) used in the fit should be similar to those employed in the multivariate model used for the actual analyzer measurement. Methodology for calculating the least square fit is discussed by Blackburn (**4**) and by Antoon, Koenig, and Koenig (**5**).

8.1.2.2 A typical least squares model could be as follows:

$$g = a_h h + a_\lambda \lambda + a_1 1 \tag{4}$$

where:

g = column vector containing the current spectrum of the check sample, the test sample or the optical filter,
h = column vector containing the historical spectrum of the check sample, the test sample or the optical filter,
λ (v for frequency based spectra) = column vector of the wavelength axis values for spectra g and h,
1 = column vector of ones,
a_h = coefficient for scaling the historical spectrum to match the current spectrum,
a_λ = coefficient which scales λ to provide a baseline correction which is linear in wavelength (or frequency), and
a_1 = coefficient for a baseline offset.

The column vectors h, λ and 1 are combined into a matrix H.

$$g = [h \; \lambda \; 1] \begin{bmatrix} a_h \\ a_\lambda \\ a_l \end{bmatrix} = Ha \tag{5}$$

8.1.2.3 The estimated coefficients $\hat{a}$ are first determined by linear least squares.

$$\hat{a} = H^{+} \; g = \left(H^{\mathrm{t}}H\right)^{-1} H^{-\mathrm{t}} g \tag{6}$$

8.1.2.4 The coefficients are then used to estimate the spectrum of the current sample $\hat{g}$.

$$\hat{g} = H\hat{a} \tag{7}$$

8.1.2.5 The residuals from the fit are the difference between the measured and estimated values for the data points, $g - \hat{g}$. The residuals from the fit are squared, and summed. The resulting measure, herein referred to as the spectral residual, is used as a measure of changes in the instrument performance. This spectral residual should be plotted on control charts.

NOTE 2—Any function of the sum of the squares of the residuals can be used, for example, the square root, or the square root of the sum divided by the number of points.

8.1.2.6 Additionally, the scaling and baseline coefficients can be monitored as an additional measure of instrument performance.

8.1.3 *Level A Tests Using a PCR or PLS Method*—To perform a Level A test using PCR or PLS, one must first develop an appropriate model. A series of historical spectra for the check/test sample, or the optical filter are analyzed by a PCR or PLS regression algorithm using 100 % for the compositional value to generate the Level A model. Generally, only one variable should be retained in the model since all the spectra are of the same material. The type of pre- or postprocessing done in the Level A test model should be comparable to that done in the multivariate calibration models being used on the spectrophotometer.

NOTE 3—Chemometricians might refer to the analysis described in 8.1.3 as principal component analysis rather than principal components regression. However, the object here is to allow the Level A test to be developed and applied using the same chemometric software employed in the development and application of the multivariate calibration model.

8.1.3.1 The PCR or PLS model is used to analyze the current spectrum of the check/test sample or optical filter. The estimate for the current spectrum is generated. The spectral residuals are calculated as the difference between the current spectrum and its estimate. The spectral residual can be charted to determine if the instrument is operating within historical specifications.

8.1.3.2 PCR and PLS models can also provide information on the scaling of the current spectrum. For simple models, variation in the estimated composition from 100 % is an indication of scaling variation.

8.2 *Level B Tests*—Level B performance tests analyze the spectrum of a check sample, a test sample or an optical filter against multivariate models that are employed during the normal use of the spectrophotometer system. As such, Level B tests can not be performed during the multivariate calibration of a spectrophotometer. Level B tests monitor the instrument performance for deviations to which a calibration model is sensitive. Tests on a limited number of samples are not rigorous, but failures in these tests are indicative that the spectrophotometer operation has changed.

8.2.1 The spectrum of the check sample, the test sample or the optical filter is analyzed using the multivariate model used during normal spectrometer operation. The predicted value (property or component concentration), the Mahalanobis distance, and the spectral residuals are again compared to historical values to detect any change in the analyzer performance.

9. Performance Test Charts

9.1 Performance test results should be plotted on charts and examined for trends. Such trend analysis may provide early warnings of possible analyzer problems.

9.2 Statistical quality control charting methods (for example, individual value control charts, exponentially weighted moving average control charts, and moving range of two control charts) can be used to detect statistically significant changes in instrument performance. However, the statistical control limits associated with these charts will not necessarily be useful in judging the performance test results. Instead, some performance test results are typically compared to action limits as described in Section 10.

9.2.1 For some performance tests, the test results are expected to trend continuously in one direction until such time as the analyzer is serviced. For example, the energy output of an infrared source is expected to decrease continuously as the source ages, until such time as the source is cleaned or replaced. The decreased energy may be observed as an increase in the Level 0 photometric noise, or as an increase in the Level A spectral residual. The daily change in energy, noise or residual may be large relative to the precision with which these values can be measured, but have tolerable effect on the spectrophotometer results for the intended application. For such tests, control charts and statistically derived limits may be inappropriate. An action limit for such tests needs to be determined from historical data or simulations as discussed in Section 10.

9.2.2 For some performance tests, the test results are expected to vary randomly about a fixed point. For example, for a properly operating instrument, the Level 0 wavelength value might be expected to vary randomly about some average value. For such tests, the statistical control charts and control limits can be usefully employed to set initial action limits in the absence of historical data. Such initial action limits may be loosened if statistically significant performance changes detected by the control charts are not found to have significant effect on the spectrophotometer results for the intended application.

9.2.3 Since, for spectrophotometers used in multivariate analyses, Level B composition or property results for check or test samples are most directly comparable to actual analyzer results, the Level B composition or property estimates are most amenable to statistical control charting. Action limits for Level B composition or property estimates can be set to statistically determined control limits.

10. Performance Test Action Limits

10.1 Spectroscopic analyses differ greatly in their sensitivity to various aspects of spectrophotometer performance, and each application differs in what constitutes an acceptable tolerance to changes in the results caused by variations in spectrophotometer performance. Although spectrophotometer performance tests are useful in their own right, the user must be concerned with how changes in the spectrophotometer performance affect results during normal operation. Historical databases or simulations that define acceptable performance for one application may not be appropriate for another application. In addition, the level of performance required by quantitative applications may be changed by the updating of the calibration.

10.2 *Setting Action Limits Based on Historical Data for Performance Tests:*

10.2.1 Performance tests provide quantitative measures of spectrophotometer performance. These measures can be compared to historical data for the same tests in order to recognize changes of spectrophotometer performance. If historical data exist, limits for each test can be set and the performance can be judged against these limits. If historical data does not exist, it will be necessary to collect them as a standard part of the spectrophotometer operation, and such collection will eventually allow performance limits to be established. The collection of the historical database for performance tests should be an integral part of the spectrophotometer operation and be continued for the life of the spectrophotometer.

10.2.2 For spectrophotometers used in qualitative analysis, what constitutes acceptable spectrophotometer performance may be difficult to quantify. The expert analyst may only know that the spectra "look wrong." If a change in instrument performance is detected, spectra of known (check or test sample) materials can be collected, and the analyst can examine the spectra to determine if the observed change in performance would distort the spectra sufficiently to cause misidentifications to occur.

10.2.3 If the normal operation of the spectrophotometer involves the use of spectral library searching or discriminative analysis for materials identification or classification, then known (check or test sample) materials should be reanalyzed whenever a change in performance is detected to determine if the change reduces the discrimination power of the analysis.

10.2.4 If the normal operation of the spectrophotometers involves quantitative analysis, then quality assurance for the quantitative analysis should be part of the normal operation. The significance of changes in spectrophotometer performance are judged by their effects on the quality control results for the normal analysis.

10.2.4.1 If the quantitative method used during normal operation is a primary method (for example, univariate calibration against quantitatively prepared or certified standards), then the quality control for the quantitative method will generally involve measurement of a standard and comparison of the results against the known value.

10.2.4.2 If the quantitative method used during normal operation is a secondary method (for example, univariate or multivariate calibration against results obtained by another primary analytical method), then the quality control for the quantitative method will generally involve periodic analyses of an unknown by both methods and statistical comparison of the results.

10.2.4.3 If the quantitative method used during normal operation is within statistical quality control, then the results for the performance tests conducted during the same time period should be considered an example of acceptable instrument performance and added to the historical database.

10.2.4.4 If the quantitative method used during normal operation is not within statistical quality control, the results from the performance tests may be examples of unacceptable instrument performance, particularly if the results from the performance tests are inconsistent with the historical database. Examples of unacceptable instrument performance can be used to set action limits for future performance tests.

10.2.4.5 It is strongly recommended that, at the time the quantitative method is developed, spectra of the check sample, the test sample or the optical filter be collected along with spectra used for calibration. Performance tests can be applied to this data to determine the level of performance at the time of calibration.

10.2.4.6 Changes in analyzer performance that are detected by Level 0 tests may or may not produce a significant change in the results during normal operation. Different types of quantitative analyses differ significantly in their sensitivity to various aspects of analyzer performance. By plotting the Level 0 test results with the quality control results for the quantitative method on control charts, conditions that lead to invalid quantitative results can be identified, and action limits for each Level 0 test can eventually be established.

10.2.4.7 For spectrophotometers where normal operation involves use of a multivariate calibration model, increases in the spectral residuals that are detected by Level A tests will generally reflect some change in the quantitative results produced by the spectrophotometer. Even if the analysis result does not change, the spectral residuals measured as part of the outlier testing will generally be expected to increase. The level of increase that can be tolerated can be determined by plotting the Level A test spectral residuals against analyzer results and determining the maximum level at which valid analysis results are produced.

10.2.4.8 For spectrophotometers where normal operation involves use of a multivariate calibration model, changes in the values produced by a Level B test are the most straightforward to interpret since the values are directly comparable to the analysis results. If the analysis of the spectrum of the check sample, the test sample, or the optical filter is an interpolation of the model, then limits can be set directly based on the desired performance of the analyzer. If the analysis of the spectrum of the check sample, the test sample or the optical filter is an extrapolation of the model, then some care must be exercised in setting limits since the extrapolated result may be more sensitive to small changes in instrument performance than analyses that are interpolations of the model. This is known as leverage. In this case, initial limits should be confirmed by plotting the Level B results against analysis results and determining the levels at which valid analysis results are produced.

NOTE 4—Any one test sample, check sample, or optical filter only tests a small portion of the multivariate model space, and may not be sensitive to all aspects of spectrophotometer performance. The Level 0, A, and B tests are intended to detect possible spectrophotometer failure modes. Acceptable performance as measured by Level 0, A and B tests is necessary but not sufficient by themselves for demonstrating valid spectrophotometer performance. Comparison of analysis results to in control, primary method laboratory values is also necessary to demonstrate the validity of analysis results.

10.3 *Determining Performance Action Limits by Simulating Instrument Response Changes:*

10.3.1 For spectrophotometers where normal operation involves use of a multivariate calibration model, an alternative procedure for determining action limits for spectrophotometer performance tests is to take actual, diverse, but representative spectra that are predicted well by the model, and to mathematically modify these spectra to simulate the expected variations in the spectrophotometer performance. The model sensitivity, for example, the change in the results per unit change in a performance parameter, can be estimated, and used to establish action limits for each performance parameter based on the error tolerance for the application. Spectrophotometer performance parameters which can be modeled include wavelength (frequency) shifts, baseline shifts, changes in photometric noise, resolution changes, and detector linearity changes. The importance of different performance parameters is both application and instrument type dependent. Historical data for Level 0 performance tests are the best guide to the type response changes that should be modeled for a given instrument type.

10.3.1.1 For example, the sensitivity of an analyzer to baseline drift can be simulated by adding various baselines to a set of representative spectra, analyzing these spectra with the calibration model, and determining the change in the results as a function of the added baseline. The added baseline can, for example, be parameterized in terms of offset, slope and curvature so that the effects of each can be determined.

10.3.1.2 For example, the sensitivity of an analyzer to wavelength (frequency) shift can be simulated by shifting the wavelength (frequency) of a set of representative spectra (see Annex A1), analyzing these spectra with the calibration model, and determining the change in the results as a function of the shift. If the shift is accomplished via interpolation of the spectra, care must be exercised that the interpolation function does not smooth or deresolve the spectra.

10.3.2 Changes in spectrophotometer performance seldom effect only one aspect of that performance. If simulations are used to set action limits for performance tests, it is essential that multiple performance parameters by varied simultaneously. The magnitude of the changes to the performance parameters that should be simulated are best obtained from examination of historical data on Level 0 performance tests conducted on the type of spectrophotometer being tested.

11. Keywords

11.1 instrument performance; level 0; molecular spectrophotometer; spectrophotometer tests

ANNEX

(Mandatory Information)

A1. PROCEDURE FOR TESTING PEAK FINDING ALGORITHMS

A1.1 Interpolation of Test Spectrum

A1.1.1 To test a peak finding algorithm, it is necessary to interpolate and shift a test spectrum by amounts equivalent to a fraction of the digital resolution of the spectrum. The following procedure can be used to interpolate and shift the spectrum.

A1.1.1.1 Four adjacent points in the spectrum are selected. The points are numbered −1, 0, 1, and 2. The absorbance at the four points is fit to a cubic equation.

$$\begin{bmatrix} A_2 \\ A_1 \\ A_0 \\ A_{-1} \end{bmatrix} = \begin{bmatrix} 1 & 2 & 4 & 8 \\ 1 & 1 & 1 & 1 \\ 1 & 0 & 0 & 0 \\ 1 & -1 & 1 & -1 \end{bmatrix} \begin{bmatrix} c_0 \\ c_1 \\ c_2 \\ c_3 \end{bmatrix} \leftrightarrow A = XC \qquad \text{(A1.1)}$$

$$C = X^{-1} A \leftrightarrow \begin{bmatrix} c_0 \\ c_1 \\ c_2 \\ c_3 \end{bmatrix} = \tfrac{1}{6} \begin{bmatrix} 0 & 0 & 6 & 0 \\ -1 & 6 & -3 & -2 \\ 0 & 3 & -6 & 3 \\ 1 & -3 & 3 & -1 \end{bmatrix} \begin{bmatrix} A_2 \\ A_1 \\ A_0 \\ A_{-1} \end{bmatrix} \qquad \text{(A1.2)}$$

A1.1.2 The cubic equation is evaluated at four intermediate points

$$\begin{bmatrix} A_{0.8} \\ A_{0.6} \\ A_{0.4} \\ A_{0.2} \end{bmatrix} = \begin{bmatrix} 1 & 0.8 & 0.64 & 0.512 \\ 1 & 0.6 & 0.36 & 0.216 \\ 1 & 0.4 & 0.16 & 0.064 \\ 1 & 0.2 & 0.04 & 0.008 \end{bmatrix} \begin{bmatrix} c_0 \\ c_1 \\ c_2 \\ c_3 \end{bmatrix} \qquad \text{(A1.3)}$$

A1.1.3 The procedure is repeated, moving the filter sideways so that each point in the spectrum (other than the two points at each end) is treated as point 0 once. The values A_i (i = 0.2, 0.4, 0.6 and 0.8) calculated for the repetitive application of the filter are collected into 4 spectral vectors. These vectors are assigned the same frequency scales as the original spectrum. If Δ is the digital resolution (data point spacing), then the vectors $A_{0.8}$, $A_{0.6}$, $A_{0.4}$, and $A_{0.2}$ generated by repetitive application of the above procedure represent spectra which are shifted by −0.2Δ, −0.4Δ, −0.6Δ, and – 0.8Δ, respectively.

NOTE A1.1—If the data points are numbered −1, 0, 1, and 2 from left to right, the interpolation estimates a value for the spectrum between point 0 and point 1. The original point at 0 is replaced with this estimate. The effect is to shift the spectrum toward the left (negative index) direction.

A1.2 The peak finding algorithm is applied to the original and shifted spectra. The peak positions for suitable peaks are calculated.

A1.2.1 If the peak positions calculated by the peak finding algorithm for the shifted spectra are shifted by −0.2Δ, −0.4Δ, −0.6Δ, and −0.8Δ, respectively, relative to the peaks for the original spectrum, then the peak finding algorithm can be used for tracking frequency (wavelength) stability.

A1.2.2 If the peak positions calculated by the peak finding algorithm for the shifted spectra are not shifted by −0.2Δ, −0.4Δ,– 0.6Δ, and −0.8Δ, respectively, relative to the peaks for the original spectrum, then the peak finding algorithm cannot be used for tracking frequency (wavelength) stability.

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