Designation: D8470 – 22

Standard Practice for
Development and Implementation of Instrument Performance Tests for Use on Multivariate Online, At-Line and Laboratory Spectroscopic Based Analyzer Systems[1]

1. Scope

1.1 This practice covers basic procedures that can be used to develop instrument performance tests for spectroscopic based online, at-line, laboratory and field analyzers. The practice is intended to be applicable to Raman spectrometers and to infrared spectrophotometers operating in the near-infrared and mid-infrared regions.

1.2 This practice 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 laboratory spectroscopic instruments. Instead, this practice is intended to provide guidelines as to how similar practices should be developed when specific practices do not exist for a particular instrument type, or when specific practices are not applicable due to sampling or safety concerns. This practice can be used to develop instrument performance tests for on-line process spectroscopic-based analyzers.

1.2.1 The performance tests described in this practice typically only evaluate the performance of the infrared spectrophotometer or Raman spectrometer part of the analyzer system, referred to herein as the instrument.

1.2.2 Instrument performance tests do not typically evaluate performance of analyzer sampling systems.

1.3 This practice describes univariate level zero and level one tests, and multivariate level A and level B tests which can be implemented to measure instrument performance. These tests are designed to be used as rapid, routine checks of instrument 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 instruments or analyzers of different manufacture.

1.4 The instrument performance tests described in this practice are used during the development of multivariate calibrations via Practice D8321 to establish the performance level at the time the calibration is developed. The same tests are used during validation of analyzers via Practice D6122 to qualify the working analyzer by demonstrating comparable performance.

1.4.1 Instrument performance tests are used to requalify instruments after analyzer maintenance.

1.4.2 Instrument performance tests are used to qualify instruments in secondary analyzers to which calibrations are being transferred after development on a primary analyzer.

1.5 *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.*

1.6 *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]

D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

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

D7940 Practice for Analysis of Liquefied Natural Gas (LNG) by Fiber-Coupled Raman Spectroscopy

D8321 Practice for Development and Validation of Multivariate Analyses for Use in Predicting Properties of Petroleum Products, Liquid Fuels, and Lubricants based on Spectroscopic Measurements

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3. Terminology

3.1 For terminology related to molecular spectroscopic methods, refer to Terminology E131. For terminology relating to petroleum products, liquid fuels and lubricants, refer to Terminology D4175.

3.2 *Definitions:*

3.2.1 *absorbance (A), n*—the logarithm to the base 10 of the reciprocal of the transmittance, (*T*).

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

E131

3.2.1.1 *Discussion*—Absorbance is a measure of the capacity of a substance to absorb light of a specific wavelength.

3.2.2 *action limit, n—for multivariate spectroscopic analyzers used in the analysis of liquid petroleum products and fuels*, the limiting value from an instrument performance test, beyond which the multivariate spectroscopic analyzer is expected to produce potentially invalid results. **D6122**

3.2.3 *calibration, n—in multivariate spectroscopic measurement*, a process for creating a multivariate model relating component concentrations or sample properties to spectra for a set of known samples, referred to as calibration samples. **D8321**

3.2.4 *control limits, n*—limits on a control chart that are used as criteria for signaling the need for action or for judging whether a set of data does or does not indicate a state of statistical control.

3.2.5 *extractive sampling, n—for spectroscopic process analyzers used in the analysis of liquid petroleum products and fuels*, the process of transporting a sample from the process, performing any necessary sample conditioning and finally presenting the sample to the analyzer so as to produce a spectrum of the process sample.

3.2.6 *in situ sampling, n—for spectroscopic process analyzers used in the analysis of liquid petroleum products and fuels*, the process of transporting light from the analyzer to a sample probe located in the process wherein the light interacts with a process sample, and collecting the transmitted or scattered light, returning it to the analyzer where it is analyzed by the instrument to produce a spectrum of the process sample.

3.2.6.1 *Discussion*—For some NIR and nearly all Raman analyzers, the light will typically be transported to and from the analyzer using fiber optics.

3.2.7 *instrument, n—for spectroscopic analyzers used in petrochemical service*, the spectrometer or spectrophotometer, associated electronics and computer, spectrometer or spectrophotometer cell, and if utilized, transfer optics. **D6122**

3.2.8 *instrument performance verification sample, n—for multivariate spectroscopic analyzers used in the analysis of liquid petroleum products and fuels which employ extractive sampling*, a material representative of the product being analyzed which is adequately stored in sufficient quantity to be used as a check on instrument performance; instrument performance verification samples are used in instrument performance tests and as checks on calibration transfer, but the samples and their spectra are generally not reproducible long term **D6122**

3.2.8.1 *Discussion*—In E1866 and previous versions of D6122 and this practice, an instrument performance verification sample was referred to as a test sample.

3.2.9 *instrument qualification sample, n—for multivariate spectroscopic analyzers used in the analysis of liquid petroleum products and fuels*, a single pure compound, or a known, reproducible mixture of compounds whose spectrum is constant over time such that it can be used in an instrument performance test. **D6122**

3.2.9.1 *Discussion*—In E1866 and previous versions of D6122 and this practice, an instrument qualification sample was referred to as a check sample.

3.2.10 *level A test, n—for spectroscopic analyzers used in the analysis of liquid petroleum products and fuels*, a pass/fail instrument performance test in which the spectrum of a check or instrument performance verification sample is compared against historical spectra of the same sample via a multivariate analysis.

3.2.11 *level B test, n—for spectroscopic analyzers used in the analysis of liquid petroleum products and fuels*, a pass/fail instrument performance test in which the spectrum of a check or instrument performance verification 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.

3.2.12 *level one (1) test, n—for spectroscopic analyzers used in the analysis of liquid petroleum products and fuels*, 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.

3.2.13 *level zero (0) test, n—for spectroscopic analyzers used in the analysis of liquid petroleum products and fuels*, a routine check of instrument performance, which can be done in a few minutes, designed to visually detect significant changes in instrument performance and provide a database to determine instrument performance over time.

3.2.14 *liquid petroleum products and fuels, n—in relation to analyzers*, any single-phase liquid material that is produced at a facility in the petroleum and petrochemical industries and will be in whole or in part of a petroleum product; it is inclusive of biofuels, renewable fuels, blendstocks, alternative blendstocks, and additives. **D8340**

3.2.15 *model variables, n—*the independent variables derived from the calibration spectra which are regressed against the calibration sample properties to produce the multivariate model. **D6122**

3.2.15.1 *Discussion—*For MLR, the model variables would be the spectral intensity at the selected wavelengths or frequencies; for PCR or PLS, the model variables are the Principal Components or latent variables.

3.2.16 *optical reference material, n—for spectroscopic analyzers used in the analysis of liquid petroleum products and fuels*, an optical filter or other device which can be inserted into the optical path in the spectrometer, spectrophotometer or probe producing a spectrum which is known to be constant over time such that it can be used in place of a check or instrument performance verification sample in a performance test.

3.2.17 *primary analyzer, n—*the analyzer(s) on which calibration spectra are collected for the purpose of building a multivariate model. **D8321**

3.2.18 *Raman Shift Standard, n—*a physical sample having known Raman shift characteristics used to determine the operating wavelength of laser module and correct for any short-term or accumulated error. The position of the spectra band(s) of this material can be used to calculate the operational wavelength of the laser:

$$\lambda_i = \frac{1}{\left(\bar{v} + \frac{1}{\lambda_s}\right)} \quad (1)$$

where λ_i is the incident wavelength (the operational wavelength of the laser) in cm, λ_s is the measured wavelength of the Raman band in cm, and $\bar{v}$ is the accepted standard position of the Raman band of the reference material in wavenumbers. **D7940**

3.2.19 *secondary analyzer, n—*an analyzer not used in the development of the multivariate model, but which will be used for analysis of new materials. **D8321**

3.2.20 *spectral intensity, n—*a generic term referring to either infrared absorbance or Raman scattering intensity. **D8321**

3.2.21 *spectral position, n—*a generic term referring to either wavelength or frequency position in a spectrum. **D8321**

3.2.22 *Spectrum Standard, n—*light source of known spectrum used to standardize/calibrate the detection module and providing correct mapping of scattered wavelength to physical pixel coordinates/location. Typically, an atomic emission source such as a neon lamp is used for this purpose. **D7940**

4. Significance and Use

4.1 If ASTM Committee E13 has not specified an appropriate test procedure for a specific type of instrument, or if the sample specified by a Committee E13 procedure is incompat-

ible with the intended instrument operation, then this practice can be used to develop practical performance tests.

4.1.1 For instruments 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 instrument configuration. For example, for FT-MIR instruments equipped with transmittance or IRS flow cells, tests based on putting polystyrene films into the sample position are impractical. In such cases, this practice suggests means by which the recommended test procedures can be modified by changing the test material or the location of the recommended test material.

4.1.2 For instruments used in process measurements, the choice of test materials may be limited due to process contamination and safety considerations. The practice suggests means of developing performance tests based on materials which are compatible with the intended use of the analyzer.

4.2 Tests developed using the practice are intended to allow the user to compare the performance of an instrument on any given day with prior performance, and specifically to compare performance during calibration of the analyzer to performance during validation of the analyzer and during routine use of the analyzer. 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 analyzers of different manufacture.

4.3 Tests developed using this practice are also intended to allow the user to compare the performance of a primary analyzer used in development of a multivariate model to the performance of secondary analyzers used to apply that model for the analysis of process or product samples.

5. Test Conditions

5.1 When conducting the performance tests, the instrument 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 instrument performance verification and instrument qualification 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. However, instrument performance tests can use data collection and computation conditions that are more demanding than those used in normal operation if advantageous for instrument standardization.

5.1.3 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. Materials Used for Performance Testing

6.1 The types of materials used for performance testing will vary depending on whether the analyzer uses extractive or in situ sampling.

6.1.1 For analyzers using extractive sampling, it is generally possible to introduce an instrument qualification or instrument performance verification sample into the transmission/scattering cell. The materials used for performance testing are chosen to be compatible with the instrument configuration, and to provide spectral features which are adequate for the tests being performed.

6.1.1.1 A liquid sample used for performance testing will generally be in the same physical state (gas, liquid, or solid) as the samples to be analyzed during normal operation of the instrument.

6.1.1.2 A liquid sample used for performance testing should be physically and chemically compatible with the samples analyzed during normal operation so as to not represent a safety or product quality issue if it ends up mixed into the process stream being analyzed.

6.1.1.3 A liquid sample used for performance testing preferably has a spectrum that is similar to the spectra which will be collected during normal operation.

6.1.1.4 For infrared systems, a liquid sample used for performance testing will preferably have several significant absorbances (0.3 < absorbance < 1.0) across the spectral range used for normal operation of the instrument.

6.1.1.5 In order to adequately determine the photometric linearity of the infrared instrument, the peak absorbance for at least one absorption band of a liquid sample will preferably be similar to or slightly greater than the largest absorbance expected for samples measured during normal operation.

6.1.1.6 A liquid sample used for performance testing will typically be introduced directly into the transmission/scattering cell and not pass through any sample conditioning system. As such, it only tests the performance of the instrument and not the total analyzer system.

6.1.2 For infrared analyzers using extractive sampling, instrument performance tests can be conducted by inserting an optical reference material into the optical path when the transmission cell is empty.

6.2 For analyzers using in situ sampling, introducing an instrument qualification sample or an instrument performance verification sample into the actual process sample probe can only be done if the probe is removed from the process. For analyzers equipped with optical multiplexers, a separate channel and probe may be used for the performance test. The performance test can be conducted on an instrument qualification sample, an instrument performance verification sample, or on an optical reference material. It should be recognized that such tests do not verify the performance of the actual process probe.

6.3 *Instrument Qualification Samples*—Instrument qualification samples can be used to conduct performance tests. Instrument qualification samples are single pure compounds or mixtures of compounds of definite composition.

6.3.1 Instrument qualification samples are used to conduct Level A tests (see 9.1).

6.3.2 If mixtures are utilized as instrument qualification 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 accu-rately pipetted or weighed at ambient temperature. It is recommended that mixtures be independently verified for composition prior to use.

6.3.3 While mixtures can be used as instrument qualification samples, their spectra may be adversely affected by temperature-sensitive interactions that may manifest themselves by wavelength (frequency) and spectral intensity changes.

6.4 *Instrument Performance Verification Samples*—An instrument performance verification 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 instrument performance verification sample must be stored in bulk quantities in controlled conditions such that the material is stable over time.

6.4.1 Instrument Performance Verification Samples are used to conduct Level B Test (see 9.2).

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

6.5 *Optical Reference Materials*—An optical reference material produces a spectrum which is known to be constant over time. This material may be automatically inserted into the optical path either within the instrument or in the fiber optic sample probe to allow instrument performance tests to be performed.

6.5.1 If an optical reference material is used routinely to check or correct the spectral data collection or computation, then the same material 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 and Raman analyzers. 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.

6.6 *Spectrum Standards and Raman Shift Standards*—Light sources with known spectra are used for standardizing and calibrating the frequency axis of Raman spectrometers. Atomic emission sources such as neon lamps are used for this purpose. The peak positions of a Raman Shift Standard such as toluene can be used in instrument performance testing (Practice

D7940). Practice E1840 lists various materials that can be used as Raman shift standards.

6.7 For Raman systems, the spectral features used in performance testing should be in the linear range for the detector, above the noise level but below the saturation level. If the linear range of the Raman detector has not previously been established, a series of mixtures should be measured at various exposure times to determine the range over which response is linear.

7. Univariate Measures of Absorbance Spectrophotometer Performance

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

7.1.1 For single beam instruments where background and sample spectra are measured separately at different times, energy level tests are generally conducted on a background spectrum. For double beam instruments 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 a minimum of two fixed frequencies (wavelengths). 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 an instrument qualification or instrument performance verification sample at regions where the spectrum is relatively flat, and the sample spectral intensity is minimal (<0.1).

7.2.1 For single beam instruments 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 instrument, 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 instruments, 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:

$$m = \frac{n\Sigma i T_i - \Sigma T_i \Sigma i}{n\Sigma i^2 - (\Sigma i)^2} = \frac{\Sigma i T_i}{\Sigma i^2} \tag{2}$$

$$b = \frac{\Sigma i^2 \Sigma T_i - \Sigma i \Sigma i T_i}{n\Sigma i^2 - (\Sigma i)^2} = \frac{\Sigma T_i}{n} \tag{3}$$

The photometric noise is calculated as follows:

$$Noise_{RMS} = \sqrt{\frac{\Sigma(T_i - (mi + b))^2}{n - 2}} \tag{4}$$

The index i in Eq 2-4 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 spectra, the spectral intensity values, A_i, are used in place of the transmittance values, T_i, in Eq 2-4. 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 2-4. 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 3 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 instrument.

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 an instrument qualification or instrument performance verification 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 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 Instrument 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 instruments 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 instrument qualification or instrument performance verification 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 instrument qualification/instrument performance verification sample or optical material, the user should be aware that changes in instrument 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 Savitzky 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 (FWHM) 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 user's responsibility to demonstrate that the peak finding algorithm is appropriate for monitoring instrument frequency (wavelength) stability.

7.7 *Resolution Stability Tests*—The resolution stability of the instrument is monitored by measuring the bandwidths of several absorption peaks in the spectrum of the instrument qualification/instrument performance verification 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 instrument is varying, suggesting a malfunction.

7.7.1 The spectral intensities for peaks used in this test are preferably in the range from 0.37 to 0.75. For peak spectral intensity 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 instrument qualification/instrument performance verification 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 Savitzky 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 FWHM 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 intensity 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.

7.8 *Photometric Linearity Tests*—Linearity of the instrument 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 instrument.

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

7.8.1 Photometric linearity is tested using the ratio of the spectral intensity of two or more peaks in the - spectrum. One peak should have a spectral intensity at or near the maximum spectral intensity 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 spectral intensity on opposite sides of the peaks. The maximum spectral intensity for each peak is corrected for the baseline, and the ratio of the spectral intensities for the two peaks is calculated. The ratio is used to track changes in the photometric linearity.

8. Univariate Measures of Raman Spectrophotometer Performance

8.1 During the development of the analytic method, correlations are established between spectra and the sample species by taking spectra of known samples. Because of the inherent linearity of the Raman effect, the method will correctly measure sample concentrations if the Raman spectra are valid. Thus, the primary task to ensure analyzer calibration is to ensure the spectra are calibrated and standardized before the analyzer is commissioned. There also needs to be a means to ensure this calibration remains valid over time by using instrument qualification approaches. A spectrum is essentially a two-dimensional chart with the number of detected photons on the vertical or intensity axis and the wavelength of those photons on the horizontal axis. The mathematical method used to generate analytic results from the spectra relies on knowing the wavelength positions and relative intensities of the various spectral features associated with the components. Each of these axes is calibrated by optical means.

8.2 *Wavelength Axis*—For the wavelength axis calibration to be standardized, and thus to know which detected vibration frequencies correspond to given spectrum features, it is necessary to determine the wavelength falling on each group of CCD pixels. This is done by exposing the detector to light that is comprised of known individual wavelengths. Typically, this is done by arranging for light from a neon bulb to be periodically and automatically imaged onto the detector. The emission spectra of neon is comprised of a large number of individual wavelengths that are known to great precision, and the physics associated with neon light ensure wavelength stability through time and over a wide range of environmental conditions, thus establishing standardization. By recording where each neon wavelength falls on the CCD, a map can be generated relating pixel to wavelength. Any changes in the position of a given wavelength on the detector as a result of thermal or mechanical effects can thus be corrected by measuring the change with the neon spectra. Ongoing instrument qualification is done analogously.

8.2.1 *Example Neon Spectrum—Y-axis*: counts, *X-axis*: Raman shift (cm^{-1}) (see Fig. 1).

8.3 *Intensity Axis Calibration—Optical Path Wavelength Transmission Efficiency*—The detection efficiency of signal photons traveling from the sample, through the probe optics, through the fiber, and finally, to the detection module, varies with wavelength. Thus, different molecular vibrations have

FIG. 1 Example Neon Spectrum