



Standard Guide for Relative Intensity Correction of Raman Spectrometers¹

This standard is issued under the fixed designation E2911; 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 is designed to enable the user to correct a Raman spectrometer for its relative spectral-intensity response function using NIST Standard Reference Materials² in the 224X series (currently SRMs 2241, 2242, 2243, 2244, 2245, 2246), or a calibrated irradiance source. This relative intensity correction procedure will enable the intercomparison of Raman spectra acquired from differing instruments, excitation wavelengths, and laboratories.

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

1.3 Because of the significant dangers associated with the use of lasers, ANSI Z136.1 or suitable regional standards should be followed in conjunction with this practice.

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:*³

[E131 Terminology Relating to Molecular Spectroscopy](#)

[E1840 Guide for Raman Shift Standards for Spectrometer Calibration](#)

[E2529 Guide for Testing the Resolution of a Raman Spectrometer](#)

2.2 *ANSI Standard:*⁴

[Z136.1 Safe Use of Lasers](#)

3. Terminology

3.1 *Definitions*—Terminology used in this practice conforms to the definitions in Terminology [E131](#).

4. Significance and Use

4.1 Generally, Raman spectra measured using grating-based dispersive or Fourier transform Raman spectrometers have not been corrected for the instrumental response (spectral responsivity of the detection system). Raman spectra obtained with different instruments may show significant variations in the measured relative peak intensities of a sample compound. This is mainly as a result of differences in their wavelength-dependent optical transmission and detector efficiencies. These variations can be particularly large when widely different laser excitation wavelengths are used, but can occur when the same laser excitation is used and spectra of the same compound are compared between instruments. This is illustrated in [Fig. 1](#), which shows the uncorrected luminescence spectrum of SRM 2241, acquired upon four different commercially available Raman spectrometers operating with 785 nm laser excitation. Instrumental response variations can also occur on the same instrument after a component change or service work has been performed. Each spectrometer, due to its unique combination of filters, grating, collection optics and detector response, has a very unique spectral response. The spectrometer dependent spectral response will of course also affect the shape of Raman spectra acquired upon these systems. The shape of this response is not to be construed as either “good or bad” but is the result of design considerations by the spectrometer manufacturer. For instance, as shown in [Fig. 1](#), spectral coverage can vary considerably between spectrometer systems. This is typically a deliberate tradeoff in spectrometer design, where spectral coverage is sacrificed for enhanced spectral resolution.

4.2 Variations in spectral peak intensities can be mostly corrected through calibration of the Raman intensity (y) axis.

¹ This guide is under the jurisdiction of ASTM Committee [E13](#) on Molecular Spectroscopy and Separation Science and is the direct responsibility of Subcommittee [E13.08](#) on Raman Spectroscopy.

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² Trademark of and available from NIST Office of Reference Materials, 100 Bureau Drive, Stop 2300, Gaithersburg, MD 20899-2300. <http://www.nist.gov/srm>.

³ 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.

⁴ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.

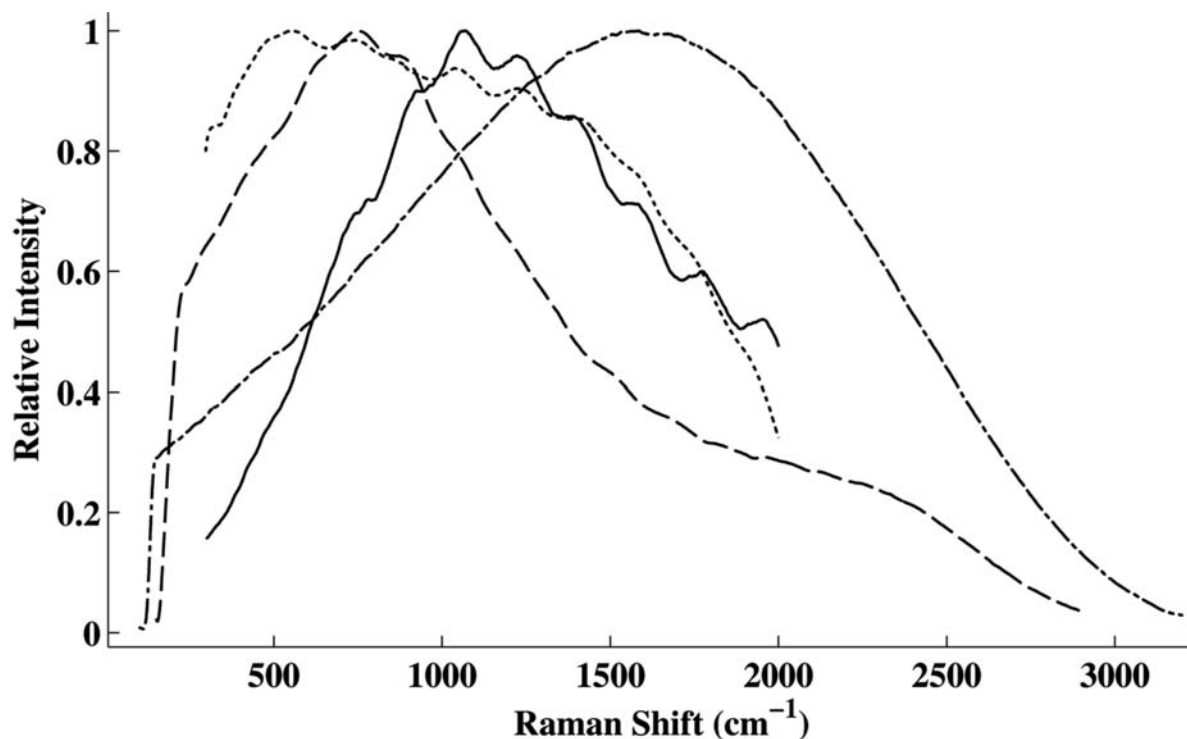


FIG. 1 SRM 2241 Measured on Four Commercial Raman Spectrometers Utilizing 785 nm Excitation

The conventional method of calibration of the spectral response of a Raman spectrometer is through the use of a National Metrology Institute (NMI), for example, NIST, traceable calibrated irradiance source. Such lamps have a defined spectral output of intensity versus wavelength and procedures for their use have been published (1)⁵. However, intensity calibration using a white-light source can present experimental difficulties, especially for routine analytical work. Calibrated tungsten halogen lamps have a limited lifetime and require periodic recalibration. These lamps are often mounted in an integrating sphere to eliminate polarization effects and provide uniform source irradiance. In practice, these sources can be difficult to align with the variety of sampling arrangements that are now typical with Raman spectrometers, especially microscope based systems and process Raman analyzers where electrical safety concerns persist in hazardous areas. The advantage of a standard lamp is that it can be used for multiple excitation wavelengths.

4.3 The spectra of materials that luminesce with irradiation can be corrected for relative luminescence intensity as a function of emission wavelength using a calibrated Raman spectrometer. An irradiance source, traceable to the SI, can be used to calibrate the spectrometer. Several groups have proposed these transfer standards to calibrate both Raman and fluorescence spectrometers (1-6). The use of a luminescent glass material has the advantage that the Raman excitation laser is used to excite the luminescence emission and this emission is measured in the same position as the sample. These glasses can be used in a variety of sampling configurations and

they require no additional instrumentation. The glasses are photostable and unlike primary calibration sources, may not require periodic recalibration. NIST provides a series of fluorescent glasses that may be used to calibrate the intensity axis of Raman spectrometers. A mathematical equation, which is a description of the corrected emission, is provided with each glass. The operator uses this mathematical relation with a measurement of the glass on their spectrometer to produce a system correction curve.

4.4 This guide describes the steps required to produce a relative intensity correction curve for a Raman spectrometer using a calibrated standard source or a NIST SRM and a means to validate the correction.

5. Reagents

5.1 Standard Reference Materials, SRM 2241, SRM 2242, SRM 2243, SRM 2244, SRM 2245, and SRM 2246 are luminescent glass standards designed and calibrated at NIST for the relative intensity correction of Raman spectrometers operating with excitation laser wavelengths of 785 nm, 532 nm, 488 nm/514.5 nm, 1064 nm, 632.8 nm and 830 nm, respectively (3-5). The corrected luminescence spectra of each is shown in Fig. 2.

5.2 Raman shift reagents (see Guide E1840).

6. Raman Shift Verification (X-Axis)

6.1 Verification of the calibration of the spectrometer's x-axis in Raman shift wavenumbers ($\Delta\nu$ cm^{-1}) is necessary before intensity correction of the y-axis is performed. The Raman shift axis is calculated from Eq 1:

$$\Delta\nu = (\nu_0 - \nu_s) \quad (1)$$

⁵ The boldface numbers in parentheses refer to the list of references at the end of this standard.

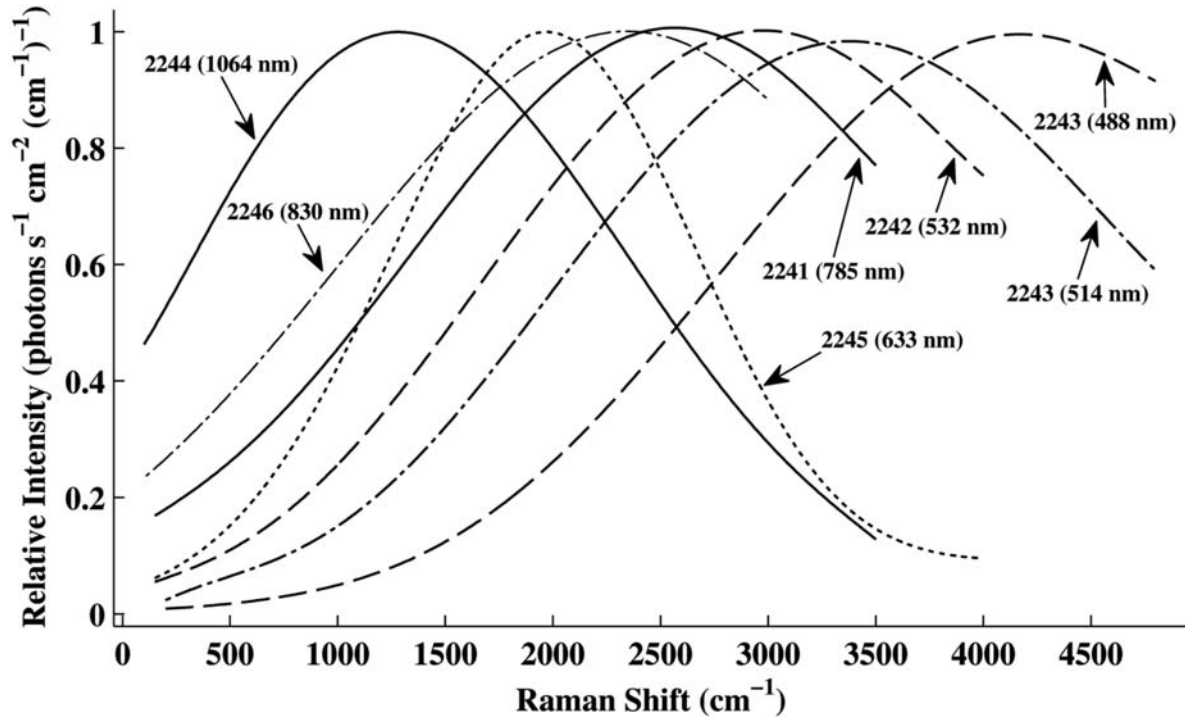


FIG. 2 Certified Models of the Corrected Luminescence Spectra of SRMs 2241 through 2246 as a Function of Raman Shift from the Specified Laser Excitation Wavelength

where:

- $\Delta\nu$ = the wavenumber in units of Raman shift (cm^{-1}),
- ν_o = the laser frequency in wavenumbers (cm^{-1}),
- ν_s = the wavelength axis of the spectrometer expressed in wavenumbers (cm^{-1}),

6.2 The laser frequency can be measured using a wavemeter while the absolute wavenumber axis of the spectrometer is calibrated with emission pen lamps. Several references (7-10) have detailed the use of the appropriate emission lamps for the relevant Raman frequency range. Users should defer to the vendor’s instructions for the purpose of Raman shift axis calibration or verification. However, independent validation of the Raman shift axis may be performed by referring to Guide E1840-96(2007).

7. Relative Instrument Response Function Calibration (Y-Axis):

7.1 General Procedure for Relative Response Calibration:

7.1.1 The most practical approach to calibrating a relative instrumental response function (IRF) involves the use of a standard of known spectral flux (intensity versus wavelength). The standard source is aligned to the spectrometer such that the emitted optical radiation is directed into the optical path to emulate Raman scattered radiation collected by the spectrometer from the sample position. The best accuracy is achieved when the calibration source radiation and Raman scatter of the sample travel the same illumination path through the collection optics of the spectrometer. The standard source spectrum is measured using, as nearly as possible, the same instrumental parameters (for example, spectral coverage, slit width, filters, or other optical elements) as used for sample data collection.

Excitation laser power, however, is sample dependent and the relative response correction of the spectrometer will be independent of this parameter. Acquisition time should be adjusted to optimize the signal-to-noise ratio (SNR).

7.1.2 The relative IRF is defined as the ratio of the measured spectrum of the standard source, $S_L(\Delta\nu)$, to the known standard output, $I_L(\Delta\nu)$. The inverse of this relation is used to calculate a relative intensity correction curve as in Eq 2:

$$I_{CORR}(\Delta\nu) = I_L(\Delta\nu)/S_L(\Delta\nu) \quad (2)$$

where:

- $I_{CORR}(\Delta\nu)$ = the relative intensity correction curve,
- $I_L(\Delta\nu)$ = the known standard output,
- $S_L(\Delta\nu)$ = the measured spectrum of the standard source (see 7.1.4).

7.1.3 Once determined, this correction curve is used to correct the measured Raman spectrum of a sample, $S_{MEAS}(\Delta\nu)$, for the system dependent response according to Eq 3:

$$S_{CORR}(\Delta\nu) = I_{CORR}(\Delta\nu) \times S_{MEAS}(\Delta\nu) \quad (3)$$

where:

- $S_{CORR}(\Delta\nu)$ = the corrected Raman spectrum of the sample,
- $I_{CORR}(\Delta\nu)$ = the relative intensity correction curve,
- $S_{MEAS}(\Delta\nu)$ = the measured Raman spectrum of the sample (see 7.1.4).

7.1.4 Prior to calculating the relative intensity correction curve or corrected sample Raman spectrum, the measured spectra should be corrected by removing contributions to the signal not originating from the sample or calibration source being measured. Background signal can arise from processes independent of light incident on the detector, such as detector