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Standard Guide for Testing the Resolution of a Raman Spectrometer¹

This standard is issued under the fixed designation E2529; 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 for routine testing and assessment of the spectral resolution of Raman spectrometers using either a low-pressure arc lamp emission lines or a calibrated Raman band of calcite.

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 shall 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *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

[E131 Terminology Relating to Molecular Spectroscopy](#)

[E1683 Practice for Testing the Performance of Scanning Raman Spectrometers](#)

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

2.2 *ANSI Standard:*³

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

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 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.

³ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.

3. Terminology

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

4. Significance and Use

4.1 Assessment of the spectrometer resolution and instrument line shape (ILS) function of a Raman spectrometer is important for intercomparability of spectra obtained among widely varying spectrometer systems, if spectra are to be transferred among systems, if various sampling accessories are to be used, or if the spectrometer can be operated at more than one laser excitation wavelength.

4.2 Low-pressure discharge lamps (pen lamps such as mercury, argon, or neon) provide a low-cost means to provide both resolution and wave number calibration for a variety of Raman systems over an extended wavelength range.

4.3 There are several disadvantages in the use of emission lines for this purpose, however.

4.3.1 First, it may be difficult to align the lamps properly with the sample position leading to distortion of the line, especially if the entrance slit of the spectrometer is underfilled or not symmetrically illuminated.

4.3.2 Second, many of the emission sources have highly dense spectra that may complicate both resolution and wave number calibration, especially on low-resolution systems.

4.3.3 Third, a significant contributor to line broadening of Raman spectral features may be the excitation laser line width itself, a component that is not assessed when evaluating the spectrometer resolution with pen lamps.

4.3.4 An alternative would use a Raman active compound in place of the emission source. This compound should be chemically inert, stable, and safe and ideally should provide Raman bands that are evenly distributed from 0 cm^{-1} (Raman shift) to the C-H stretching region 3000 cm^{-1} and above. These Raman bands should be of varying bandwidth.

4.4 To date, no such ideal sample has been identified; however carbon tetrachloride (see Practice [E1683](#)) and naphthalene (see Guide [E1840](#)) have been used previously for both resolution and Raman shift calibration.

Calcite

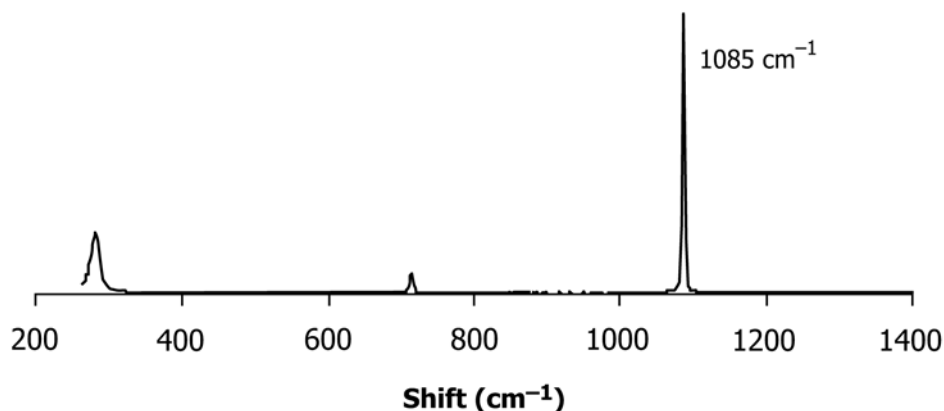


FIG. 1 Calcite Raman Spectrum

4.5 The use of calcite to assess the resolution of a Raman system will be addressed in this guide. Calcite is a naturally occurring mineral that possesses many of the desired optical properties for a Raman resolution standard and is inexpensive, safe, and readily available.

4.6 The spectral bandwidth of dispersive Raman spectrometers is determined primarily by the focal length of the spectrometer, the dispersion of the grating, and the slit width. Field portable systems typically operate with fixed slits and gratings and thus operate with a fixed spectral bandwidth, while in many laboratory systems the slit widths and gratings are variable. The spectral bandwidth of Fourier-Transform (FT)-Raman systems is continuously variable by altering the optical path difference of the interferometer and furthermore is capable of obtaining much lower spectral bandwidth than most practical dispersive systems. Therefore, data obtained of a narrow Raman band on a FT-Raman system can be used to determine the resolution of a dispersive Raman system. A calibration curve of the full width at half height (FWHH) for the 1085-cm⁻¹ band of calcite as a function of spectral resolution has been reported for this purpose.⁴ Measurement of this calcite band on a test dispersive instrument enables an estimation of the spectrometer resolution.

4.7 This guide will describe the use of calcite and pen lamps for the evaluation of Raman spectrometer resolution for dispersive (grating based) Raman systems operating with a 785 nm laser wavelength.

5. Reagents

5.1 Calcite and calcium carbonate (CaCO₃) come in many forms. Iceland spar, from Iceland and, more commonly, Mexico, is easily cleavable into a rhombohedron and is the clear crystal commonly found in retail stores. It is readily available and inexpensive but may fluoresce under blue excitation. In addition, it is birefringent.

⁴ Bowie, B. T. and Griffiths, P. R., "Determination of the Resolution of a Multichannel Raman Spectrometer Using Fourier Transform Raman Spectra," *Applied Spectroscopy*, Vol 57, No 2, 2003, pp 190-196.

5.2 Low-pressure discharge emission (pen) lamps are widely available from optical supply companies. They are typically made with noble gases or a metal vapor. Argon, krypton, and xenon pen lamps are applicable as resolution calibration sources for Raman spectrometers operating with 785 nm excitation. These pen lamps cover a wide wave number range but have reasonably sparse spectra.

6. Procedure

6.1 Calcite Calibration:

6.1.1 Measure the Raman spectrum of calcite using the vendor's recommended procedure for producing a Raman spectrum of a sample with good signal to noise. The Raman spectrum of calcite is shown in Fig. 1. Because the Raman scattering of the 1085 cm⁻¹ band is polarized, the peak height will depend upon the polarization of the laser and the location of the sample with respect to the excitation laser. Rotate the sample under excitation laser beam to obtain the maximum signal from the 1085 cm⁻¹ band. The calibration relation determined in 4.6 is:

$$B_{w1085} (\text{cm}^{-1}) = 1.0209 * S_{\text{resolution}} + 0.684 \quad (1)$$

where:

- B_{w1085} = the measured bandwidth of the 1085 cm⁻¹ CaCO₃ Raman band, and
- $S_{\text{resolution}}$ = the nominal resolution of the reference FT-Raman spectrometer described in 4.6.

6.1.2 After acquiring the Raman spectrum of the calcite sample, determine the FWHH of the 1085 cm⁻¹ band, B_{w1085} , by using the spectral analysis feature commonly found in the control software provided with the spectrometer. These programs typically use a Levenburg-Marquardt nonlinear least squares to determine the line shape of the Raman band.⁵ The calibration equation (Eq 1) was determined using a fit to a mixed Gaussian and Lorentzian function. Solve for the nominal resolution of the spectrometer under test by rearranging Eq 1 to:

⁵ Marquardt, D. W., *J. Soc. Ind. Appl. Math.*, Vol 11, 1963, pp. 431-441.

Argon

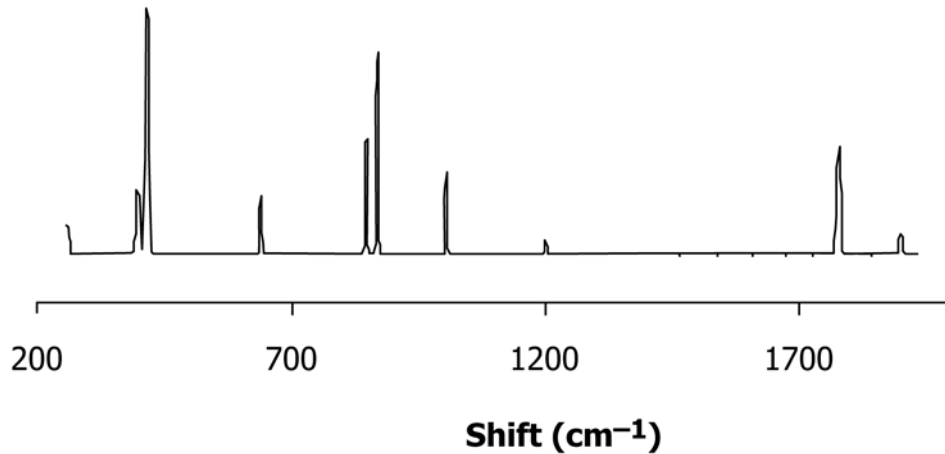


FIG. 2 Emission Spectra of Argon Plotted in Shift Units from 12 738.85 cm^{-1} (785 nm)

$$S_{\text{resolution}} = (B_{w1085} - 0.684)/1.0209 \quad (2)$$

6.1.3 This fit is reported to be good to approximately 20 % accuracy, which is adequate for validation purposes. The 1085 cm^{-1} band is a good approximation for system resolution estimation as it is centered in the Raman spectra for fixed grating systems that typically operate from 200 cm^{-1} to approx. 2000 cm^{-1} . This material is suitable for use with all laser wavelengths; however, many samples have been observed to fluoresce with excitation wavelengths below 532 nm excitation.

6.2 *Pen Lamp Calibration*—The spectra of xenon, argon, and krypton in Raman shift from 12 739 cm^{-1} (785 nm excitation) are shown in Figs. 2-4. The associated emission lines from each source is listed in Table 1 in air wavelength, absolute cm^{-1} (air), and Raman shift from 12739 cm^{-1} . If a fiber-probe-based Raman system is to be calibrated, a convenient source of an argon spectra is the light emitted from older backlit laptop computer screens or overhead fluorescent lights. Place a translucent target at the focal point of the fiber collection system. An example would be several thicknesses of scotch tape placed on a glass slide. Otherwise, illuminate the slit as evenly as possible. Check for symmetric lines in the collected spectrum and use integration times that prevent saturation of

the detector. This is especially true for the xenon source in which the 881.9 nm line is very intense. Determine the FWHH of bands in the low, middle, and long Raman shift region of the spectra. The resolution (FWHH) shall not be constant, but vary from the low to high Raman shift region. Gratings disperse light nearly linearly in wavelength and therefore the reciprocal linear dispersion in wavelength units (nm) will be nearly constant. The reciprocal linear dispersion in wave number (cm^{-1}) units will increase at higher Raman (Stokes) shift due to the inverse relation between wavelength and wave number. For Raman systems based upon the commonly used spectrometer designs, the resolution will theoretically increase (FWHH decreases) on the Stokes-shifted (longer wavelength) side of the excitation laser line. It is not unusual, however, to observe the center of the spectra of fixed grating systems to have the smallest FWHH (highest resolution) while the edges (low and high Raman shift region) exhibit lower resolution. This effect is due to error incurred by the curvature of the focal plane for low f-number spectrometers.

7. Keywords

7.1 calcite; low-pressure arc lamp calibration; Raman spectroscopy; resolution calibration