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Standard Guide for Testing the Resolution of a Raman Spectrometer¹

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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 given in SI units are to be regarded as the 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 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

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

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.

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,

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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>.

Calcite

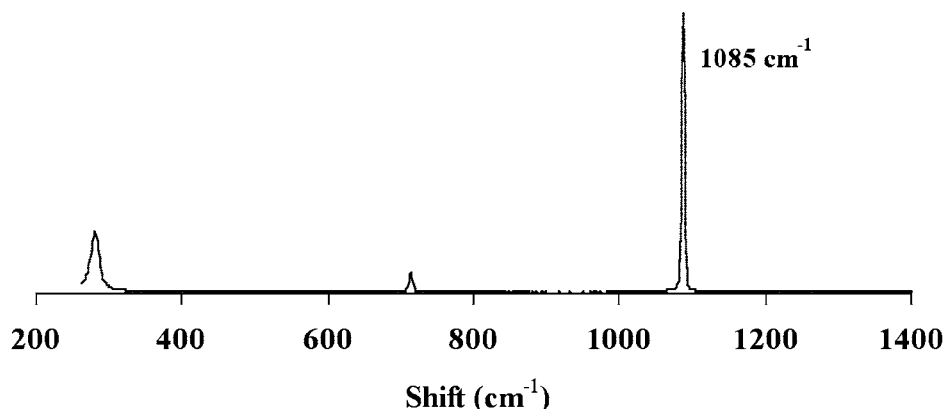


FIG. 1 Calcite Raman Spectrum

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.

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:

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

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 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.

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

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