Lightnovo

Spectral resolution measurement according to ASTM E2529-06 (calcite)

KEYWORDS

Raman spectrometer; spectral resolution; calcite; spectral peak; spectral band; Full Width at Half Height (FWHH).

INTRODUCTION

In traditional Raman spectroscopy, the sample under investigation is excited by monochromatic light with a certain wavelength λ_0, whereas the intensity I of inelastically scattered light with a changed wavelength $\lambda \neq \lambda_0$ is measured at different λ over some range. The result is a Raman spectrum, which is usually represented by the $I(\nu)$ dependence, where $\nu = (1/\lambda_0 - 1/\lambda)\cdot 10^7$ is the Raman shift (wavenumber) expressed in cm^{-1} units, while λ_0 and λ are taken in nm. The $I(\nu)$ spectrum contains a baseline ($I = 0$ in the ideal case) and a number of peaks (bands), the positions, heights and widths of which reflect the unique features of the chemical composition and structure of the sample.

For a Raman spectrometer, one of the key characteristics is the spectral resolution S – a measure of the instrument's ability to distinguish between two adjacent peaks. If the spectrum is represented as $I(\nu)$, then S is usually expressed in units of ν (i.e. in cm^{-1}). In other words, S shows how many peaks the spectrometer can resolve for the covered range of shifts ν (spectral range), and thus how much detailed information about the sample can be gained from the Raman spectrum. Typically, the lower the S value, the higher the cost and size of the instrument. This has led to the emergence of different classes of spectrometers depending on the analysis tasks (required resolution). Simple averaging of data from [1] gives mean resolution values for modern commercially available instruments:

- S = 2 cm^{-1} (research tasks),
- S = 6 cm^{-1} (routine and process control tasks),
- S = 8 cm^{-1} (hand-held instruments).

Spectral resolution is highly dependent on the spectrometer design. For example, when using a dispersive optical system, S is mainly determined by the parameters of the entrance diaphragm (slit or pinhole), dispersive element (prism or diffraction grating), light detector, as well as by the spectrometer focal length (the distance between the dispersive element and the detector) [2]. Thus, for the correct and efficient application of any Raman spectrometer, it is necessary to carry out an experimental assessment of its spectral resolution.

This Technical Note describes the procedure for measuring spectral resolution S for the miniRaman spectrometers from Lightnovo ApS [3].

MEASURING SYSTEM: MINIRAMAN SPECTROMETER

The miniRaman is a series of ultra-compact Raman spectrometers, Figure 1, having the record low sizes (112×39×34 mm^3) and mass (200 g in aluminum housing). These devises are suitable for most typical applications of Raman spectroscopy, and allow for a variety of use scenarios: the autonomous field hand-held instrument, benchtop instrument, component of a confocal 2D/3D scanning Raman microscope, distant instrument with wireless control etc.

Figure 1. Lightnovo miniRaman Power spectrometer (λ_0 = 785 nm).

The miniRaman is the dispersive spectrometer that operates in 180°-backscattering mode. The solid-state laser is used to generate light with a wavelength λ_0, which is output to the sample through an entrance lens and a special optical probe (Raman probe). Reflected light is collected by the same components and passes through an entrance slit and an edge filter, which rejects the elastically scattered part of the light having a wavelength λ_0. Then a transmission diffraction grating splits the remaining light into a spectrum, and a CMOS image sensor records them simultaneously across whole instrument's spectral range.

The patented optical scheme of the spectrometer [4] has a number of original solutions and improvements that eliminate the use of expensive, bulky, cooled and moving components significantly reducing the mass-size parameters. At the same time, they made it possible to overcome the main issues inherent in Raman spectrometers, obtain the ~ 92 % throughput from the sample to the detector, effectively decrease the impact of fluorescence on Raman signal, and, as a result, measure the Raman spectrum I(ν) with high sensitivity and signal-to-noise ratio.

Details for miniRaman MRs patent

The miniRaman series includes five models: Standard, Power, SERS, Standard Dual and Power Dual. The first three have a single laser with λ_0 = 785 nm providing the spectral range ν = (400...2700) cm^{-1}. The Dual models have two lasers with λ_0 = 785 nm and 660 nm providing extended spectral range ν = (400...4000) cm^{-1}. The models differ in the power of the laser(s). All instruments have the same optical scheme with fixed entrance lens and slit, grating, and focal length. Different interchangeable Raman probes can be installed to handle various types of samples and/or to arrange required working distances of the instrument.

SPECTRAL RESOLUTION MEASUREMENT PROCEDURE

ASTM E2529-06 (2022) "Standard guide for testing the resolution of a Raman spectrometer" [5] provides the most convenient technique for determining the spectral resolution of dispersive (grating-based) Raman spectrometers with laser excitation at λ_0 = 785 nm. It involves the use of a calibrated peak in the Raman spectrum of the calcite sample.

Calcite is a wide-spread natural mineral, a form of calcium carbonate $CaCO_3$. Its Raman spectrum has only three strong peaks in the range ν = (200...1200) cm^{-1}, and they are completely resolved [5]. This makes calcite attractive as a reference material. Unfortunately, it is birefringent, so that the peak heights are highly dependent on the laser polarization and the beam orientation relative to the sample. Therefore, using the height values as calibrated data is problematic.

Nevertheless, the study [6], which underlies the standard [5], showed that the birefringence has almost no affect the Full-Width at Half-Height (FWHH) value for all peaks. Experiments carried out using a precision Fourier-transform Raman spectrometer with the λ_0 = 1064 nm excitation have demonstrated a linear relationship:

$$S = \frac{\Delta\nu_{1085} - 0.684}{1.0209}, \qquad \text{(Eq.1)}$$

where S is the spectral resolution;

$\Delta\nu_{1085}$ is the FWHH value for the most intensive calcite peak at ν = 1085 cm^{-1}.

It was then shown that this dependence is applicable with an accuracy of 20 % for a grating-based spectrometer having the λ_0 = 782 nm excitation [6]. Finally, equation (Eq.1) was adopted as a standard for the spectral resolution assessment in dispersive spectrometers with λ_0 = 785 nm [5].

To measure spectral resolution S in accordance with the ASTM E2529-06 (2022) standard [5] the following main steps must be performed:

1. Matching the optimal measurement parameters (exposure time, number of repetitions) that provide a suitable signal-to-noise ratio for a calcite sample.
2. Choosing the sample orientation relative to the excitation light beam, which gains the maximum Raman signal for the peak at ν = 1085 cm^{-1}.
3. Measuring the Raman spectrum.
4. Fitting of the measured datapoints for the ν = 1085 cm^{-1} peak by some analytical curve.
5. Determining FWHH $\Delta\nu_{1085}$ for the ν = 1085 cm^{-1} peak from the fitting curve.
6. Calculating spectral resolution S using (Eq.1).

It should be noted that the standard does not contain restrictions regarding the calcite's origin, as well as any instructions for the manufacture of a reference sample based on this material. In addition, there are no strict requirements for the type of fitting curve for the ν = 1085 cm^{-1} peak in [5]. Moreover, nothing is said about the applicability of equation (Eq.1) for other excitation wavelengths λ_0, whereas it is recognized that calcite can be used for a laser with any values of λ_0.

EXAMPLE OF SPECTRAL RESOLUTION MEASUREMENT

The miniRaman Power model with an excitation wavelength λ_0 = 785 nm and a slit width of 25 μm was used to demonstrate the procedure. Data acquisition parameters used:

- laser power 100 mW;
- image sensor gain 0;
- exposure 250 ms;
- number of repetitions 10.

The instrument was equipped with the middle working distance (10 mm) Raman probe. The space between the probe and the calcite sample was not specially optically isolated. The measurements were carried out in an ordinary office (laboratory) space with common lightning, at room temperature and humidity. Besides a native instrument housing, no special means were taken to isolate the spectrometers form background electromagnetic environment.

Figure 2 shows baseline corrected Raman spectrum I(ν) of calcite. The following parameters were used for baseline correction: radius 300, scale Y: 0.1. Intensity I is expressed as a percentage of the saturation level of the spectrometer's CMOS image sensor.

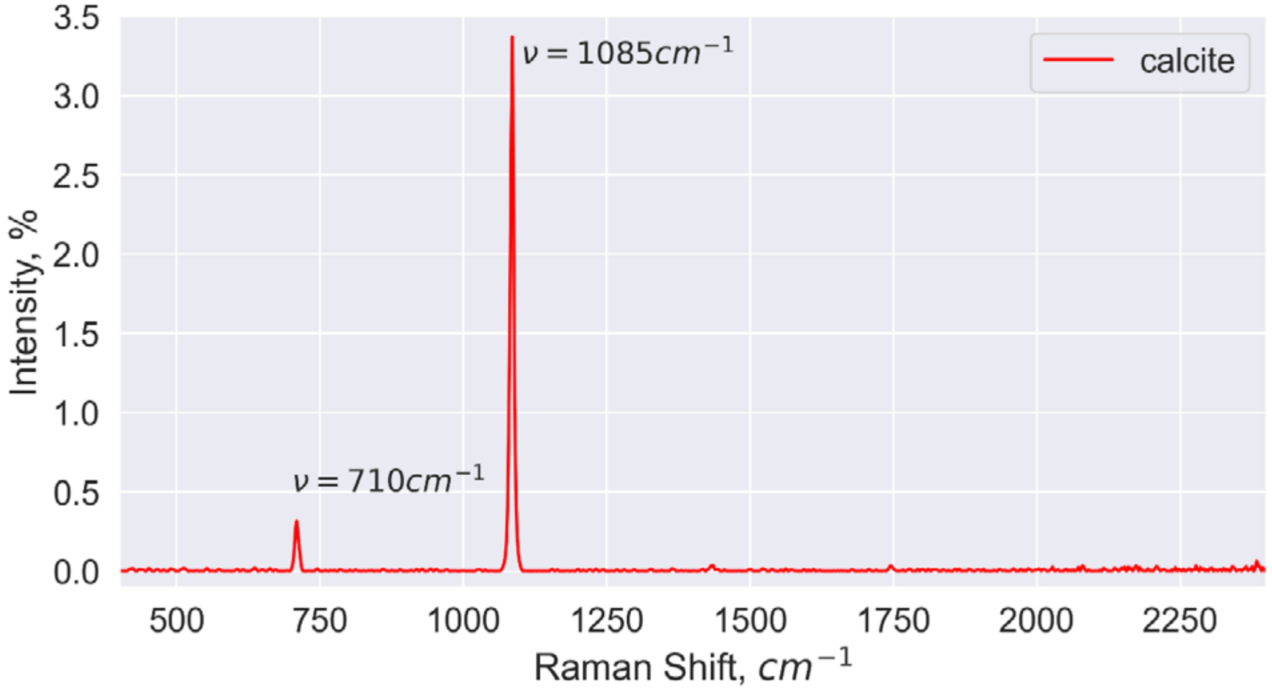

Figure 2. Baseline corrected Raman spectrum I(ν) of the calcite sample.

The obtained spectrum contains two of the three sharp peaks typical for calcite: at **ν** = 710 cm^{-1} and **ν** = 1085 cm^{-1} [5, 6]. The third one, at **ν** = 280 cm^{-1}, lies out of the spectral range. As can be seen, the selected experiment conditions provide a fairly high signal-to-noise ratio, and the baseline and peaks are clearly distinguishable. Note that, the maximum intensity value is far from the saturation level, which eliminates the risk of additional errors.

The observed baseline incline can be explained by the overlap with fluorescent spectrum, that is a typical situation for Raman spectroscopy [2]. When analyzing an unknown material, such interference can significantly complicate its identification, since, as a rule, library spectra are stored clean from the fluorescence impact. It can also lead to errors in the calculation of low-intensity peaks height, which in turn will negatively affect quantitative analysis. In these cases, the spectrum must be processed using some mathematical tools in order to remove the fluorescence and other spurious components (so called background or baseline correction). The miniRaman spectrometer's software has appropriate program instruments for this [3].

However, for the described measuring procedure, there is no need to make additional background correction. This is because the calcite peak at **ν** = 1085 cm^{-1} is isolated from another ones, and is quite intensive and narrow. Hence, a baseline incline will not affect the symmetry of this peak, and therefore will not lead to a significant error in determining its height. This can be seen from Figure 3 which shows a zoomed fragment of the spectrum. The peak is enough symmetrical, and the baseline level from which its height is measured can be determined quite accurately.

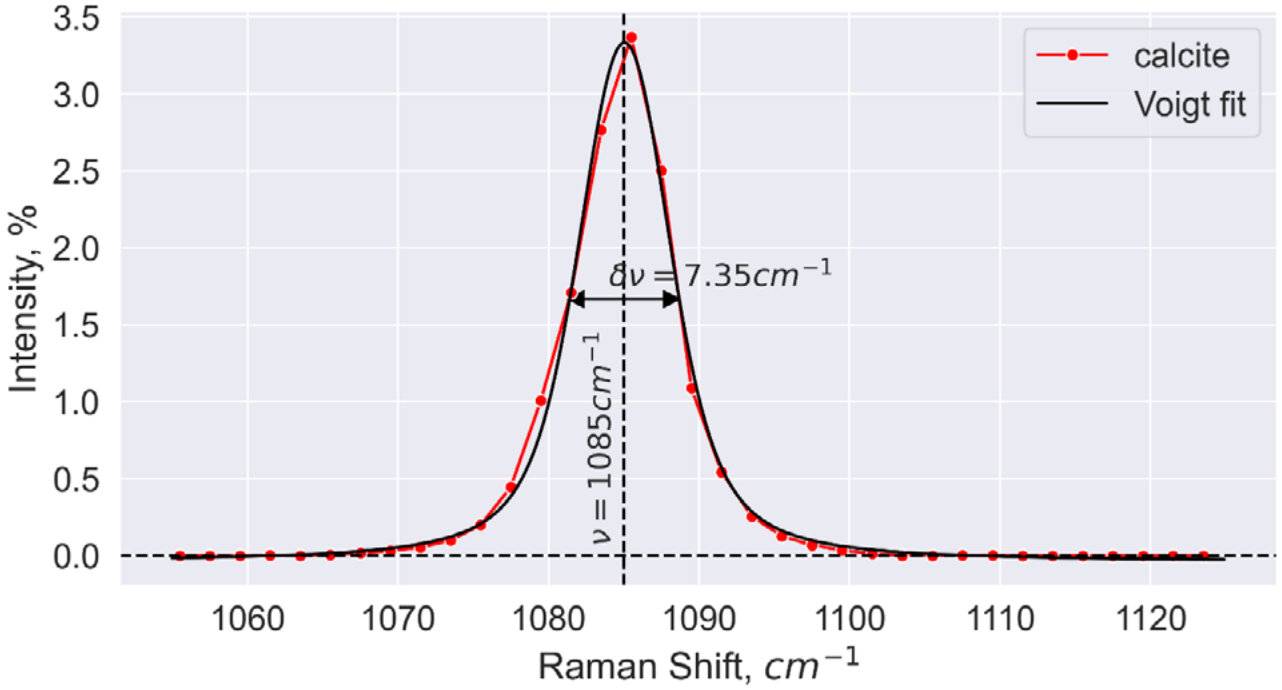

Figure 3. The ν = 1085 cm^{-1} peak in the calcite spectrum I(ν): the experimental results (in red; a zoomed fragment from Figure 2); and the correspondent Voigt fit curve (in black).

The data points related to the $\mathbf{\nu}$= 1085 cm^{-1} peak were fitted by the Voigt profile (a convolution of the Gaussian and Lorentzian distributions), that is shown by the black curve in Figure 3. The goodness of the fit was estimated by reduced chi-squared criterion.

The calculated position of the peak maximum is $\mathbf{\nu} \approx$ 1085.06 cm^{-1}, i.e. it is displaced by ≈ 0.06 cm^{-1} from the nominal value specified in [5, 6]. This corresponds to the wavenumber accuracy ±2.5 cm^{-1} declared for the miniRaman instrument [3]. It should be noted, that this displacement isn't influencing the spectral resolution measurement according with ASTM E2529-06 [5] because the standard relies on the measurement of peak width, that is, the difference between two Raman shift $\mathbf{\nu}$ values.

The Voigt fit allows to estimate FWHH value as $\mathbf{\Delta\nu}_{1085}$ = 7.35 cm^{-1}, that after substitution in (Eq.1) gives the spectral resolution value S = 6.53 cm^{-1}.

CONCLUSION

The described procedure for measuring spectral resolution is simple, fast, inexpensive, and applicable to any miniRaman spectrometer. It doesn't require the use of specially made standard samples, dedicated environment or the involvement of service engineers. In fact, measurements can be performed even in the field by any person who is acquainted with the spectrometer operation. Nevertheless, the procedure doesn't replace factory calibration of the instrument, but rather should be used to verify its performances within a periodical inspection and/or when the spectrometer is combined with some new external optical components.

The measured spectral resolution of about 6.5 cm^{-1} allows the miniRaman spectrometers to be used in most known routine and process applications of Raman spectroscopy. In combination with record low mass-size indicators, it makes miniRaman one of the best spectrometers in the hand-held class. Besides, the high adaptability of the miniRaman makes them convenient and inexpensive desk-mounted instruments for undemanding scientific investigation.

LITERATURE

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Harness the power of Raman spectroscopy and make it widely accessible for the benefit of mankind.

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Lightnovo ApS
Blokken 15, 1. tv.
3460 Birkerød
Denmark (DK)
CVR: 40979603
+45 71 37 04 10
info@lightnovo.com
https://lightnovo.com