Date of Issue:
07 January 2022

Standard Reference Material® 2241

Relative Intensity Correction Standard for Raman Spectroscopy: 785 nm Excitation

CERTIFICATE

Purpose: The certified values delivered by this Standard Reference Material (SRM) are intended for the correction of the relative intensity of Raman spectra obtained with instruments employing 785 nm laser excitation.

Description: A unit of SRM 2241 consists of an optical glass slide that emits a broadband luminescence spectrum when excited at a 785 nm laser wavelength, measuring approximately 10 mm in width × 10 mm in length × 1.65 mm in thickness, with one surface optically polished and the opposite surface ground to a frosted finish using a 400 grit polish. SRM 2241 is a chromium-doped (mole fraction of 0.02 % Cr_2O_3) sodium borosilicate matrix glass.

Certified Values: A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or taken into account [1]. The measurements of the relative spectral intensity are traceable to a lamp-illuminated integrating sphere source which has been calibrated for its spectral radiance at NIST. The shape of the mean luminescence spectrum of this glass is described by a mathematical expression that relates the relative spectral intensity to the wavenumber (cm^{-1}) expressed as the Raman shift from the excitation laser wavelength. This model, together with a measurement of the luminescence spectrum of the standard, can be used to determine the spectral intensity-response correction that is unique to each Raman system. The resulting instrument-intensity-response correction may then be used to obtain Raman spectra that are largely free from instrument-induced spectral artifacts. The certified values of the coefficients of the model describing the mean shape of the luminescence spectrum of SRM 2241, excited at 785 nm, are listed in Table 1. The spectrum and its associated expanded uncertainty [± 95 % confidence curves (CC)] are shown in Figure 1 [2,3]. This model is certified to describe the luminescent response of the SRM when it is measured in the temperature range of 20 °C to 25 °C. This model certifies the shape of the luminescence spectrum between 200 cm^{-1} and 3500 cm^{-1} Raman shift for excitation with a 785 nm laser. The measurand is relative luminescence measured as a function of Raman shift (cm^{-1}) from the laser excitation wavelength of 785 nm. Metrological traceability is to the NIST spectral radiance scale.

Period of Validity: The certified values delivered by **SRM 2241** are valid within the measurement uncertainty specified until **31 December 2026**. The certified values are nullified if the material is stored or used improperly, damaged, contaminated, or otherwise modified.

Maintenance of Certified Values: NIST will monitor this SRM to the end of the period of validity. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

Carlos A. Gonzalez, Chief
Chemical Sciences Division

Steven J. Choquette, Director
Office of Reference Materials

Certificate Revision History on Last Page

Certification Uncertainty: The coefficients of the models that express the expanded uncertainty (± 95 % confidence curves) of the certified model of $I_{SRM}(\Delta\upsilon)$ are listed in Table 1. These models are used to calculate the upper and lower 95 % confidence curves for the mean luminescence spectrum of SRM 2241. The upper and lower bounds are shown in Figure 1.

The confidence curves were calculated by applying point-by-point uncertainty analysis to the data from which the certified model was derived [2,3]. The curves represent the uncertainties on the mean luminescence spectrum of SRM 2241 based on measurements using three different spectrometers. Components of the uncertainty include the uncertainty in the calibration source and various estimable systematic errors from the operation of the Raman instruments used in the measurements. Careful measurements of the glass have shown it to be spatially homogeneous in spectral luminescence. No significant changes in the shape of the luminescence spectrum occur over the range of laser power densities commonly used in Raman instruments.

Table 1. Coefficients of the Certified Polynomial and of the 95 % Confidence Curves[(a)]
Describing the Mean Luminescence Spectrum of SRM 2241 for 785 nm excitation.
(Valid for Temperatures of 20 °C to 25 °C)

Polynomial Coefficient	Certified Value Polynomial Coefficient[(b)] 20 °C to 25 °C	Polynomial Coefficient[(b)] of the ± 95 % Confidence Curves[(b)]	
		+95 % CC	–95 % CC
A_0	9.71 937 E–02	1.04 276 E–01	9.01 111 E–02
A_1	2.28 325 E–04	2.39 131 E–04	2.17 519 E–04
A_2	–5.86 762 E–08	–7.81 489 E–08	–3.92 035 E–08
A_3	2.16 023 E–10	2.32 243 E–10	1.99 803 E–10
A_4	–9.77 171 E–14	–1.03 769 E–13	–9.16 653 E–14
A_5	1.15 596 E–17	1.23 774 E–17	1.07 417 E–17

(a) The consensus curve is a point-by-point weighted mean of the average responses of three instruments [4,5], fitted by the polynomial model. The uncertainty curves are polynomial models of point-by-point expanded uncertainties, with coverage factor $k = t_{0.975,2} = 4.303$ (95 % confidence), calculated by combining a between-instrument variance incorporating interinstrumental Type B uncertainties with a pooled within-method variance [3], following the ISO/JCGM Guide [2].

(b) Where $I_{SRM}(\Delta\upsilon) = A_0 + A_1 \times (\Delta\upsilon)^1 + A_2 \times (\Delta\upsilon)^2 + A_3 \times (\Delta\upsilon)^3 + A_4 \times (\Delta\upsilon)^4 + A_5 \times (\Delta\upsilon)^5$,
for $\Delta\upsilon$ = **200 cm^{-1} to 3500 cm^{-1}** Raman Shift relative to 785 nm excitation.
$I_{SRM}(\Delta\upsilon)$ has units of photons s^{-1} (cm^{-2}) $(cm^{-1})^{-1}$.

Measurement Conditions: The certification measurements of the luminescence spectrum of SRM 2241 were made using three spectrometer systems: one commercial Raman microscopy system operated in a 180° backscatter geometry, one Raman system based on 460 mm focal length spectrograph designed for array detectors operated in a 180° backscatter geometry, and one commercial near-IR spectrofluorometer operated in a 90° geometry [6]. Excitation laser wavelength was measured daily using a wavemeter. Excitation laser sources included an argon ion laser pumped titanium:sapphire solid-state tunable laser (785.00 nm ± 0.01 nm) and a frequency-stabilized 785 nm diode laser source (784.98 nm ± 0.02 nm). Either edge or notch Rayleigh rejection filters were used on all systems. The absolute wavenumber or wavelength axis of each spectrometer was calibrated using emission lines from low-pressure pen lamps operated with a DC power supply. The y-axis (relative spectral intensity) of each system was calibrated with a white-light, uniform-source, integrating sphere that had been calibrated for irradiance at NIST or by a high-emissivity blackbody radiator with furnace temperature calibrated by the manufacturer. All certification data were acquired at nominal room temperature (22 °C).

Storage: The glass slide should be handled only in its mount. Although not recommended, the glass standard may be removed from its mount without altering the certified properties of the glass. When not in use, the SRM should be stored in the container provided or in one providing comparable mechanical protection.

Use: SRM 2241 is used to provide Raman spectra corrected for relative intensity and is not intended for use as a standard for the determination of absolute spectral irradiance or radiance. This requires a measurement of its luminescence spectrum on the Raman instrument and then a mathematical treatment of both this observed luminescence spectrum, and the observed Raman spectrum of the sample. This SRM is intended for use in measurements over the temperature range of 20 °C to 25 °C. It may also be used for Raman excitation with lasers that range from 784 nm to 786 nm in excitation wavelength. Use of this SRM at temperatures outside of the certification temperature range is not currently supported.

For proper use of this procedure, attention must be paid to the following experimental conditions. The spectrometer laser and x-axis should be calibrated using the manufacturer's recommended methods. Validation of the Raman shift axis may be accomplished by referring to ASTM E1840-96 [7]. It is important that the laser excitation be incident only on the frosted surface of the glass. The shape of the spectral luminescence will have some sensitivity to the placement of the glass surface relative to the collection optics of the spectrometer, which is minimized by scattering from the frosted surface. Measurement conditions should be arranged to furnish a spectrum of optimum signal-to-noise ratio of the SRM. The luminescence spectrum must be acquired over the same Raman range as that of the sample.

The relative intensity of the measured Raman spectrum of the sample can be corrected for the instrument-specific response by a computational procedure that uses a correction curve. This curve is generated using the certified model and the measured luminescence spectrum of the SRM glass. For the spectral range of certification, $\Delta\upsilon = 200\ \mathrm{cm^{-1}}$ to $3500\ \mathrm{cm^{-1}}$, compute the elements of the certified relative mean spectral intensity of SRM 2241, $I_{SRM}(\Delta\upsilon)$, according to equation (1)

$$I_{SRM}(\Delta\upsilon) = A_0 + A_1 \times (\Delta\upsilon)^1 + A_2 \times (\Delta\upsilon)^2 + A_3 \times (\Delta\upsilon)^3 + A_4 \times (\Delta\upsilon)^4 + A_5 \times (\Delta\upsilon)^5 \quad (1)$$

where $(\Delta\upsilon)$ is the wavenumber in units of Raman shift ($\mathrm{cm^{-1}}$) and the A_n's are the coefficients listed in Table 1. The elements of $I_{SRM}(\Delta\upsilon)$ are obtained by evaluating equation (1) at the same data point spacing used for the acquisition of the luminescence spectrum of the SRM and of the Raman spectrum of the sample. $I_{SRM}(\Delta\upsilon)$ has been normalized to unity and is a relative unit expressed in terms of photons $\mathrm{s^{-1}\ cm^{-2}\ (cm^{-1})^{-1}}$. The data sets that are the measured glass luminescence spectrum, S_{SRM}, and the measured Raman spectrum of the sample, S_{MEAS}, must have the units of Raman shift ($\mathrm{cm^{-1}}$). The elements of the correction curve $I_{CORR}(\Delta\upsilon)$, defined by equation (2), are obtained from $I_{SRM}(\Delta\upsilon)$ and the elements of the glass luminescence spectrum, $S_{SRM}(\Delta\upsilon)$, by

$$I_{CORR}(\Delta\upsilon) = I_{SRM}(\Delta\upsilon) / S_{SRM}(\Delta\upsilon). \quad (2)$$

The elements of the intensity-corrected Raman spectrum, $S_{CORR}(\Delta\upsilon)$, are derived by multiplication of the elements of the measured Raman spectrum of the sample, $S_{MEAS}(\Delta\upsilon)$, by the elements of the correction curve [8]

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

The certified model, equation (1), is certified for use **between 200 $\mathrm{cm^{-1}}$ and 3500 $\mathrm{cm^{-1}}$**. The certified model is intended as a simple numerical descriptor of the spectral response observed over the wavenumber range studied. It is not intended as a physically meaningful model. **The model coefficients listed in Table 1 cannot be used to extrapolate the limits of certification without incurring significant error. Extrapolation of the model outside the certification limits of 200 $\mathrm{cm^{-1}}$ and 3500 $\mathrm{cm^{-1}}$ is not a supported use of this SRM**.

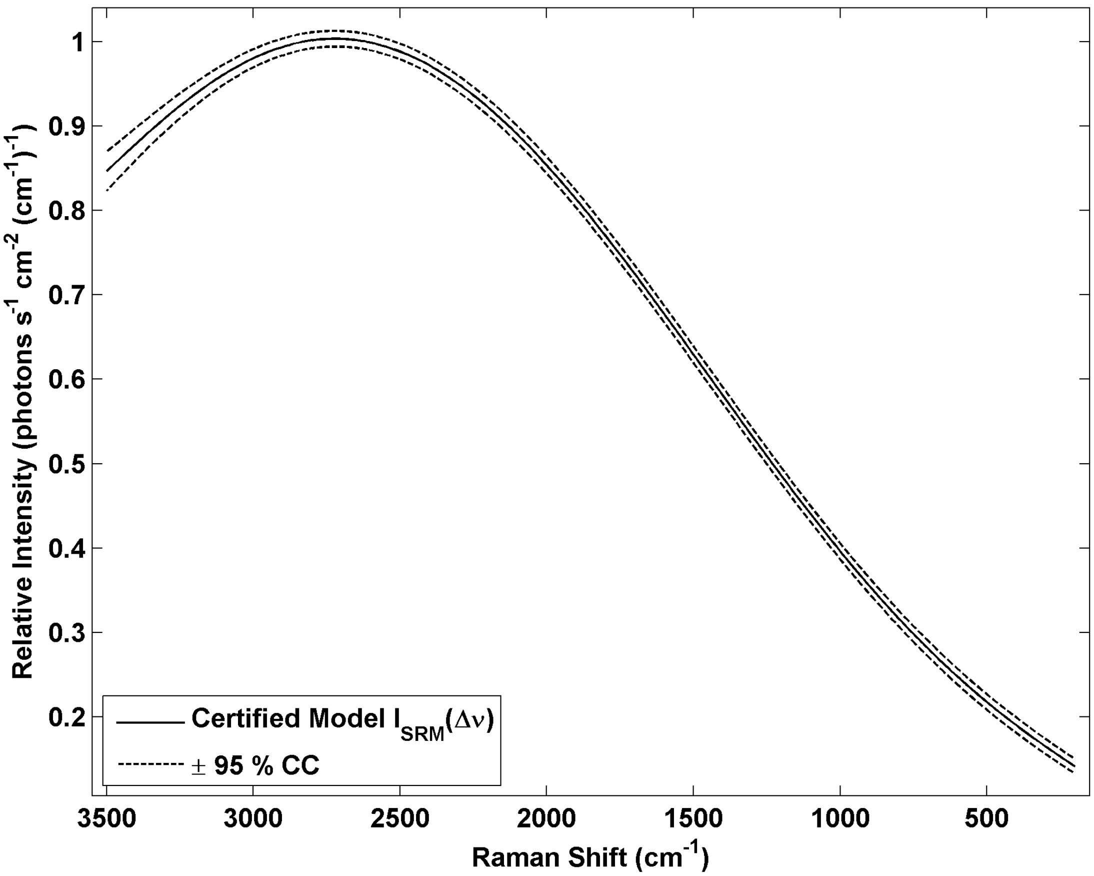
Luminescence Spectrum on the Wavelength Scale: The equation describing the mean luminescence spectrum of the glass SRM is given in equation (1), where $(\Delta\upsilon)$ is the wavenumber in units of Raman shift ($\mathrm{cm^{-1}}$). For correction of spectra where the x-axis is in wavelength with units of nanometers, the same model coefficients can be used to calculate $I_{SRM}(\lambda)$ through the following coordinate transformation:

$$I_{SRM}(\lambda) = [10^7/\lambda^2] \times [A_0 + A_1 \times Z^1 + A_2 \times Z^2 + A_3 \times Z^3 + A_4 \times Z^4 + A_5 \times Z^5] \quad (4)$$

where

$$Z = 10^7 \times [(1.0/\lambda_L) - (1.0/\lambda)] \quad (5)$$

and λ_L is the wavelength of the laser in nanometers and λ is the wavelength in nanometers. The prefactor of 10^7 in the first term of equation (4) is needed only if it is desired to preserve the numerical value of spectral areas computed relative to the two x-axis coordinate systems.



REFERENCES

[1] Beauchamp, C.R.; Camara, J.E.; Carney, J.; Choquette, S.J.; Cole, K.D.; DeRose, P.C.; Duewer, D.L.; Epstein, M.S.; Kline, M.C.; Lippa, K.A.; Lucon, E.; Molloy, J.; Nelson, M.A.; Phinney, K.W.; Polakoski, M.; Possolo, A.; Sander, L.C.; Schiel, J.E.; Sharpless, K.E.; Toman, B.; Winchester, M.R.; Windover, D.; *Metrological Tools for the Reference Materials and Reference Instruments of the NIST Material Measurement Laboratory*; NIST Special Publication (NIST SP) 260-136, 2021 edition; U.S. Government Printing Office: Washington, DC (2021); available at https://nvlpubs.nist.gov/nistpubs/SpecialPublications/NIST.SP.260-136-2021.pdf (accessed Jan 2022).

[2] JCGM 100:2008; *Evaluation of Measurement Data — Guide to the Expression of Uncertainty in Measurement* (GUM 1995 with Minor Corrections); Joint Committee for Guides in Metrology (2008); available at https://www.bipm.org/en/publications/guides (accessed Jan 2022); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; U.S. Government Printing Office: Washington, DC (1994); available at https://www.nist.gov/pml/nist-technical-note-1297 (accessed Jan 2022).

[3] Horn, S.D.; Horn, R.A.; Duncan, D.B.; *Estimating Heteroscedastic Variances in Linear Models*; J. Am. Stat. Assoc., Vol. 70(350), pp. 380–385 (1975).

[4] Rukhin, A.L.; *Weighted Means Statistics in Interlaboratory Studies*; Metrologia, Vol. 46, pp. 323–331 (2009).

[5] DerSimonian, R.; Laird, N.; *Meta-Analysis in Clinical Trials*; Control. Clin. Trials, Vol. 7(3), pp. 177–188 (1986).

[6] Choquette, S.J.; Etz, E.S.; Hurst, W.S.; Blackburn, D.H.; Leigh, S.D.; *Relative Intensity Correction of Raman Spectrometers: NIST SRMs 2241 Through 2243 for 785 nm, 532 nm, and 488 nm/514.5 nm Excitation*; Appl. Spectrosc., Vol. 61, pp. 117–129 (2007).

[7] ASTM E1840–96, *Standard Guide for Raman Shift Standards for Spectrometer Calibration*; Annu. Book ASTM Stand., Vol. 03.06 (2007).
[8] Frost, K.J.; McCreery, R.L.; *Calibration of Raman Spectrometer Response Function with Luminescence Standards: An Update*; Appl. Spectrosc., Vol. 52(12), pp. 1614–1618 (1998).

Certificate Revision History: 07 January 2022 (Change of expiration date; updated certificate format; editorial changes) **17 November 2020** (Update to physical description; editorial changes); **30 July 2020** (Change of expiration date; editorial changes); **24 August 2015** (Change of expiration date; editorial changes); **28 February 2014** (Update of storage information; editorial changes); **02 December 2010** (SRM 2241 Recertification; extension of certification period; editorial changes); **30 May 2008** (Extension of certification period); **08 May 2007** (Update of expiration date); **27 June 2002** (Original certificate date).

* * * * * * * * * * ** * * End of Certificate * * * * * * * * * * ** * *