

Standard Reference Material® 2246a

Relative Intensity Correction Standard for Raman Spectroscopy: 830 nm Excitation

CERTIFICATE

Purpose: The certified values delivered by this Standard Reference Material (SRM) are for the correction of the relative intensity of Raman spectra obtained with instruments employing 830 nm continuous wave laser excitation.

Description: SRM 2246a is a chromium oxide doped (0.30 % mole fraction) borosilicate glass that emits a broadband luminescence spectrum when excited at 830 nm. A unit of this SRM consists of a glass slide that is 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. The glass slide is mounted in a 2.5 cm × 7.6 cm × 0.3 cm microscope slide-style holder. On the top face is a rectangular slot to retain the glass slide over a circular aperture in the center of the holder. Two plastic springs serve to hold the glass slide in the slot centered over the circular aperture. Removal of the SRM glass for measurements that are physically hindered by the holders does not alter the certified properties of this SRM.

Certified Values: The certified value [1] of SRM 2246a is relative spectral luminescence measured as a function of Raman shift (cm⁻¹) from the laser excitation wavelength of 830 nm modeled by a linearly shifted lognormal function. Metrological traceability is to the NIST spectral irradiance scale [2].

Table 1. Coefficients of the certified (CERT), linearly shifted lognormal model^(a,b) that describes the mean luminescence spectrum of SRM 2246a for 830 nm excitation, and coefficients of the analytical approximations (with the same functional form as the model itself) to the upper and lower envelopes of the 95 % confidence (L_{CONF} , U_{CONF}) bands depicted in Figure 1 (includes the results of the Type A and Type B evaluations of uncertainty)

	L_{CONF}	CERT	U_{CONF}
H	1.0142 E +00	1.0178 E +00	1.0213 E +00
w	3.0919 E +03	3.0823 E +03	3.0729 E +03
ρ	9.8303 E -01	9.8252 E -01	9.8201 E -01
x_0	2.3537 E +03	2.3531 E +03	2.3526 E +03
m	-4.3629 E -07	-1.1825 E -07	2.0664 E -07
b	-3.5124 E -02	-1.7500 E -02	9.3692 E -05

^(a) The consensus (CERT) curve coefficients are for an unweighted lognormal model fit to the response data from three data sets. The uncertainty curve coefficients (CONF) are for lognormal model fits to 95 % confidence band expanded uncertainties, combining uncertainty components evaluated by Type A and Type B methods, with a coverage factor of $k = 2$, following the ISO/JCGM Guide [3].

^(b) Where $I_{SRM}(\Delta\nu) = H \cdot e^{\left[\frac{-\ln 2}{(\ln \rho)^2} \left(\ln \left[\frac{(\Delta\nu - x_0)(\rho^2 - 1)}{w \cdot \rho} + 1 \right] \right)^2 \right]} + m \cdot \Delta\nu + b$;

for $\Delta\nu = 110 \text{ cm}^{-1}$ to 3000 cm^{-1} Raman Shift relative to 830 nm excitation.

$I_{SRM}(\Delta\nu)$ is a ratio expressed as (photons per wavenumber)/(spectral maximum photons per wavenumber).

Period of Validity: The certified values delivered by **SRM 2246a** are valid within the measurement uncertainty specified until 31 January 2034. 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 over the period of its validity. If substantive technical changes occur that affect the certification, NIST will issue an amended certificate through the NIST SRM website (<https://www.nist.gov/srm>) and notify registered users. SRM users can register online from a link available on the NIST SRM website or fill out the user registration form that is supplied with the SRM. Registration will facilitate notification. Before making use of any of the values delivered by this material, users should verify they have the most recent version of this documentation, available through the NIST SRM website (<https://www.nist.gov/srm>).

The certified values of the coefficients of the model describing the mean shape of the luminescence spectrum of SRM 2246a, excited at 830 nm, are listed in Table 1. The dependent variable of this model is the relative spectral intensity of the luminescence. The independent variable of this model is the wavenumber expressed in units of Raman shift (cm^{-1}) from a laser excitation wavelength of 830 nm. This model is certified to describe the shape of the luminescence spectrum between 110 cm^{-1} and 3000 cm^{-1} Raman shift for excitation with an 830 nm laser when the SRM is measured in the temperature range of 20°C to 25°C . The spectrum and its associated expanded uncertainty bands (for 95 % coverage probability) are shown in Figure 1. The expanded uncertainties include contributions from short term repeatability, batch uniformity, temperature dependence within the certified temperature range, and inter-instrument variability. See “Laser Power Density Warning” section below for additional information on excitation laser power.

The certified model of SRM 2246a was determined via careful comparison to the original issue of SRM 2246. The relative luminescence spectrum of SRM 2246 was determined using a white light, uniform source, integrating sphere that was calibrated for its irradiance at NIST and a high emissivity black body radiator with furnace temperature calibrated by the manufacturer.

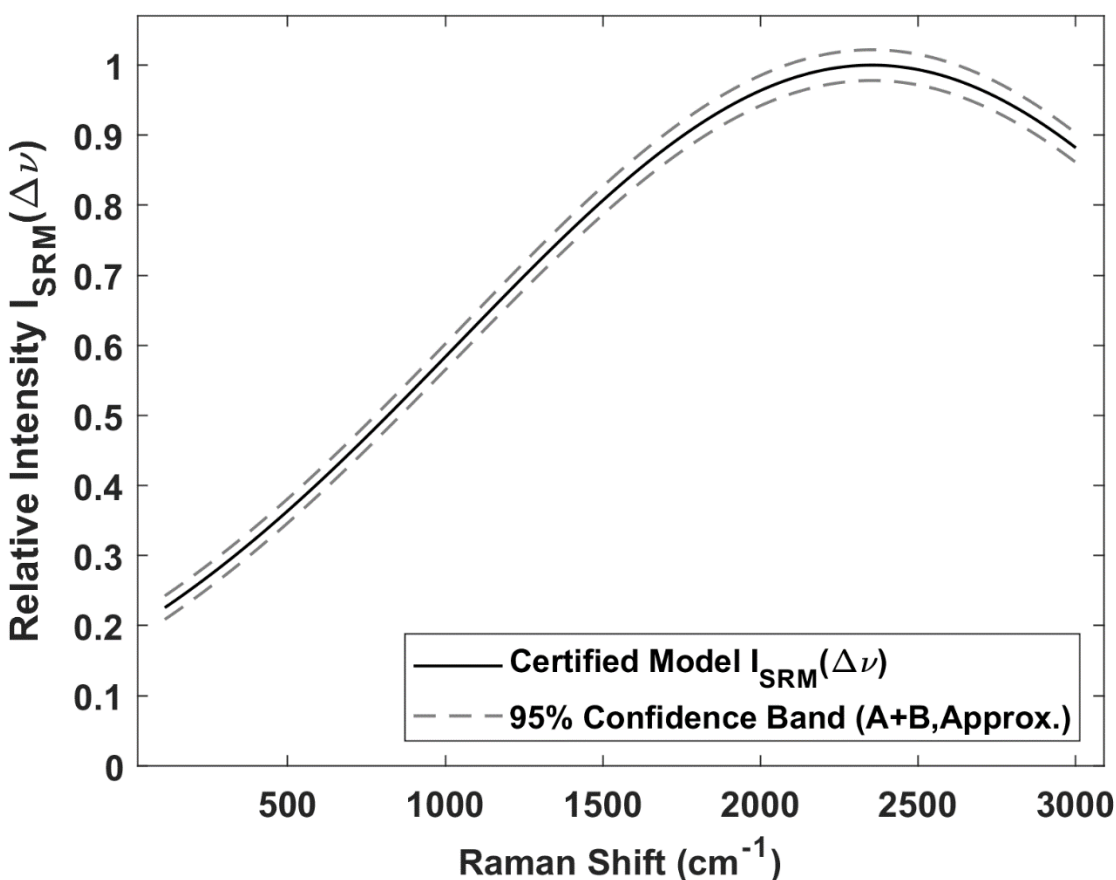


Figure 1. Certified SRM 2246a lognormal model and associated 95% confidence bands.

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

Use: SRM 2246a is used to provide Raman spectra corrected for relative intensity. 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 in the temperature range of 20 °C to 25 °C. This SRM has only been tested under continuous wave laser excitation and use of pulsed lasers is not supported. **See “Laser Power Density Warning” section below for additional information on excitation laser power.** Additional guidance and considerations for the use of SRM 2246a and other SRMs in the 224X series can be found in ASTM E2911-23 [4].

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 [5]. For certification, SRM 2246a is measured in a 180° backscatter measurement configuration with the laser excitation and emission collection system focused on the frosted surface of the glass. Illumination of the frosted surface of the glass is recommended but measurements on the polished face of the SRM may yield more reproducible results on some instruments. Back reflections of the excitation laser into the optical system may cause more issues (e.g. increase in observed Rayleigh laser line intensity) with measurements on the polished surface. Alternatively, smaller focal spot sizes on the surface of the frosted face of the SRM (e.g. in a microscope-based Raman system) can give rise to reproducibility issues in the measured spectrum. The effect of laser spot size and focal point relative to the SRM surface have not been extensively studied outside of investigating reproducibility with focused excitation directly on the frosted and polished faces of SRM units with 5X-50X objectives on a micro-Raman system. In these studies, variability in the profile of measured spectra from different locations increased with increasing objective magnification on the frosted face. These effects were reduced to a large extent when the frosted face was out of focus or when illuminating the polished face of the SRM. 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. Users are encouraged to investigate these effects on their instrumentation to ensure the SRM can be measured in a reproducible manner. 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, $\Delta\nu = 110 \text{ cm}^{-1}$ to 3000 cm^{-1} , compute the elements of the certified relative mean spectral intensity of SRM 2246a, $I_{\text{SRM}}(\Delta\nu)$, according to

$$I_{\text{SRM}}(\Delta\nu) = H \cdot e^{\left[\frac{-\ln 2}{(\ln \rho)^2} \left(\ln \left[\frac{(\Delta\nu - x_0)(\rho^2 - 1)}{w \cdot \rho} + 1 \right] \right)^2 \right]} + m \cdot \Delta\nu + b \quad (1)$$

where $(\Delta\nu)$ is the wavenumber in units of Raman shift (cm^{-1}), H is peak height, w is peak width, ρ is half width ratio, x_0 is a location parameter for the lognormal profile, while m and b are the slope and intercept terms, respectively, for the linear term, with values as listed in Table 1. The elements of $I_{\text{SRM}}(\Delta\nu)$ 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. $I_{\text{SRM}}(\Delta\nu)$ has been normalized to unity and is a ratio expressed as (photons per wavenumber)/(spectral maximum photons per wavenumber). The data sets that are the measured glass luminescence spectrum, $S_{\text{SRM}}(\Delta\nu)$, and the measured Raman spectrum of the sample, $S_{\text{MEAS}}(\Delta\nu)$, which must have the units of Raman shift (cm^{-1}). The elements of the correction curve $I_{\text{CORR}}(\Delta\nu)$, defined by Equation 2, are obtained from $I_{\text{SRM}}(\Delta\nu)$ and the elements of the glass luminescence spectrum, $S_{\text{SRM}}(\Delta\nu)$, by

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

The elements of the intensity-corrected Raman spectrum, $S_{\text{CORR}}(\Delta\nu)$, are derived by multiplication of the elements of the measured Raman spectrum of the sample, $S_{\text{MEAS}}(\Delta\nu)$, by the elements of the correction curve [7]

$$S_{\text{CORR}}(\Delta\nu) = S_{\text{MEAS}}(\Delta\nu) \cdot I_{\text{CORR}}(\Delta\nu). \quad (3)$$

The Table 1 coefficients are **certified for use between 110 cm^{-1} and 3000 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 claimed to be physically meaningful. **Extrapolation of the model outside the certification limits of 110 cm^{-1} and 3000 cm^{-1} is not a supported use of this SRM.** However, the model coefficients listed in Table 1 were fit to data spanning the Raman shift range from 60 cm^{-1} to 3750 cm^{-1} .

Use of this SRM at temperatures outside the certification temperature range of 20 °C to 25 °C is not currently supported.

This SRM is not intended for use as a standard for the determination of absolute spectral irradiance or radiance.

This SRM was shown to be photostable under extended exposure to approximately 50 mW of 830 nm laser light focused through a 50X magnification microscope objective. **See “*Laser Power Density Warning*” section below for more information.**

Luminescence Spectrum on the Wavelength Scale: The equation describing the mean luminescence spectrum of the glass SRM is given in Equation 1, where $\Delta\nu$ is the Raman shift in units of wavenumbers (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 $I_{\text{SRM}}(\lambda)$ through the following transformation:

$$I_{\text{SRM}}(\lambda) = \left[\frac{10^7}{\lambda^2} \right] \cdot \left(H \cdot e^{\left[\frac{-\ln 2}{(\ln \rho)^2} \left(\ln \left[\frac{(z-x_0)(\rho^2-1)}{w \cdot \rho} + 1 \right] \right)^2 \right]} + m \cdot z + b \right) \quad (4)$$

where

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

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 required only if it is desired to preserve the numerical value of spectral areas computed relative to the two x-axis coordinate systems.

Laser Power Density Warning: The luminescence from SRM 2246a exhibits a temperature dependence that manifests as a hypsochromic (blue) shift and reduction in absolute intensity of the emission with increasing temperature. Laser illumination has been shown to affect a temperature increase in the glass that is evidenced by this behavior. The effect is reversible and has been found to depend on both the laser power density and illumination spot size. Users of SRM 2246a are strongly encouraged to investigate the impacts on the measured spectrum of this SRM at different laser power settings on their instrumentation and determine suitable measurement conditions for their application. The laser power used should be at a level below the point when perturbations are detectable or, alternatively, below a user specified tolerance. For reference, investigations during the certification of SRM 2246a found that no perturbations were observed in the following two measurement scenarios, (1) below 6 mW with an approximately 250 μm focal spot size, and (2) below 1.5 mW with an approximately 5 μm focal spot size. Neither of these scenarios involved evaluation on a microscope-based Raman system or with confocal spatial filtering of the collected emission.

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 260-136, 2021 edition; National Institute of Standards and Technology, Gaithersburg, MD (2021); available at <https://nvlpubs.nist.gov/nistpubs/SpecialPublications/NIST.SP.260-136-2021.pdf> (accessed Mar 2024).
- [2] Yoon, H. and Gibson, C. (2011), *SP250 Spectral Irradiance Calibrations*, NIST Special Publication 260-244; National Institute of Standards and Technology, Gaithersburg, MD, (2024); available at <https://doi.org/10.6028/NIST.SP.250-89> (accessed Mar 2024).
- [3] 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 (JCGM) (2008); available at <https://www.bipm.org/en/committees/jc/jcgm/publications> (accessed Mar 2024); 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 Mar 2024).
- [4] ASTM E2911-23; *Standard Guide for Relative Intensity Correction of Raman Spectrometers*; ASTM International, West Conshohocken, PA (2023).
- [5] ASTM E1840-96(2022); *Standard Guide for Raman Shift Standards for Spectrometer Calibration*; ASTM International, West Conshohocken, PA (2022).

- [6] Urbas, A.; Gierz, K.; Leber, D. *Certification of Standard Reference Material® 2246a Relative Intensity Correction Standard for Raman Spectroscopy: 830 nm Excitation*; NIST Special Publication 260-244; National Institute of Standards and Technology, Gaithersburg, MD, (2024); available at <https://nvlpubs.nist.gov/nistpubs/SpecialPublications/NIST.SP.260-244.pdf> (accessed Mar 2024).

If you use this SRM in published work, please reference:

Urbas A, Gierz K, Leber, D (2024) Certification of Standard Reference Material® 2246a Relative Intensity Correction Standard for Raman Spectroscopy: 830 nm Excitation. (National Institute of Standards and Technology, Gaithersburg, MD), NIST Special Publication (SP) 260-244. <https://doi.org/10.6028/NIST.SP.260-244>

Certain commercial equipment, instruments, or materials may be identified in this Certificate to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Users of this SRM should ensure that the Certificate in their possession is current. This can be accomplished by contacting the Office of Reference Materials 100 Bureau Drive, Stop 2300, Gaithersburg, MD 20899-2300; telephone (301) 975-2200; e-mail srminfo@nist.gov; or the Internet at <https://www.nist.gov/srm>.

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APPENDIX A

Measurement Conditions: The certification measurements of the luminescence spectrum of SRM 2246a were made using purpose-built Raman spectrometer system based on a 320 mm focal-length spectrograph designed for array detectors operated in a 180° backscatter geometry. The excitation laser source was a frequency-stabilized 830 nm diode laser source (830.0 nm). Longpass edge filters were utilized for Rayleigh rejection. The absolute wavenumber axis of each spectrometer was calibrated using emission lines from low-pressure pen lamps operated with DC power supplies. The y-axis (relative spectral response) of the spectrometer system was calibrated via measurements of multiple SRM 2246 units measured under identical conditions and concurrently with multiple SRM 2246a units. All certification data were acquired at nominal room temperature (approximately 22 °C) or with SRM units held at a controlled temperature of 22.5 °C.

Traceability: $I_{\text{SRM}}(\Delta\nu)$ is a ratio expressed as (photons per wavenumber)/(spectral maximum photons per wavenumber). The relative luminescence spectrum is traceable to the NIST spectral radiance scale through comparison measurements to SRM 2246. The relative luminescence spectrum of SRM 2246 was calibrated using a white-light, uniform, integrating sphere source that had been calibrated for irradiance at NIST and a high emissivity black body radiator with furnace temperature calibrated by the manufacturer. Metrological traceability is to the NIST spectral radiance scale [2].

Determination of Expanded Uncertainties: The combined standard measurement uncertainty comprises one set of components evaluated by application of statistical methods (Type A evaluation) and one set of components evaluated by other methods (Type B evaluation), combined in root sum of squares.

The Type A uncertainties include contributions attributable to repeatability of measurements conducted during the certification process and contributions from uncontrolled experimental factors, all of which find expression in the dispersion of the values of luminescent intensity that were obtained experimentally. The Type B uncertainties includes contributions from measured batch uniformity, temperature dependence within the certified temperature range (20 °C to 25 °C), inter-instrument variability assessed from the certification data of the original SRM 2246 release, and from uncertainty in the irradiance calibration of the integrating sphere used in the certification of SRM 2246. A more thorough characterization of the uncertainty associated with this curve will have to take into account not only the standard uncertainties of its coefficients, but also the correlations between them. Both are captured in Table 6 of reference 6, whose section 6.2.7 explains how such uncertainty can be propagated to quantities derived from the spectrum, in applications of this reference material where such propagation is called for.

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