



National Institute of Standards & Technology

Certificate

Standard Reference Material[®] 2244

Relative Intensity Correction Standard for Raman Spectroscopy: 1064 nm Excitation

This Standard Reference Material (SRM) is a certified spectroscopic standard for the correction of the relative intensity of Raman spectra obtained with instruments employing 1064 nm laser excitation. SRM 2244 consists of an optical glass that emits a broadband luminescence spectrum when excited at this laser wavelength. The relative spectral intensity of the glass luminescence has been determined through the use of a white-light, uniform-source, integrating sphere that has been calibrated for its irradiance at NIST and a high-emissivity blackbody source. 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 polynomial, 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.

This SRM is the fourth in a series of SRMs (2241, 2242, 2243) that provide relative intensity corrections for Raman spectrometers employing lasers commonly used for Raman spectroscopy. This SRM is intended for use in measurements over the temperature range of 20 °C to 25 °C.

Certification: The polynomials describing the mean relative luminescence spectrum of SRM 2244 and associated confidence curves are given in Table 1.

Expiration of Certification: The certification of **SRM 2244** is valid, within the measurement uncertainty specified, until **01 February 2015**, provided the SRM is handled in accordance with instructions given in this certificate (see "Instructions for Use"). The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

Production and certification of this SRM were performed by S.J. Choquette, A. Urbas, and D.H. Blackburn of the NIST Biochemical Science Division.

The SRM units were cut and polished by J. Fuller of the NIST Fabrication Technology Division.

Statistical consultation was provided by S.D. Leigh of the NIST Statistical Engineering Division.

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Support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

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Table 1. Coefficients of the Certified Polynomial^(a) and of the Relative $\pm 2\sigma$ Confidence Curves^(b) Describing the Mean Luminescence Spectrum of SRM 2244 for 1064 nm excitation. (Valid for Temperatures of 20 °C to 25 °C)

Polynomial Coefficient	Certified Value Polynomial Coefficient ^(c) 20 °C to 25 °C	Polynomial Coefficient ^(c) of the $\pm 2\sigma$ Confidence Curves ^(b)	
		+ 2 σ CC	- 2 σ CC
A ₀	0.405953	0.436911	0.374995
A ₁	5.20345E-04	5.58855E-04	4.81831E-04
A ₂	5.30390E-07	3.66027E-07	6.94759E-07
A ₃	-6.84463E-10	-5.33614E-10	-8.35316E-10
A ₄	2.10286E-13	1.59882E-13	2.60690E-13
A ₅	-2.05741E-17	-1.49463E-17	-2.62019E-17

- ^(a) A NIST certified value represents a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been fully investigated or taken into account [1].
- ^(b) The confidence curves were calculated point-by-point using the uncertainty analysis of [3].
- ^(c) Where $I_{\text{SRM}}(\Delta\nu) = A_0 + A_1 \times (\Delta\nu)^1 + A_2 \times (\Delta\nu)^2 + A_3 \times (\Delta\nu)^3 + A_4 \times (\Delta\nu)^4 + A_5 \times (\Delta\nu)^5$; for $\Delta\nu = 100 \text{ cm}^{-1}$ to 3500 cm^{-1} Raman Shift relative to 1064 nm excitation. $I_{\text{SRM}}(\Delta\nu)$ has units of photons $\text{s}^{-1} (\text{cm}^{-2})(\text{cm}^{-1})^{-1}$

Certified Values: A NIST certified value [1] is a value for which NIST has the highest confidence in its accuracy to the extent that all known or suspected sources of bias have been fully investigated or taken into account. The certified values of the coefficients of the fifth-order polynomial describing the mean shape of the luminescence spectrum of SRM 2244, excited at $\approx 1064 \text{ nm}$ (exact value in absolute cm^{-1} will depend upon the system laser), are listed in Table 1. The spectrum and its associated expanded uncertainty [2] ($\pm 2\sigma$ confidence curves (CC)) are shown in Figure 1. The dependent variable of this polynomial expression is the relative spectral intensity of the luminescence. The independent variable of this polynomial is the wavenumber expressed in units of Raman shift (cm^{-1}) from the laser excitation wavelength of 1064 nm. This polynomial 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 polynomial certifies the shape of the luminescence spectrum between 100 cm^{-1} and 3500 cm^{-1} Raman shift for excitation with a 1064 nm laser.

Certification Uncertainty: The coefficients of the polynomials that express the expanded uncertainty ($\pm 2\sigma$ confidence curves) of the certified polynomial of $I_{\text{SRM}}(\Delta\nu)$ are listed in Table 1. These polynomial expressions are used to calculate the upper and lower 95 % confidence curves for the mean luminescence spectrum of SRM 2244. These upper and lower bounds are shown in Figure 1.

The confidence curves were calculated by applying the point-by-point uncertainty analysis of [3] to the data from which the certified polynomial was derived. The curves represent the uncertainties on the mean luminescence spectrum of SRM 2244 based on measurements using two different spectrometers. Components of the uncertainty include the uncertainty in the white-light, uniform-source, integrating sphere irradiance calibration and various 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.

Physical Description: SRM 2244 is a chromium-doped (mass fraction 0.7 % Cr_2O_3) oxide in a borosilicate matrix glass. Each unit of this SRM consists of a glass slide that is approximately 10.7 mm in width \times 30.4 mm in length \times 2.0 mm in thickness, with one surface optically polished and the opposite surface ground to a frosted finish using a 400 grit polish. The frosted surface of the slide is characterized by a surface average roughness (root-mean-square) in the range of 1.30 μm to 1.49 μm , as determined by stylus profilometry [4]. The slide is held in a 12.5 mm square cuvette-style optical mount. This mount is designed for the typical 12.5 mm sampling accessories

widely used in chemical spectroscopy, i.e., absorbance, fluorescence, etc. This mount can easily be placed on its side for use on a microscope stage. The mount holds the glass slide, frosted side up, in place with a clip. The glass slide extends approximately 0.3 mm above the sides of the mount to allow its use with close-focus objectives. Removal of the SRM glass for measurements that are physically hindered by its protective holder do not alter the certified properties of this SRM.

Measurement Conditions: The certification measurements of the luminescence spectrum of SRM 2244 were made using two commercially available FT-Raman spectrometers. Each had its own dedicated Nd:YAG laser, utilized Si:CaF₂ beamsplitters, liquid nitrogen cooled germanium detectors, and proprietary beamsplitters. One system utilized a Rayleigh rejection filter that enabled measurement of the anti-Stokes spectra to -1000 cm^{-1} relative. The other spectrometer utilized a cutoff filter. The common spectral range for certification was 100 cm^{-1} to 3500 cm^{-1} Raman shift. All Raman systems were operated in a 180° backscattering geometry. The absolute wavenumber axis of each spectrometer was calibrated using water vapor bands and validated with neon emission lines from a low-pressure pen lamp 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. For comparison, a high-emissivity (0.995) blackbody radiator was used at three temperatures ($950\text{ }^\circ\text{C}$, $1050\text{ }^\circ\text{C}$, and $1100\text{ }^\circ\text{C}$) and its spectral irradiance calculated using Planck's distribution [5]. The data were acquired at 4 cm^{-1} spectral resolution. All certification data were acquired at nominal room temperature ($21^\circ\text{C} \pm 1^\circ\text{C}$).

INSTRUCTIONS FOR USE

SRM 2244 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.

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 [6]. 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 polynomial and the measured luminescence spectrum of the SRM glass. For the spectral range of certification, $\Delta\nu = 100\text{ cm}^{-1}$ to 3500 cm^{-1} , compute the elements of the certified relative mean spectral intensity of SRM 2244, $I_{\text{SRM}}(\Delta\nu)$, according to eq. 1

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

where $(\Delta\nu)$ is the wavenumber in units of Raman shift (cm^{-1}) and the A_n 's are the coefficients listed in Table 1. The elements of $I_{\text{SRM}}(\Delta\nu)$ are obtained by evaluating eq. 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 relative unit expressed in terms of photons $\text{s}^{-1}\text{cm}^{-2}(\text{cm}^{-1})^{-1}$. 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 (cm^{-1}). The elements of the correction curve $I_{\text{CORR}}(\Delta\nu)$, defined by eq 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]

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

The polynomial expression, eq 1, is certified for use **between 100 cm⁻¹ and 3500 cm⁻¹**. This is the spectral range common to the two instruments used for the certification. The polynomial fits are intended as simple numerical descriptors of the spectral response observed over the wavenumber range studied. They are not intended as physically meaningful models. **The polynomial coefficients listed in Table 1 can not be used to extrapolate the limits of certification without incurring significant error. Extrapolation of the polynomial outside the certification limits of 100 cm⁻¹ and 3500 cm⁻¹ is not a supported use of this SRM.**

Use of this SRM at temperatures other than the certification temperature is not currently supported.

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

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

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

$$I_{\text{SRM}}(\lambda) = [10^7/\lambda^2] \times [A_0 + A_1 \times Z^1 + A_2 \times Z^2 + A_3 \times Z^3 + A_4 \times Z^4 + A_5 \times Z^5] \quad (6)$$

where

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

and λ_L is the wavelength of the laser in nm and λ is the wavelength in nanometers. The prefactor of 10^7 in the first term of eq. 6 and eq. 7 is needed only if it is desired to preserve the numerical value of spectral areas computed relative to the two x-axis coordinate systems.

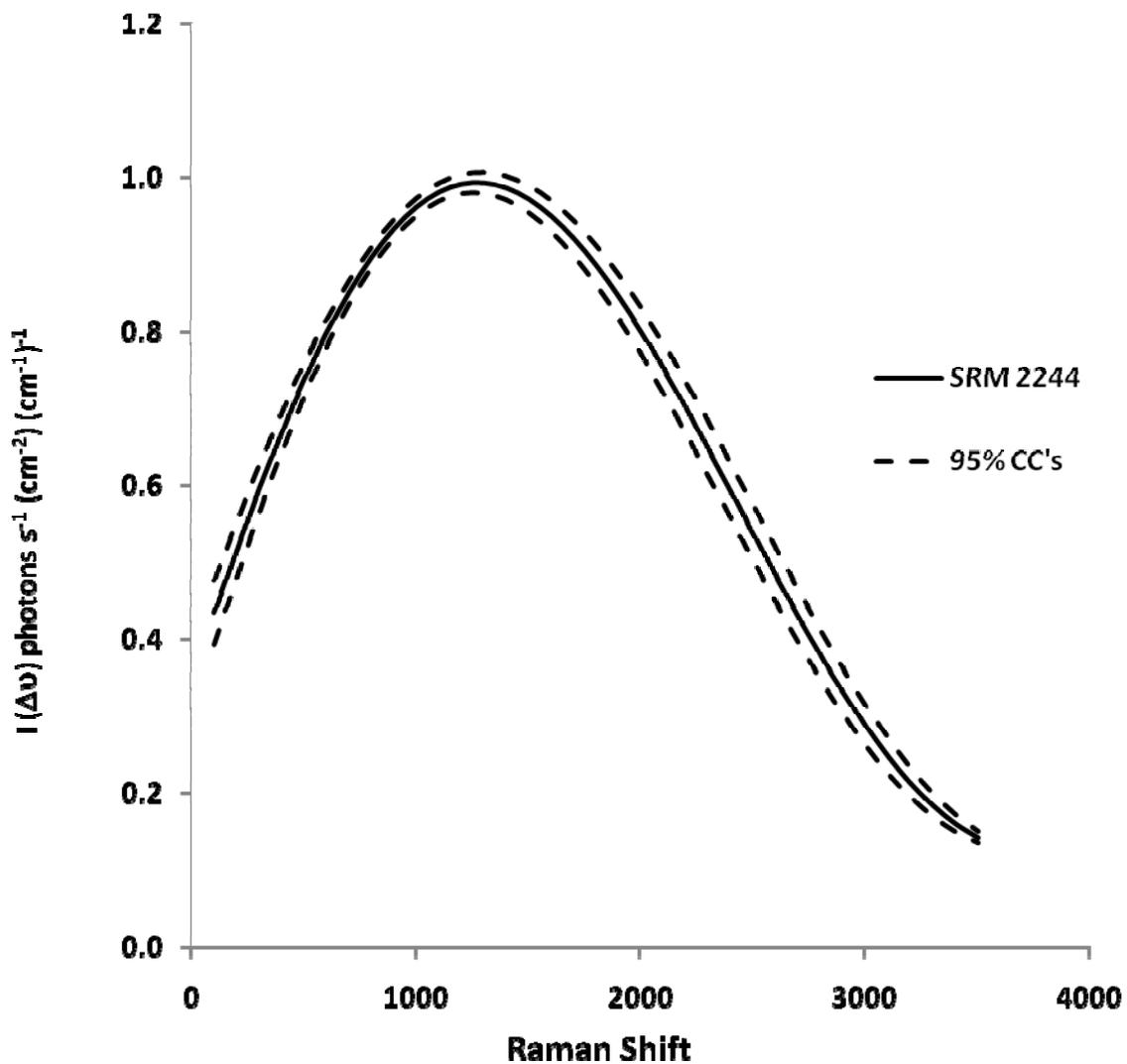


Figure 1. Fifth-order certified polynomial for SRM 2244 when excited at 1064 nm. The x-axis is expressed in Raman shift (cm⁻¹). The y-axis is on a relative scale and normalized to unity with the dimensions of photons s⁻¹ cm⁻² (cm⁻¹)⁻¹. Dashed lines denote 95% confidence curves.

REFERENCES

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- [7] Frost, K.J.; McCreery, R.L.; *Calibration of Raman Spectrometer Response Function with Luminescence Standards: An Update*; Appl. Spectrosc., Vol. 52, Number 12, pp. 1614-1618 (1998).
- [8] Additional information regarding this SRM may be obtained by contacting Steven Choquette at Steven.Choquette@nist.gov, 301-975-3096, NIST, Gaithersburg, MD 20899-8312.

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-2200; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet at <http://www.nist.gov/srm>.