National Institute of Standards & Technology

Certificate

Standard Reference Material® 2242a

Relative Intensity Correction Standard for Raman Spectroscopy: 532 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 532 nm laser excitation. A unit of SRM 2242a consists of an optical glass slide that emits a broadband luminescence spectrum when excited at 532 nm. This SRM is approximately 10 mm in width × 10 mm in length × 1.65 mm in thickness, with both surfaces optically polished, and furnished with two mounts. The relative spectral intensity of the glass luminescence has been determined using a white-light, uniform-source, integrating sphere calibrated at NIST for its irradiance. 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.

Certified Values: A NIST certified value [1] 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. The measurand is relative luminescence measured as a function of Raman shift (cm^{-1}) from the laser excitation wavelength of 532 nm. Metrological traceability is to the NIST spectral irradiance scale.

Equation 1 defines a log-normal model used to describe the mean shape of the SRM 2242a luminescence spectrum when excited at 532 nm. Table 1 lists the certified values of the coefficients of Equation 1. Figure 1 shows the spectrum and its associated 95 % level of confidence expanded confidence and prediction uncertainty bands.

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 the laser excitation wavelength of 532 nm. 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 150 cm^{-1} and 4000 cm^{-1} Raman shift for excitation with a 532 nm laser.

Expiration of Certification: The certification of **SRM 2242a** is valid, within the measurement uncertainty specified, until **31 December 2024**, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see “Instructions for Handling, Storage, and Use”). The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Production and certification of this SRM were performed by A.A. Urbas of the NIST Chemical Sciences Division. The glass was produced, cut and polished by A. Kirchhoff of the NIST Fabrication Technology Division.

Statistical consultation was provided by D.V. Samarov of the NIST Statistical Engineering Division. Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive 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

Gaithersburg, MD 20899
Certificate Issue Date: 15 October 2019

Steven J. Choquette, Director
Office of Reference Materials

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

$I_{\mathrm{SRM}}(\Delta\upsilon)$ is relative mean spectral intensity of SRM 2242a at $\Delta\upsilon$, $\Delta\upsilon$ is the wavenumber in units of Raman shift ($\mathrm{cm^{-1}}$), H is peak height, w is peak width, ρ is half width ratio, x_0 is a location parameter for the log-normal profile, m is the slope and b is the intercept.

Table 1. Coefficients of the certified, linearly shifted log-normal model defined in Equation 1 that describes the mean luminescence spectrum of SRM 2242a for 532 nm excitation[a,b,c].

Coefficient	L_{PRED}	L_{CONF}	Mean Value	U_{CONF}	U_{PRED}
H	9.9563 E-01	9.8378 E-01	9.9747 E-01	1.0112 E+00	9.9931 E-01
w	3.1045 E+03	3.1006 E+03	3.1006 E+03	3.1005 E+03	3.0966 E+03
ρ	1.1580 E+00	1.1572 E+00	1.1573 E+00	1.1573 E+00	1.1566 E+00
x_0	2.9723 E+03	2.9720 E+03	2.9721 E+03	2.9721 E+03	2.9719 E+03
m	-3.8550 E-06	-3.6481 E-06	-3.7168 E-06	-3.7841 E-06	-3.5804 E-06
b	-1.1574 E-02	1.2598 E-02	1.2864 E-02	1.3114 E-02	3.7302 E-02

[a] The mean values of the coefficients are for an unweighted log-normal model fit to the response data from three spectrometers. The lower and upper curve coefficients are for log-normal model fits to 95 % prediction, [L_{PRED},U_{PRED}] and 95 % confidence [L_{CONF},U_{CONF}] band expanded uncertainties.

[b] The confidence band expresses the uncertainty associated with the model and the NIST measurements that were used to assign the coefficient values. If the NIST measurements were repeated, mean luminescence spectra would be expected, with about a 95 % level of confidence, to be within the confidence bands generated using the L_{CONF} and U_{CONF} coefficients.

[b] The prediction band expresses the uncertainty associated with the model and measurements that could be made by a competent laboratory using methods comparable to that used at NIST. Individual luminescence spectra are expected, with about a 95 % level of confidence, to be within the prediction bands generated using the L_{PRED} and U_{PRED} coefficients.

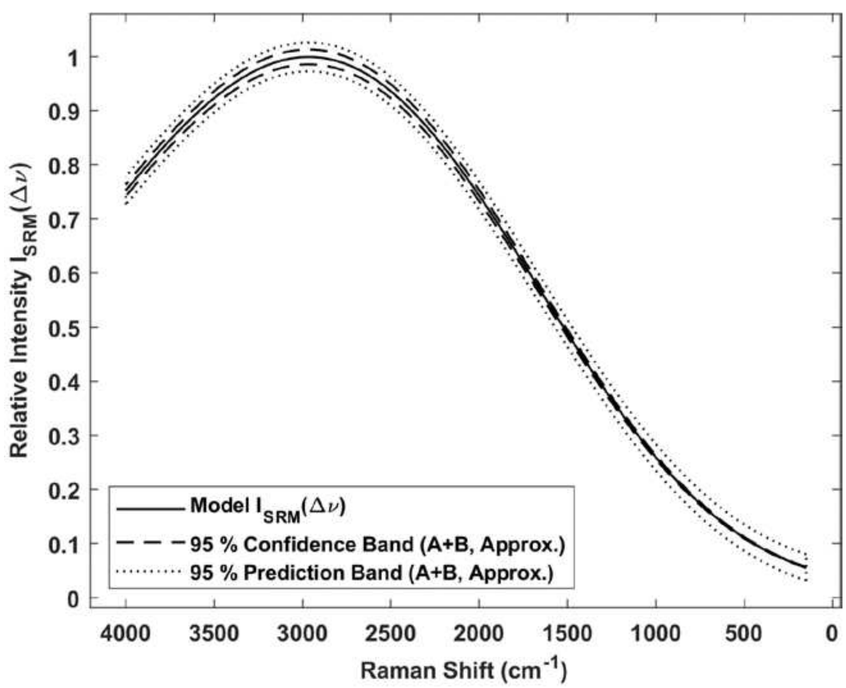

Figure 1. Certified, linearly shifted log-normal model describing the luminescence spectrum of SRM 2242a when excited at 532 nm. The horizontal axis has dimensions of Raman shift ($\mathrm{cm^{-1}}$). The vertical axis is on a relative scale and normalized to unity with the dimensions of number of photons per second per square centimeter per wavenumber. The dashed lines (---) represent an approximate 95 % confidence band for the spectrum. The wider, dotted lines (···), are the corresponding 95 % prediction band for individual spectra measured using methods and instruments comparable to those that were used in the certification.

Physical Description: SRM 2242a is a manganese-doped (0.15 wt % MnO_2) borate matrix glass. One mount is 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. The glass slide is retained in a slot on the front face of the holder. Two plastic springs, also retained in the slot, hold the glass slide in place while allowing for positioning within the slot to accommodate different beam heights. Grooves on the sides of the slot require that the glass slide and springs be loaded into the slot from the bottom of the holder. The other mount is 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.

The glass matrix of SRM 2242a is susceptible to corrosion when exposed to water vapor for extended periods of time. Storage at high relative humidity (RH) or direct contact with liquid water can rapidly deteriorate the surface. To improve stability, a bilayer nanolaminate was deposited on the glass substrate to serves as a moisture barrier. The thin film with applied to the substrates by atomic layer deposition (ALD) and consists of a base layer of 30 nm Al_2O_3 with a 20 nm SiO_2 capping layer. While this moisture barrier greatly reduces humidity related surface corrosion it does not prevent it. Due to the potential use of these SRMs on microscope systems with high magnification objectives, thicker films that may offer superior performance were not investigated. The emission profile of the coated and uncoated units could not be distinguished on a confocal Raman microscope using a 50X objective.

Measurement Conditions: The certification measurements of the luminescence spectrum of SRM 2242a were made using two spectrometer systems: one commercial micro-Raman spectrometer system operated in a 180° backscatter geometry and one home-built Raman system that utilized two spectrograph and detector combinations. Measurements on all instruments were conducted in a 180° backscatter geometry. Two diode-pumped continuous wave laser excitation sources were used with nominal laser wavelength of 532.2 nm. Laser excitation wavelength was measured periodically using a wavemeter. Longpass edge filters were utilized for Rayleigh rejection on all systems. The absolute wavenumber axis of each spectrometer was calibrated using emission lines from low-pressure pen lamps. 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. Most certification data were acquired at nominal room temperature, which typically varied from 22 °C to 23 °C. Additional measurements were conducted with sample temperature control from 20 °C to 25 °C.

INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

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. **The glass substrate is susceptible to surface corrosion when exposed to elevated levels of humidity. Therefore, when not in use it is strongly recommended that the SRM unit be stored in an environment with a stable humidity of 20 % or lower.**

Use: SRM 2242a is used to provide 532 nm laser excitation Raman spectra corrected for relative intensity; it is not intended for use as a standard for the determination of absolute spectral irradiance or radiance.

For user convenience, a spreadsheet containing the coefficients of the certified model, confidence band and prediction interval as well as an example relative spectral intensity correction calculation can be obtained at https://www-s.nist.gov/srmors/view_datafiles.cfm?srm=2242a.

This SRM is intended for use in measurements in the temperature range of 20 °C to 25 °C. Use of this SRM at temperatures other than the certification temperature is not supported. This SRM was shown to be photostable under extended exposure to approximately 50 mW of 532 nm laser light focused through a 50X magnification microscope objective. While it is expected that higher power densities could be used without incurring damage, this is not recommended.

Correcting the Raman spectrum of a sample requires a measurement of the SRM 2242a luminescence spectrum on the Raman instrument and then a mathematical treatment of both this luminescence spectrum and the observed Raman spectrum of the sample. For proper use, attention must be paid to the following experimental conditions: (1) The spectrometer laser and x-axis should be calibrated using the manufacturer's recommended methods. (2) Validation of the Raman shift axis may be accomplished by referring to ASTM E1840-96 [2]. It should be noted that the shape of the spectral luminescence may have some sensitivity to the placement of the glass surface relative to the illumination and collection optics of the spectrometer. (3) Measurement conditions should be arranged to furnish a spectrum of optimum signal-to-noise ratio of the SRM. (4) 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. A detailed description of this procedure for the intensity correction of Raman spectra can be found in references [3–5]. This curve is generated using the certified coefficient values for the model defined in Equation 1 and the measured luminescence spectrum of the SRM glass. For the spectral range of certification, $\Delta\upsilon = 150\ \mathrm{cm^{-1}}$ to $4000\ \mathrm{cm^{-1}}$, compute the elements of the certified relative mean spectral intensity of SRM 2242a, $I_{SRM}(\Delta\upsilon)$, using 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 photons per second per square centimeter per wavenumber. The data sets that are the measured glass luminescence spectrum, $S_{SRM}(\Delta\upsilon)$, and the measured Raman spectrum of the sample, $S_{MEAS}(\Delta\upsilon)$, 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

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

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:

$$S_{CORR}(\Delta\upsilon) = S_{MEAS}(\Delta\upsilon) \bullet I_{CORR}(\Delta\upsilon). \qquad (3)$$

The Table 1 coefficients are **certified for use between 150 cm^{-1} and 4000 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 150 cm^{-1} and 4000 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 Raman shift in units of wavenumbers ($\mathrm{cm^{-1}}$). 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 transformation:

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

where

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

and λ is the wavelength in nanometers and λ_L is the wavelength of the laser 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.

REFERENCES

[1] May, W.; Parris, R.; Beck II, C.; Fassett, J.; Greenberg, R.; Guenther, F.; Kramer, G.; Wise, S.; Gills, T.; Colbert, J.; Gettings, R.; MacDonald, B.; *Definition of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements*; NIST Special Publication 260-136 (2000); available at https://www.nist.gov/sites/default/files/documents/srm/SP260-136.PDF (accessed Oct 2019)

[2] ASTM E1840-96; *Standard Guide for Raman Shift Standards for Spectrometer Calibration;* ASTM International, West Conshohocken, PA (2007).

[3] Frost, K.J.; McCreery, R.L.; *Calibration of Raman Spectrometer Response Function with Luminescence Standards: An Update*; Appl. Spectrosc., Vol. 52, pp. 1614–1618 (1998).

[4] 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 488/514.5 nm Excitation*; Appl Spectrosc., Vol. 61, pp. 117–129 (2007).

[5] ASTM Standard E2911-13, *Standard Guide for The Relative Intensity Correction of Raman Spectrometers*; Annu. Book ASTM Stand., West Conshohocken, PA.

Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 948-3730, email srminfo@nist.gov; or via the Internet at https://www.nist.gov/srm.