Relative Intensity Standards for Raman Spectroscopy

NIST has developed luminescent glasses for intensity calibration for use with popular laser excitation wavelengths that are available as a set of SRMs traceable to NIST primary radiometric standards. The advantage of these glasses is their ease of use, the photostability of the luminescence, and their cost relative to a calibrated white-light irradiance source. Contact with the Raman community of major chemical industries, instrument manufacturers, regulatory agencies, and initiatives adopted by the ASTM E13.08 Subcommittee on Raman Standards is being maintained so that methods, standards, and techniques developed by NIST are widely accepted by the industry.

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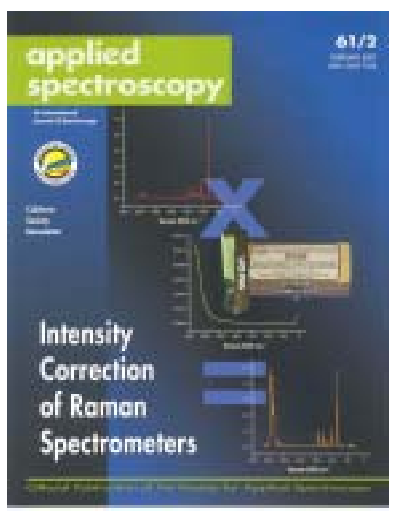
Raman spectroscopy is now finding its place in the industrial environment for process measurements and quality control. The lack of accepted practices, standards and spectral libraries has been a main obstacle to the acceptance of Raman in industrial settings and is a barrier to its use in the regulated industries. Intensity calibration of Raman spectra can be accomplished using white light sources, but this procedure requires expensive equipment, has a source with a limited lifetime, and employs a radiation source that is spatially different from the Raman process. These limitations can be avoided by using luminescent glass artifacts of known relative irradiance.

Standard Reference Materials® SRMs 2241 through 2243 are certified spectroscopic standards intended for the correction of the relative intensity of Raman spectra obtained with instruments employing laser excitation wavelengths of 785 nm, 532 nm or 488 nm/514.5 nm. These SRMs each consist of an optical glass that emits a broadband luminescence spectrum when illuminated with the Raman excitation laser. The shape of the luminescence spectrum is described by a polynomial expression that relates the relative spectral intensity to the Raman shift with units in wavenumber (cm^{-1}). This polynomial, together with a measurement of the luminescence spectrum of the standard, can be used to determine the spectral intensity-response correction which is unique to each Raman system. The resulting instrument intensity-response correction may then be used to obtain Raman spectra which are corrected for a number of, but not all, instrument dependent artifacts.

In addition to the spectrometer intensity calibration, there is interest in developing a methodology for the validation of the calibration process. This validation can be accomplished by the determination of peak area ratios of intensity corrected spectra obtained from spectral measurements of previously characterized spectra. A current choice is to use the spectrum of cyclohexane, since this chemical is currently an ASTM standard for the measurement of Raman shift, as a check on the spectrometer wavelength calibration. NIST has shown that measurements of the peak area ratios of cyclohexane can exhibit significant systematic variations that are dependent upon the cuvette placement relative to the collection lens focal point of the spectrometer and on the properties of the laser beam. This result has implications for the development of protocols for the validation of the intensity correction procedure and was included in the paper. Work this year was to finish these measurements to complete a study that covered excitation wavelengths of 488 nm, 514 nm, 532 nm, 647 nm, 752 nm and 785 nm.

In addition, NIST wrote for ASTM Subcommittee E13.08 a Standard Guide for the determination of Raman spectrometer resolution that is currently in the process of being adopted by the Subcommittee.

NIST standards will promote the acceptance of Raman spectroscopy as a tool for process control in the chemical and pharmaceutical industries and will provide a means for instrument qualification as required by regulatory agencies such as the FDA.



Expected to be a "Definitive" Publication:

S.J. Choquette, E.S. Etz, W.S. Hurst, D.H. Blackburn and S.D. Leigh, **"Relative Intensity Correction of Raman Spectrometers: NIST SRMs 2241 through 2243 for 785 nm, 532 nm and 44/514.5 nm Excitation",** Applied Spectroscopy, advanced publication, 61/2, Feb. 2007.

Future Plans: A study will be done on the systematic errors that can result from either white light-based or luminescent-based relative intensity calibration of dispersive spectrometers that use two-dimensional CCD detectors (as is the case with almost all modern dispersive instruments). NIST is developing a luminescent glass SRM for use at 1064 nm (FT-Raman spectrometers). Collaborative work with ASTM E13.08 will continue.