8. Standards for Raman Spectroscopy

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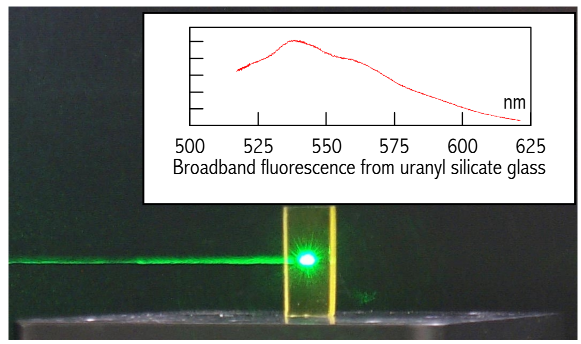
Objective: Critically evaluate existing approaches and develop new methods and associated standards that will provide for calibration of the frequency and intensity of Raman spectral data.

Problem: It is widely acknowledged that major advances in analytical Raman instrumentation have virtually revolutionized Raman spectroscopic measurement, so that Raman spectroscopy is now finding its place in the industrial environment for process measurements and quality control. Calibration of both the Raman intensity and frequency are important. Intensity calibration is needed to make process-control Raman measurements instrument independent, for analysis of unknown mixtures, and for reliable and robust quantification. Maintaining a highly accurate frequency calibration on all spectra is needed if the training sets of multivariate analyses used in process control algorithms are to maintain their validity. 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.

Approach: One approach for intensity calibration will be to evaluate the use of fluorescent materials. NIST will research the choice of fluorescent materials by evaluating the fluorescence spectra of rare-earth doped glasses to provide both broad-band and narrow-band emissions over the common Raman spectral domains. These glasses will lead to the certification of a set of Standard Reference Materials (SRMs) traceable to NIST primary radiometric standards. While fluorescence can be exploited for intensity calibration, a more fundamental approach rests upon the determination of absolute Raman cross sections to provide an absolute intensity calibration that is verifiably instrument independent. A Raman gain spectrometer will be developed for the measurement of the Raman cross sections of judiciously chosen liquids and solids that may serve as absolute Raman intensity standards. Frequency calibration issues will be studied, with reference to the ASTM adopted Raman shift standards of selected compounds. 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 will be maintained so that methods, standards, and techniques developed by NIST are widely accepted by the industry.

Results and Future Plans: In FY01, efforts focused on identifying and controlling several issues (sample focusing and NIR absorption effects, and issues regarding carrying out reliable white light calibration measurements) that had large systematic effects on the measured spectral shape. It was discovered that the technique given in the literature for the correction of the intensity axis of Raman spectra and for the effects of instrumental response has an unsuspected source of substantial error.



A systematic difference in spectral shape for both Raman and fluorescent scattered light occurs that is particularly pronounced for transparent materials several millimeters thick and for laser excitation at 785 nm. Its source is in the off-axis light that is collected by the measurement system. Measurement techniques were developed for the Raman and fluorescence measurements that give reproducible results and agree with samples that approximate infinite thinness. A round robin test will be conducted in FY01 through the ASTM E13.08 subcommittee to ascertain the variability in intensity-corrected Raman spectra that are obtained using a chromium-based glass at 785 nm laser excitation. The results of this test will enable production of this glass for the ASTM user community. A glass suitable for use at 532 nm will be developed this coming year.