Simplified Calibration of Instrument Response Function for Raman Spectrometers Based on Luminescent Intensity Standards

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Published Raman spectra are rarely corrected for variations in spectrometer sensitivity across the Raman spectrum, which leads to often severe distortion of relative peak intensities that impede calibration transfer and library searching. A method was developed that uses the known luminescence of standards which fluoresce in response to laser irradiation. Since the standards are observed with the same sampling geometry as the Raman sample of interest, their spectra are subject to the same instrumental response function. After one-time calibration of the standards' fluorescence output against a known tungsten source, the unknown Raman spectrum may be corrected for instrumental response by a simple formula. In practice, the user need only run the standard under the same conditions as the Raman sample, then apply a short GRAMS algorithm. The approach is demonstrated for coumarin 540a and Kopp 2412 glass standards, with 514.5- and 785-nm laser light, respectively. Once the corrected spectrum is in hand, the absolute Raman cross section of a given Raman feature may be determined by comparison to known scatterers such as benzene.

Index Headings: Raman; Calibration; Intensity; Instrument response function.

INTRODUCTION

The surge of interest in Raman spectroscopy as an analytical technique was stimulated by the development of FT-Raman[1–5] in the mid 1980s, and later by compact dispersive spectrometers with charge-coupled devices (CCDs) in the early 1990s.[6–9] The historical disadvantages of Raman spectroscopy such as complexity, low sensitivity, and fluorescence interference have largely been eliminated with improved instrumentation. One of the main obstacles still preventing broader acceptance of Raman is the problem of widely varying instrumental response. Spectrometers vary in transmission efficiency and detector quantum efficiency with wavelength, thus perturbing the true spectrum of intensity vs. Raman shift. The resulting uncertainties in relative intensity result from the fact that Raman spectroscopy is a single-beam technique lacking the internal response calibration inherent in absorbance measurements. The vast majority of published Raman spectra are uncorrected for instrumental response and are subject to large variations in relative peak intensities when obtained on different instruments. Such variations greatly complicate useful spectroscopic operations, such as library searches and calibration transfer, and affect long-term stability. Even if one restricts a series of measurements to a single instrument, relative intensities can vary for such mundane reasons as routine replacement of a detector.

Several groups have reported procedures for correcting for the spectrometer response function,[11–16] all of which depend on a reference source with a known output of intensity vs. wavelength. By taking a spectrum of the reference material or source, it is possible to determine the response function of the spectrometer by dividing the observed reference spectrum by the known reference output. The ideal reference source for correcting Raman spectra would have several characteristics:

1. It should have a broad, featureless output over the relevant wavelength range.
2. It should exactly reproduce the Raman sampling geometry.
3. It should be simple and easy to implement.
4. It should require no additional equipment other than what is required to take the Raman spectrum.
5. It should be relatively inexpensive.
6. It should exhibit long-term stability.

Petty et al. used a graphite furnace at a fixed temperature as a black-body radiator to correct for instrumental response.[13] Fryling et al. used a standard tungsten source operating at a fixed current as a broad-band emitter over several hundred nanometers.[16] While both approaches accurately correct for instrumental response, they require fairly expensive and cumbersome sources. Furthermore, it is important that the calibration source closely approximate the size and geometry of the Raman sample, so that both Raman scattering and source output follow the same light path through the spectrometer. Chromatic aberrations can yield quite different response curves for different sample positions, resulting in miscalibration if standard and source differ in size or geometry. Hamaguchi and co-workers[11,12] realized the importance of placing the correcting source in the same position as the Raman sample and suggested using the known, broad-band fluorescence output of quinine to correct for the spectrometer response function. Although this technique assures similarity of standard and sample positioning, quinine requires UV excitation and is not applicable to the visible and NIR laser wavelengths common to many Raman spectrometers. For the tungsten, black-body, or quinine standards, the calibration procedure is generally too complex for routine use. In order for the procedure to be practical for daily use in a routine analytical laboratory, alternative calibration sources are required.

In the current report, we considered the use of fluorophores which produce broad-band emission when excited by 514.5- or 785-nm light. Secondary standards made from a fluorescent laser dye and a colored-glass filter were established by comparing their emission

APPLIED SPECTROSCOPY

curves to those of a standard tungsten source. Once these secondary standards are in hand, a Raman spectrum excited with the same laser wavelength may be corrected by comparison to the emission spectrum of the standard. The standard spectrum is obtained in the same manner as a sample but can be used to correct the intensities of all spectra obtained under the same experimental configuration.

THEORY

The theoretical basis of the procedure is very similar to that discussed previously for a tungsten source,[16] except that the luminescent output of the standard replaces that of the bulb. Starting with the signal expression for a Raman sample (equation 4 of ref. 16),

$$S_A = P_D \beta_A D_A \Omega T A_D QKt \qquad (1)$$
$$S_S = P_D \beta_S D_S \Omega T A_D QKt \qquad (2)$$

where S_A is the signal in e^- for the analyte; S_S is the signal in e^- for the standard; P_D is the laser power density at the sample, (photon s^{-1} cm^{-2}); β_A is the differential Raman cross section of the analyte (cm^2 molecule^{-1} sr^{-1}); β_S is the cross section for standard luminescence (cm^2 molecule^{-1} sr^{-1}); D_A is the number density of the analyte (molecules cm^3); D_S is the number density of the standard (molecule cm^{-1}); Ω is the collection angle (sr^{-1}); Q is the detector quantum efficiency (e^- photon^{-1}); T is the transmission of the spectrometer and collection optics (unitless); A_D is the area of illuminated sample monitored by the spectrograph (cm^2); K is the geometric factor, equal to depth of field for liquids in cm; and t is the observation time (seconds).

Note that the product $\beta_S D_S$ determines the strength of luminescence from the standard, from fluorescence or some other process, even though the luminescence may not originate from individual molecules. In addition, K may differ for sample and standard because of optical absorption, but this difference, if present, does not affect the shape of the standard's luminescence spectrum. Raman cross sections are normally integrated over the spectral linewidth, to avoid the effects of varying spectrometer resolution. However, Raman spectra are not integrated over wavelength, and Eqs. 1 and 2 must be modified to express the signal for a given resolution element. Defining S'_A as signal per resolution element $[e^-(cm^{-1})^{-1}]$, s as the spectral bandpass in cm^{-1} [equal to $\Delta(\Delta\bar{v})$], and β'_A as the cross section in cm^2 molecule^{-1} sr^{-1} $(cm^{-1})^{-1}$ yields Eq. 3:

$$S'_A = P_D \beta'_A s D_A (\Omega T A_D Q K)t. \qquad (3)$$

β'_A is the derivative of β_A with respect to $\Delta\bar{v}$ and is related to the integrated cross section σ_A by Eq. 4:

$$\beta'_A = \frac{\delta^2 \sigma_A}{\delta\Omega\delta(\Delta\bar{v})}. \qquad (4)$$

Since β varies with observation angle for Raman scattering, a given determination of β' will apply to a particular observation geometry and polarization. Let R represent the instrument response function so that

$$R = s\Omega TQA_D K, \qquad (5)$$
$$S'_A = P_D \beta'_A D_A Rt, \qquad (6)$$
$$S'_S = P_D \beta_S D_S Rt. \qquad (7)$$

As noted elsewhere,[16] a tungsten source has a specific intensity, L_w, which is proportional to its calibrated output curve, and

$$S'_W = L_W s \Omega T Q A_D t. \qquad (8)$$

Certain constants such as A_D may differ for the standard and the tungsten source, but these will affect the spectrum magnitude, not shape. Neglecting these possible differences yields Eq. 9:

$$S'_W = L_W R t. \qquad (9)$$

Taking the ratio of Eqs. 7 and 9 and rearranging yields 10:

$$\beta'_S D_S = \frac{S'_S L_w}{S'_W P_D}. \qquad (10)$$

Since the shape of L_W is known and P_D is a constant, the shape of $\beta'_S D_S$ may be determined from the standard and tungsten spectra. The ratio of Eqs. 6 and 7 yields Eq. 11:

$$\beta'_A D_A = \beta'_S D_S \frac{S'_A}{S'_S}. \qquad (11)$$

Note that the shape of $\beta'_A D_A$ has now been corrected for instrument response.

The correction procedure for a particular laser wavelength involves two steps. First, the shape of $\beta'_S D_S$ as a function of wavelength is determined by comparing the spectrum of the standard to that of a calibrated tungsten source. This shape may be described by a fourth-order polynomial that is valid for a particular standard and laser wavelength. Second, the corrected Raman spectrum of the analyte ($\beta'_A D_A$) is calculated from this polynomial and the uncorrected analyte and standard spectra, via Eq. 11. Since P_D and L_W are usually not determined on an absolute scale, the β'_A and β'_S functions determined from Eqs. 10 and 11 have accurate shapes, but arbitrary magnitudes.

EXPERIMENTAL

All data were acquired with an ISA 640 single spectrograph (300 lines/mm) equipped with a Photometrix EEV05-10 CCD liquid nitrogen-cooled camera. Both the focusing and objective lens were 120-mm-focal-length $fl4$ lenses from Melles Griot. The laser was either a Coherent Ti:sapphire 890 operating at 785 nm or a Coherent Innova 90-5 at 514.5 nm. A Kaiser (Ann Arbor, MI) holographic notch filter tuned for 785 nm was used to reject the laser line in the red, while a Pomfret (Orange, NJ) dielectric filter was used to attenuate the 514.5-nm line. It was necessary to use a polarization scrambler from Melles Griot to remove any grating-induced variation due to polarization. The tungsten irradiance standard from Eppley Labs (Q100t4/cl) was operated at 6.5 amps. An 800-nm long-pass filter was used to eliminate the higher-order diffraction of the tungsten bulb from interfering with the correction procedure at 785 nm. All chemicals were reagent grade and obtained from either Sigma or Mallinckrodt, except for the coumarin 540a, which was obtained from Exciton (Dayton, OH). The secondary standard for 514.5-nm excitation was 0.84 mM coumarin
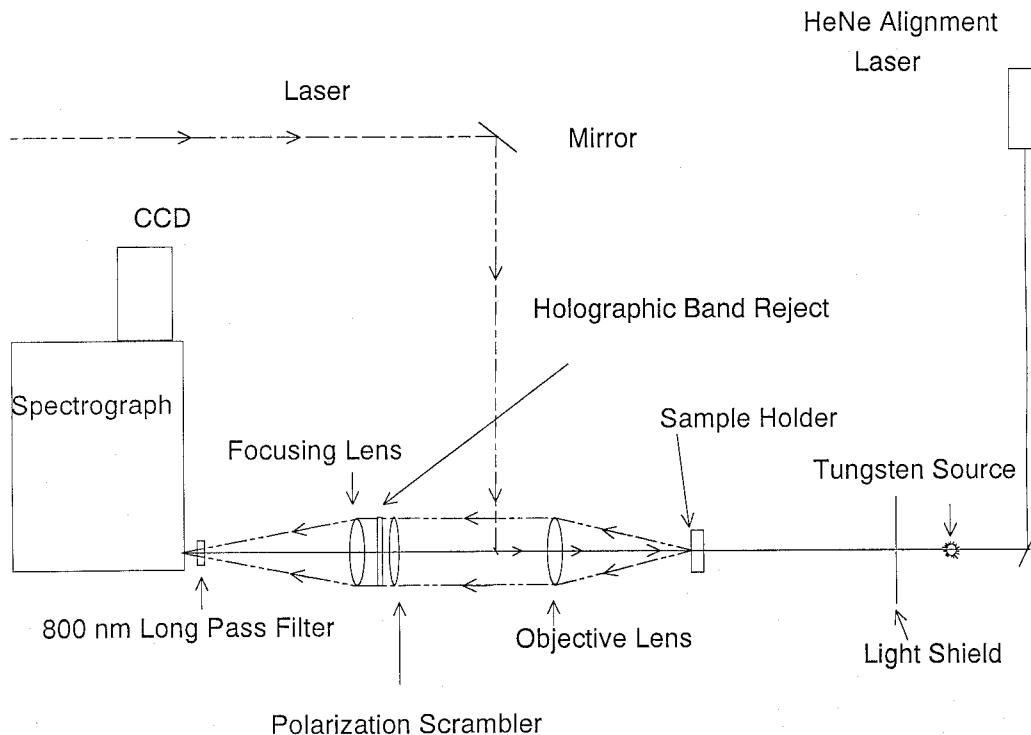
FIG. 1. Experimental apparatus. The Raman sample was a liquid in a quartz cuvette or a free-standing solid. When the tungsten source was observed, the sample was replaced with a 0.2-mm-diameter hole in poster board and a "Kimwipe" diffuser.

540a in methanol, in a 1-mm quartz cuvette. The secondary standard for 785-nm excitation was a commercially available red filter made from semiconductor-doped glass with inherent luminescence.[17] Corning sold such glass as type "2-61"; it is currently manufactured by Kopp Glass Co. as type 2412 and sold by F. J. Gray & Co., Jamaica, NY. One 3-mm-thick sample of Corning type 2-61 and three of Kopp type 2412 glass (also 3 mm thick) were compared for use as a standard for 785-nm excitation. Raman shift calibration was performed by using a second-order polynomial fit to the known bands of cyclohexane and benzonitrile.

RESULTS

By using the apparatus shown in Fig. 1 along with Eq. 10, we determined the shape of the $\beta'_s \, D_s$ function for each standard. The tungsten source was directed through a 0.2-mm hole and a diffuser (Kimwipe) in order to scatter the light before entering the collection optics, thus generating an approximately spherical distribution of light similar to a Raman sample. The spectrum of the lamp was compared to that of each fluorescent standard, to yield the corrected emission curves shown in Fig. 2. The magnitude of these curves depends on P_D, D_S, and s, but their shapes accurately reflect the changes in emission intensities with wavelength. The curves for the coumarin and glass standards are more conveniently plotted against Raman shift relative to either 514.5 or 785 nm, as shown in Fig. 3. Also shown are fourth-order polynomials fit to these curves and normalized to a maximum intensity of 1.0, with their coefficients listed in Table I.

Once the polynomials describing the corrected emission spectra were in hand, Eq. 11 was applied to obtain corrected Raman spectra. The spectrum of the appropriate

standard was recorded under exactly the same conditions (slit width, grating position, sample position, etc.) as the Raman spectrum to be corrected. Then a GRAMS/386 Array Basic subroutine was used to calculate the shape of the $\beta'_s \, D_s$ function from the polynomial coefficients. Finally, the corrected spectrum was calculated with Eq. 11. Recall that the resulting spectrum has an arbitrary intensity scale, but corrected relative intensities. It may be converted to an absolute scale with another standard, as described below. To obtain corrected spectra on a routine basis, the user need only obtain a spectrum of the appropriate standard, then use one operation in GRAMS/386 to read the appropriate polynomial coefficients from a disk file and calculate the corrected spectrum.

The procedure is illustrated in Fig. 4 for methylene chloride, corrected with the tungsten source and both standards. The uncorrected spectra (4A and 4B) show large variations in relative intensity due mainly to differences in detector Q in the visible and NIR. Correction with all three standards yields similar relative intensities, which compare favorably with those reported by Petty et al.[13] for 1064-nm excitation and by Fryling et al.[16] The tungsten, coumarin, and glass standards were evaluated more quantitatively by comparing the ratios of two peak areas for methylene chloride and acetonitrile. Table II lists the uncorrected and corrected peak area ratios for CH_2Cl_2 (2986 to 701 cm^{-1}) and CH_3CN (2252 to 918 cm^{-1}) at the two laser wavelengths. The peak area ratios vary with laser wavelength greatly before correction mainly because of the difference in detector quantum efficiency. Correction with coumarin or glass yields ratios close to those observed after tungsten correction for a given laser wavelength. The peak ratios observed with the 785-nm laser are lower than those observed with
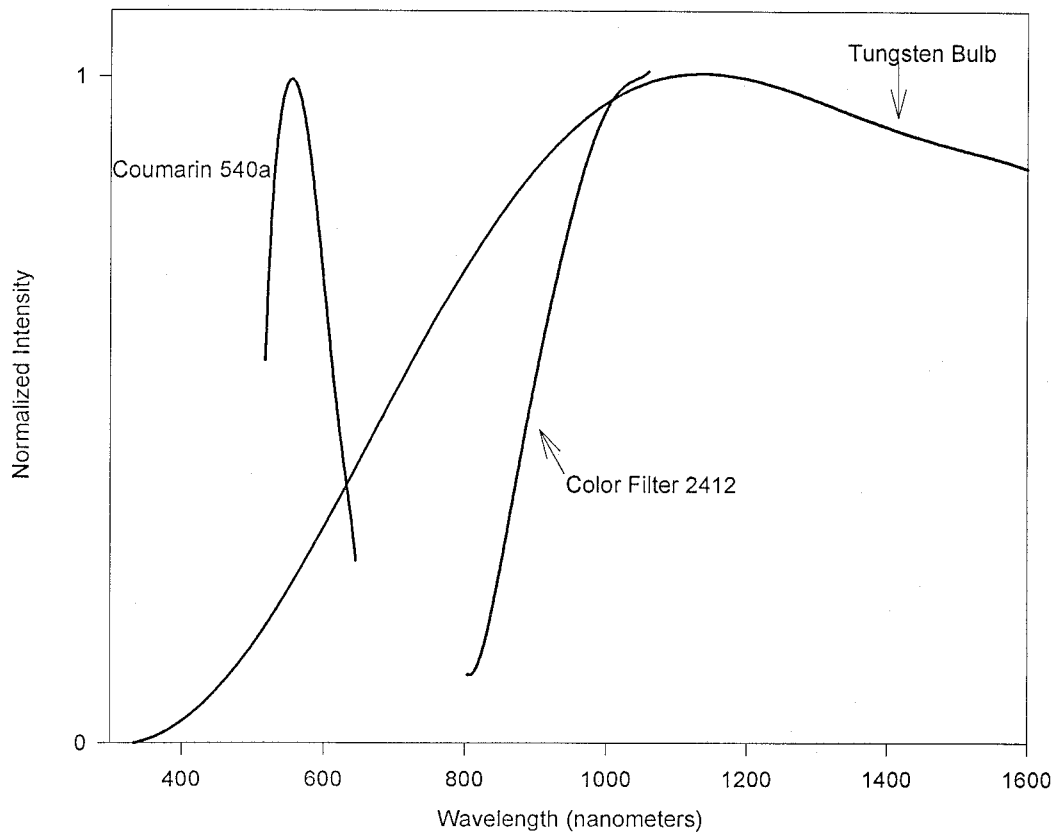
FIG. 2. Corrected emission spectra for coumarin solution, type 2412 glass, and tungsten bulb. Bulb curve is a fifth-order polynomial fit to the intensities provided by the manufacturer. The other curves were determined by comparison to the bulb via Eq. 10. All three curves are normalized to maximum intensities of 1.0. Coumarin was illuminated by a 514.5-nm laser, 2412 glass by a 785-nm laser.
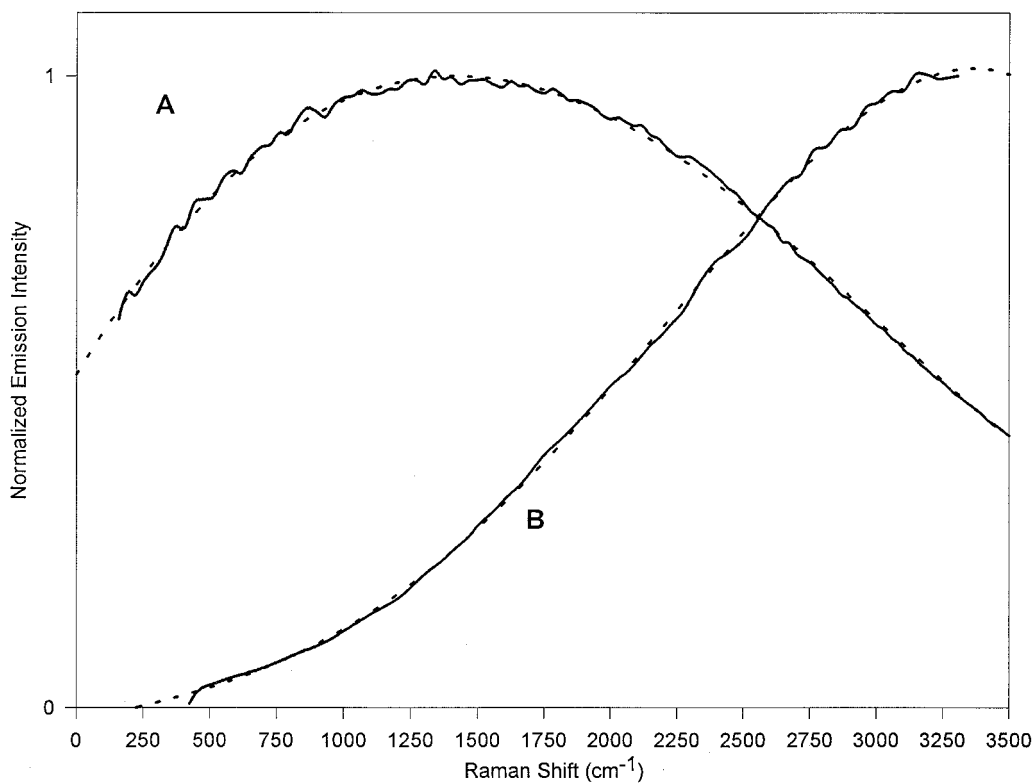

FIG. 3. Coumarin (*A*) and Kopp 2412 (*B*) emission from Fig. 2 plotted as functions of Raman shift relative to 514.5 nm (coumarin) or 785 nm (glass). Solid lines are corrected spectra, dashed lines are fourth-order polynomial fits.

TABLE I. Polynomial coefficients for coumarin and Kopp 2412 standards, for maximum intensity = 1.0.

Coefficient of	Coumarin excited at 514.5 nm	2412 Glass excited at 785 nm
$(\Delta\bar{\nu})^0$	0.494771	-0.0241981
$(\Delta\bar{\nu})^1$	7.773929×10^{-4}	1.145194×10^{-4}
$(\Delta\bar{\nu})^2$	-3.305342×10^{-7}	-5.312753×10^{-8}
$(\Delta\bar{\nu})^3$	2.113758×10^{-11}	$1.0989663 \times 10^{-10}$
$(\Delta\bar{\nu})^4$	2.371421×10^{-15}	$-2.288769 \times 10^{-14}$

FIG. 4. Raman spectra of $CH_2 Cl_2$ obtained as follows: (**A**) uncorrected, 514.5 nm; (**B**) uncorrected, 785 nm; (**C**) 514.5 nm, corrected with tungsten bulb; (**D**) 514.5 nm, corrected with coumarin standard; (**E**) 785 nm, corrected with 2412 glass.

514.5-nm laser, but this difference is attributable to the variation in scattering cross section with wavelength. Solely on the basis of the $\nu_0 (\nu_0 - \nu_1)^3$ term, the 2986/701 peak area ratio for CH_2Cl_2 for a 785-nm laser should be 79% as large as it is for a 514.5-nm laser. Similarly, the 2252/918 peak area ratio for CH_3CN at 785 nm should be 89% of its value at 514.5 nm. Dudik et al. have noted that the 2252-cm^{-1} band of CH_3CN is preresonantly enhanced[18] and therefore does not follow a simple $\nu_0 (\nu_0 - \nu_1)^3$ dependence. As noted earlier, the coumarin and glass standards (yielding spectra 4D and 4E) have the advantage of low cost and ease of use, plus precise reproduction of sampling geometry.

Reproducibility of fluorescence emission from standard to standard, as well as stability of the emission curve shape, is of obvious importance to a reliable secondary standard. Coumarin 540 solutions had a shelf life of at least four months, with no observable changes in the fluorescence curve shape of Fig. 3. Observation of 28 different spots on a single Kopp glass filter exhibited a standard deviation of less than 1% in curve shape, defined as the ratio of the intensity at 526 to 1553 cm^{-1}, relative to 785 nm. This ratio showed a standard deviation of 5.1% ($N = 20$) when determined on five spots for each of four different glass samples. Extended exposure of a single spot on the glass filter did result in some photobleaching, as shown in Fig. 5. Although the emission intensity decreased by 12% after 90 min (55 mW on a 100-μm-diameter spot), the decrease was uniform over the 0–3500-cm^{-1} Raman shift range. The constant ratio of the intensities before and after prolonged illumination indicates that this slow degradation will not affect corrected relative intensities.

An issue that often arises with multichannel detectors applied to Raman is the trade-off between resolution and spectral coverage. Since CCDs have a finite number of pixels, increasing spectral resolution often requires spectral acquisition in segments, interspersed with grating motion or generated optically with an echelle or split-grating spectrograph. Since spectrometer transmission can vary for a given wavelength observed at different positions on the CCD, discontinuities can appear, such as those illustrated in Fig. 6. The uncorrected emission spectrum of a red filter obtained with three CCD exposures shows artifacts at the splice points, which can distort Raman features. Since these artifacts, as well as any fixed pattern gain variation in the CCD, will appear in both the analyte and standard Raman spectra, they will be corrected by the intensity correction procedure outlined above. To illustrate, the spectrum of 2412 glass shown in Fig. 6A was corrected with the spectrum and polynomial of a *different* 2412 glass filter, to yield spectrum 6B. 6C
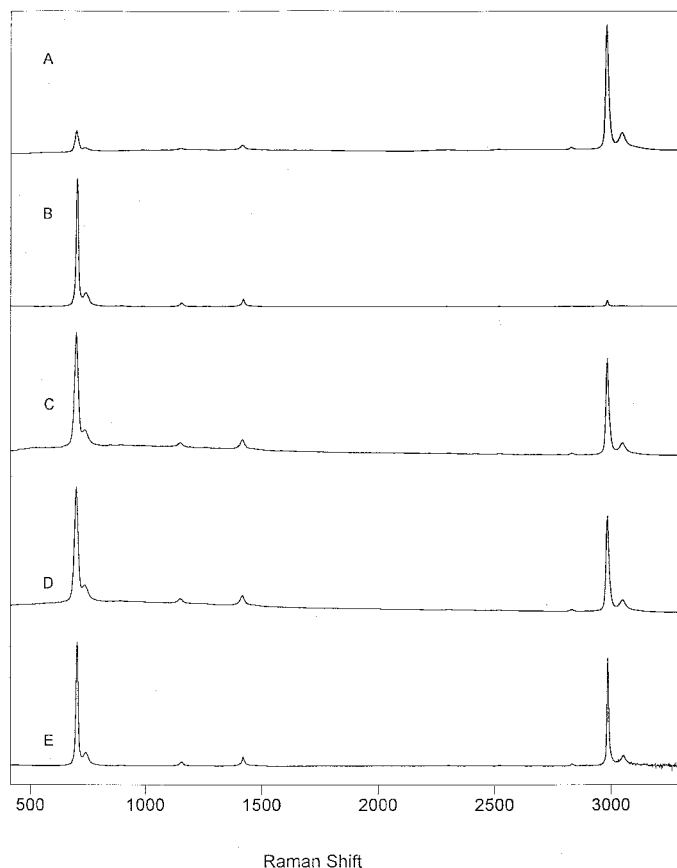
is the ratio of the spectra of the two glass samples, showing noise of about 5%. The flatness of curve 6C indicates that the discontinuities are removed, and that the "sample" and "standard" glass materials have the same emission spectra. Also shown in Fig. 6D is the instrument response function, determined by dividing 6A by 6B. Finally, Figs. 7 and 8 show spectra of caffeine and 4-acetamidophenol (acetaminophen) obtained in one segment at 514.5 nm and two segments at 785 nm, and corrected with the coumarin 540a and 2412 glass standards.

TABLE II. Peak area ratios.

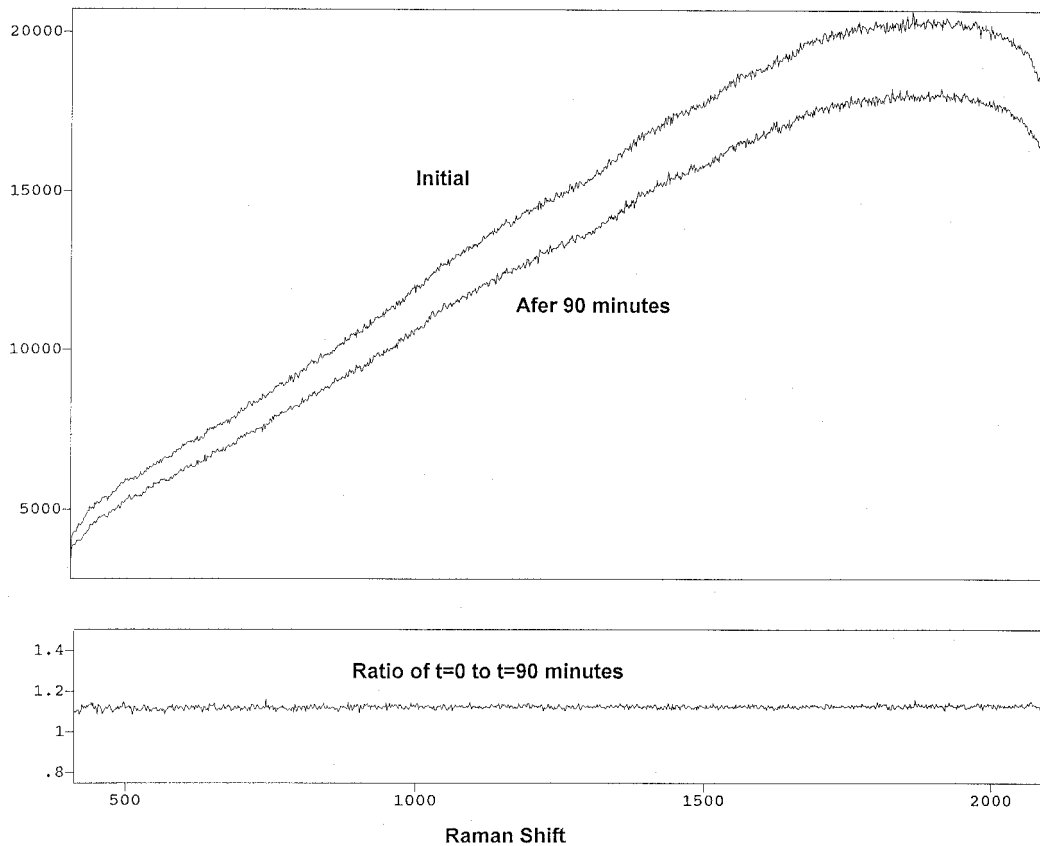|	Excitation at 514.5 nm	Excitation at 785 nm
CH_2Cl_2 (2986/701-cm^{-1} bands)		
Uncorrected	5.9	0.028
Corrected with:		
Tungsten	0.71	0.51
Coumarin	0.65	—
Kopp 2412	—	0.41
CH_3CN (2252/918-cm^{-1} bands)		
Uncorrected	10.2	1.06
Corrected with:		
Tungsten	3.53	2.86
Coumarin	3.53	—
Kopp 2412	—	2.67

FIG. 5. Luminescence spectra of a single location on a 2412 glass filter illuminated with 55 mW of 785-nm light on a 100-μm spot.
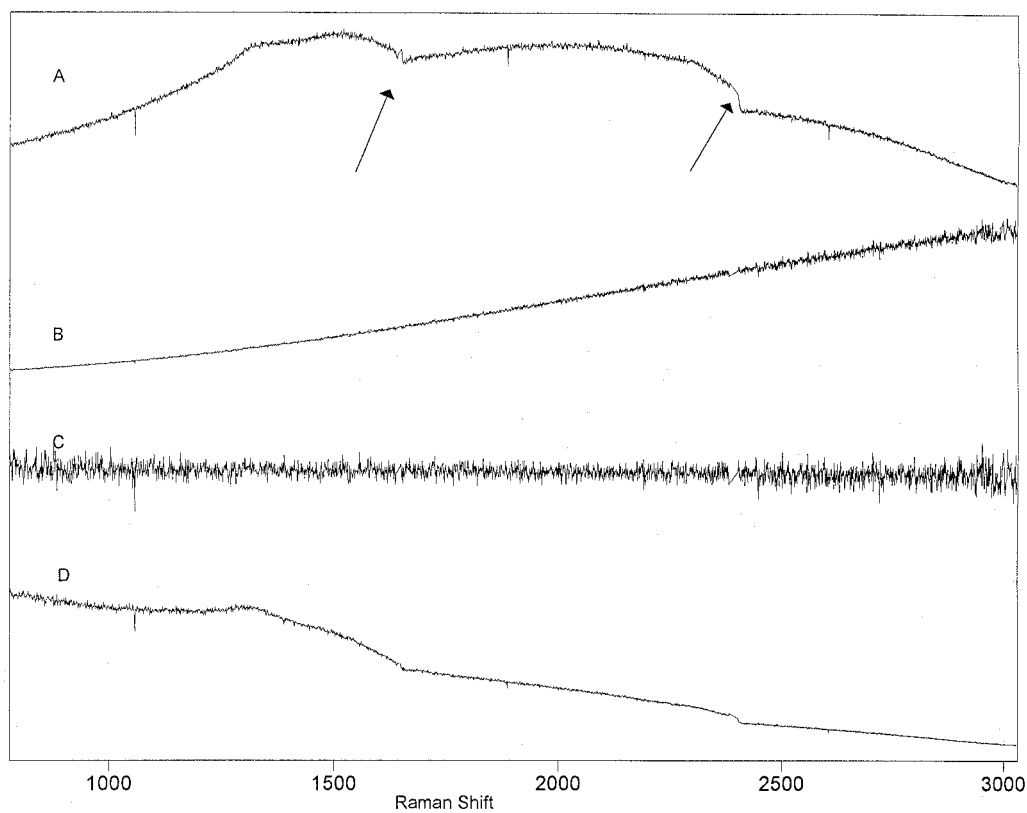

FIG. 6. (**A**) Uncorrected luminescence spectrum of 2412 glass obtained in three spectral segments, with a 785-nm laser. Arrows indicate splices between segments. (**B**) Spectrum **A** after correction with a different 2412 glass sample and its polynomial. (**C**) Ratio of spectra of two different glass samples. (**D**) Instrument response function determined by dividing curve **A** by curve **B**.
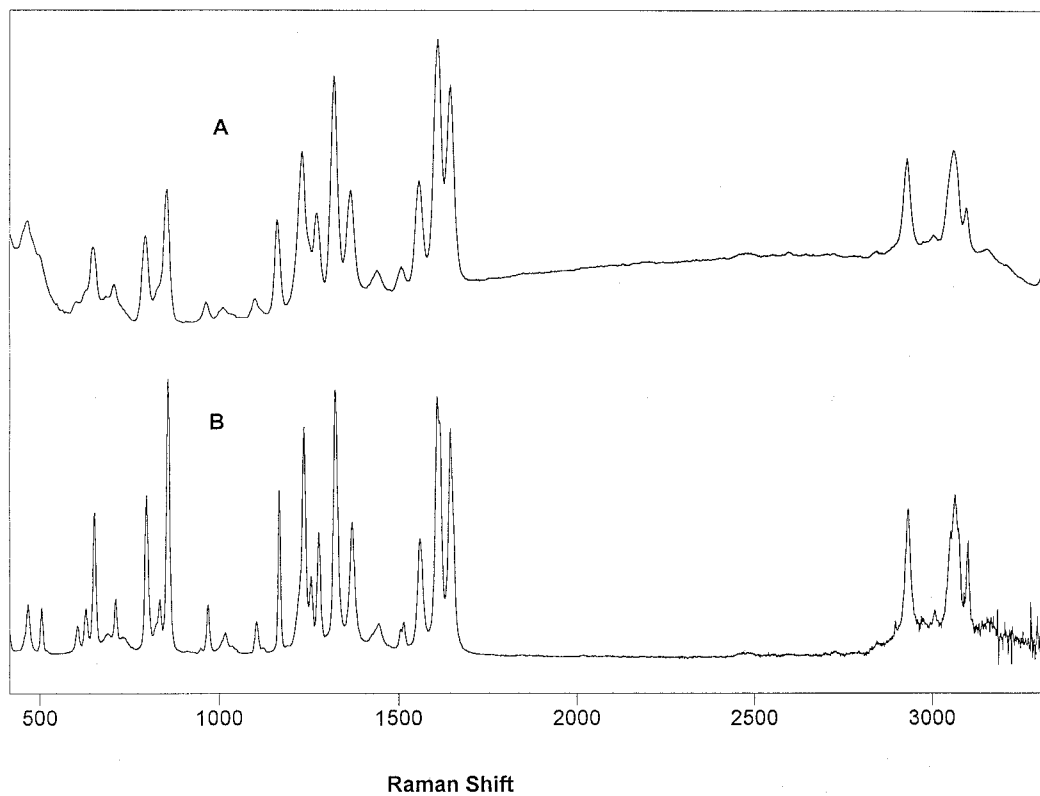
Raman Shift

FIG. 7.   (**A**) Spectrum of acetamidophenol obtained with a 514.5-nm laser in one CCD segment, and corrected with coumarin 540. (**B**) Spectrum of acetamidophenol obtained with two CCD segments and corrected with 2412 glass.
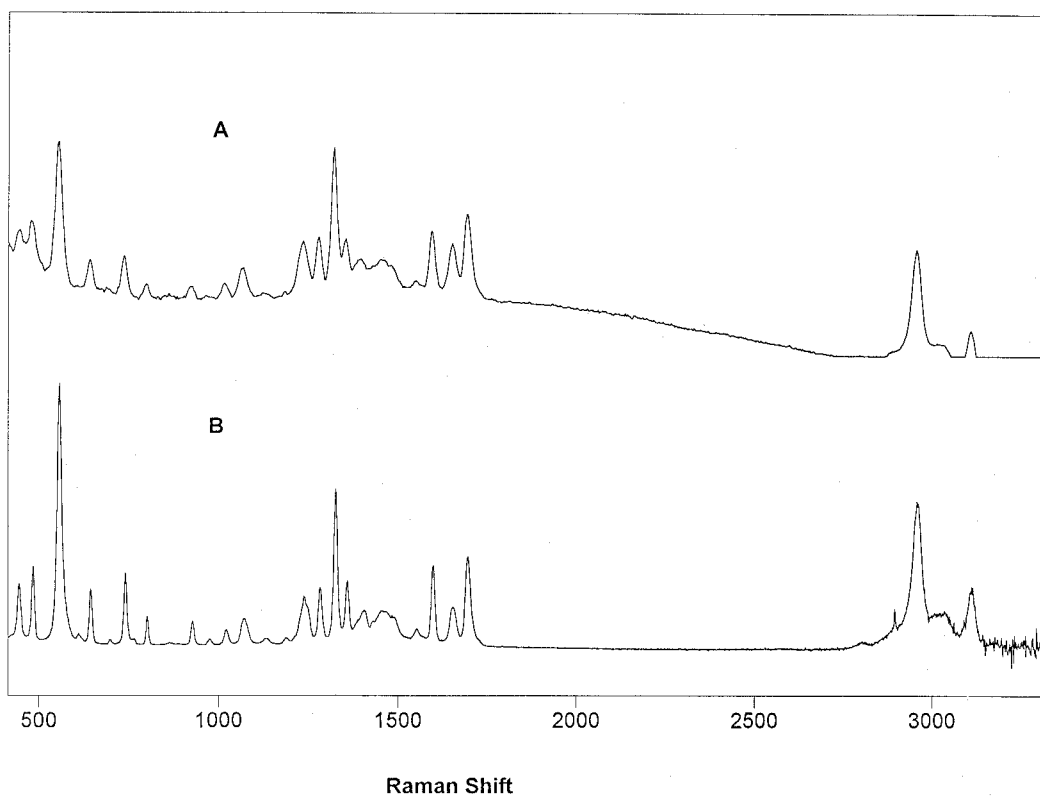

Raman Shift

FIG. 8.   Spectra of caffeine; same conditions as Fig. 7.

DISCUSSION

Although the coumarin 540a dye solution and 2412 glass filter are not necessarily the optimum secondary standards for intensity correction with 514.5- and 785-nm lasers, they do meet most of the criteria. Unlike the tungsten bulb correction, a procedure based on fluorescent secondary standards requires a different material (or at least a different polynomial) for each laser wavelength. So the procedure presented here will be most useful for common, fixed laser wavelengths such as 488, 514.5, 532, 785, and 1064 nm. It is quite possible that such standards, along with their polynomials, will become available commercially.

With a universally available and easily implementable relative intensity correction procedure available, several important issues may be addressed. One of the major benefits of relative spectral intensity correction is the ability to compare spectra taken with different instruments. In most spectra published to date, no effort is made to correct for the spectrometer response function, and it is difficult to compare the results of one instrument to another. In principle, at least, a response function correction will reduce errors caused by instrumental drift with time, as well as variations between different units of the same design and between instruments of different designs or from different vendors. It should be possible to develop an analytical procedure such as multivariate calibration in the research lab, then transfer it to different instruments in the field without sacrificing quantitative accuracy. Furthermore, spectral libraries which are corrected for instrumental response should be transferable from one instrument to another, even if the two spectrometers differ in response function. Finally, a response calibration permits a check on instrument performance over time and permits correction of any changes induced by detector replacement, aging optics, etc. Overall, the response calibrations bring many of the advantages of a double-beam method (such as absorbance) to Raman, which is inherently a single-beam technique.

As pointed out by Petty et al.,[13,15] and as recognized by users of FT-IR libraries, relative peak intensities are resolution-dependent. Since the instrumental linewidth is rarely narrow in comparison to Raman features, the instrument can only approximately determine β' as a function of $\Delta\bar{v}$. The instrumental linewidth is easily varied with FT-Raman spectrometers, but for dispersive/CCD, it will depend on entrance slit width, reciprocal linear dispersion, and pixel width. Thus any attempt to compare corrected spectra from different instruments should avoid significant resolution differences. The correction procedure adequately corrects for variations in spectrometer response with laser wavelength, as demonstrated in Fig. 3 and Table II. However, comparisons of spectra resulting from different laser wavelengths should be made with caution, since fully corrected spectra can exhibit varying relative intensity for varying laser wavelength. The v_0 ($v_0 - v_1$)^3 dependence affects relative intensity, as noted earlier, and preresonant or resonant affects can produce much larger effects on relative intensities.

As described previously, the tungsten bulb standard can, in principle, be used to determine absolute cross sections for Raman features, after suitable calibration.[16] The coumarin and glass standards could also be calibrated to yield absolute cross sections, but the procedure would be quite cumbersome. A simpler procedure depends on knowing the absolute cross section of a known Raman feature, such as the 992-cm^{-1} band of benzene. Raman peak *areas* (rather than heights) do not depend on the relationship between instrumental and Raman linewidth, so the area of unknown Raman features may be accurately compared to that of benzene. A spectrum of the sample of interest is obtained, along with one of benzene under the same conditions. Both spectra are then corrected for instrumental response, as described above. Then the cross section of an unknown feature (integrated over Δv and having units of cm^2 molecule^{-1} sr^{-1}) may be calculated from Eq. 12:

$$\beta_A = \frac{\beta_{992}\gamma_A D_{992}}{\gamma_{992}D_A} \qquad (12)$$

where γ_A and γ_{992} represent the integrated peak areas of the Raman feature of interest and the benzene 992 band; D_A and D_{992} are the number densities of analyte and benzene, respectively; and β_{992} is the known cross section of benzene's 992-cm^{-1} band, 2.9×10^{-29} cm^2 sr^{-1} at 514.5 nm.[19] This procedure applies to transparent liquids but may be modified for solids or absorbing samples. Cross sections (514.5 nm) for the CH$_3$CN 2252- and 918-cm^{-1} bands determined in this manner were 4.1×10^{-30} and 1.4×10^{-30} cm^2 molecule^{-1} sr^{-1} for the 180° backscattered geometry, with both polarizations analyzed. Dudik et al.[18] reported values of (5.6–8.2) $\times 10^{-30}$ and 1.0 $\times 10^{-30}$ cm^2 molecule^{-1} sr^{-1} for the same bands observed at 90° and both polarizations.

The primary objective of this work was a relative intensity correction that is sufficiently simple to be used widely. Once the standard and its polynomial are available for a particular laser wavelength, the correction procedure consists of running the standard as if it were another sample and then using a straightforward and automatable data treatment step. Provided that the samples and standard are positioned identically and their spectra obtained under the same instrumental conditions, the corrected relative intensities should be quantitatively comparable to those from other instruments. A detailed error analysis was not performed in the present work, but experience indicates that corrected relative intensities vary by about ±5% from day to day. The comparison of spectra corrected with different standards (e.g., tungsten vs. 2412 glass) will depend on the accuracy of the determination of the polynomials but is about ±15% on the basis of the results listed in Table II. Until more results are available, we estimate the precision of the corrected relative intensities to be ±5% and their accuracy to be ±15%.

does indicate the importance of determining a correct polynomial for each standard.

ACKNOWLEDGMENTS

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