Raman Intensities and Detection Limits of Geochemically Relevant Gas Mixtures for a Laser Raman Microprobe

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We describe Raman experiments on gas mixtures of known composition containing N_2 plus two or more of the following species: SO_2, CO_2, O_2, CO, H_2S, CH_4, and H_2. The mixtures were used to calibrate a RAMANOR U-1000 with the goal of increasing the accuracy of compositional analyses of fluid inclusions in geological samples. We derived instrument-specific "Raman quantification factors" that incorporate both relative (to N_2) Raman scattering cross sections and instrumental efficiencies. The experiments were done on gases in thin-walled, silica glass capillaries at <15 atm pressure. The application of these quantification factors eliminates the need to choose among the widely differing literature values for Raman scattering cross sections and permits better correction for specific optical and geometric effects than does the use of a calibration lamp. Detection limits for analysis of fluid inclusions exceeding about 10 μm in diameter range from about 0.3 to 1.6 atm partial pressure.

The quantification of different species in fluid inclusions in geological samples is one of the major fields of application in laser Raman *microprobe* spectroscopy (e.g., ref 1–5). The fact that several instrument- and sample-specific parameters (e.g., irradiance of the scattering volume and absolute Raman scattering cross sections) are not known, makes the Raman determination of *absolute* quantities of species in fluid inclusions impossible. Thus, the challenge is to determine the molar proportions ("relative quantification") of the individual species. The quantitative result is based on an *intensity* ratio, which is calculated from the areas of two (or more) Raman peaks for two (or more) different species in the same inclusion.

Knowledge of the instrumental response is absolutely necessary for any kind of quantification, even in the relative mode. Among the most important instrumental factors are the different sensitivities of the gratings and the detector system for Raman scattered light of different polarization orientations and/or wavelengths. Those instrumental effects have to be taken into account and compensated for, in order that the calculated Raman intensity ratio be a meaningful quantitative result and not just a reflection of instrumental artifacts. The use of the microprobe mode of a laser Raman spectrometer will cause additional optical effects due to components in the microscope (e.g., objective, beam splitter, lenses), which the exciting laser light and/or the Raman scattered light has to pass through before it hits the sample and eventually enters the monochromator. Since each optical component has its own spectral characteristics (i.e., transmission, absorption, reflection, diffraction, etc.) that are a function of both wavelength and polarization orientation of the interacting light, an empirical calibration of each individual instrument in a particular configuration is necessary.

This paper is addressed to both applied spectroscopists and geologists concerned with the quantitative use of laser Raman microprobes. It describes an empirical approach to quantitative analysis of microsamples (on the order of picomoles) of mixed gases. A method of calibration that is believed to yield the most accurate quantitative results on low-pressure gaseous species in fluid inclusions is described.

Table I. Raman Active Vibrational Frequencies (in cm^{-1}) of Gases of Geological Interest

species	theoretical[a] $\bar{\nu}_1$	$\bar{\nu}_2$	$\bar{\nu}_3$	$\bar{\nu}_4$	practical[b] $\bar{\nu}_{vib}$
SO_2	1151	518	1362		1152
CO_2	(1337)[c]				1285.5
					1388.0[c]
O_2	1555				1555.0
CO	2143.16				2142.5
N_2	2331				2329.0
H_2S	2615	1183	(2627)		2612.0
CH_4	2917	1534	3019	1306	2918.0
H_2O	3657	1595	3756		*d*
H_2	4161.13				4156.5

[a] As listed in ref 11. [b] Band used in this quantification study. [c] Average of two frequencies split by Fermi resonance. [d] H_2O is difficult to quantify and is not included in this study.

Species of Interest. Fluid inclusions in rocks can be subdivided into two major types: aqueous and volatile-bearing (not mutually exclusive). The aqueous inclusions have a wide range of compositions and concentrations of dissolved salts (and in some cases dissolved volatiles). There are also inclusions dominated by mixtures of simple gases such as CO_2, CH_4, N_2, H_2S, and to a lesser extent CO, O_2, H_2, SO_2, and C_2H_6 (see Table 2 in ref 4). Geologists are concerned with both simple identification of the gases (as indicators of fluid composition) and with quantitative analysis of molar proportions (to infer gas fugacities). These data are used, for instance, to reconstruct fluid mixing histories in rocks, the development of ore deposits, and the processes of the breakdown of organic matter and the maturation of hydrocarbons in sedimentary basins.

In order to quantify the composition of fluid inclusions in minerals, numerous analytical techniques (including instrumental neutron activation and atomic absorption) have been used, many of which involve extraction of the fluid inclusions from bulk rock samples (for references, see ref 6 and 7). Because a single rock or mineral grain in many cases has recorded the passage of several generations of fluids, by capturing the fluids in inclusions, one frequently opts for the technique that allows analysis of individual fluid inclusions. The most promising and powerful techniques are microthermometry (use of a microscope to observe phase changes in inclusions under controlled temperature), laser Raman microprobe (LRM) spectroscopy, and laser- or heat-induced bursting of individual fluid inclusions combined with different methods of volatile analysis (e.g., ref 8–10). Microthermometry and LRM analysis are the only two nondestructive techniques that permit the observation and analysis of chosen, single inclusions. Whereas LRM analysis can *uniquely identify* the covalently bonded volatiles in a fluid inclusion, from microthermometry one can only *infer* compositions (qualitatively

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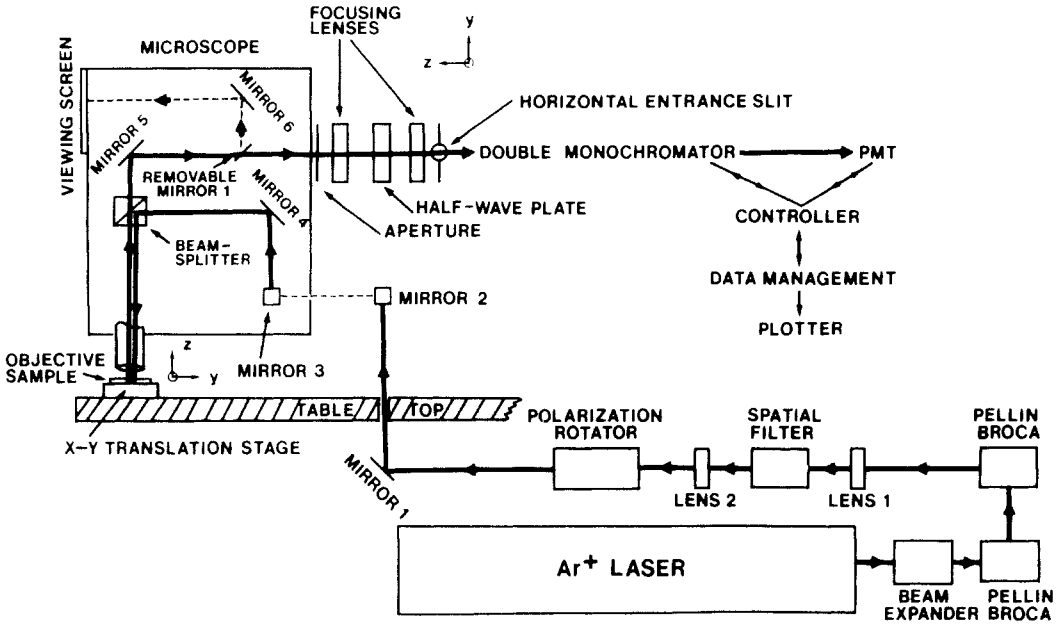

Figure 1. Diagrammatic sketch of optical components and beam path in RAMANOR U-1000 laser Raman microprobe. Mirrors 2 and 3 are oriented in the *xz* direction; --- light is traveling in the *x* direction. Optical path expressed in Porto notation: Z(XX)Z for an analyzer used in horizontal, and Z(XY)Z for an analyzer used in vertical position. For the experiments in this work, no analyzer was used.

as well as quantitatively) that are consistent with the observed phase changes.

Most of the LRM work on fluid inclusions has been devoted to the volatile-bearing inclusions. Table I lists the Raman-active modes of simple gases of geological importance, not all of which are strong enough to be used for routine fluid inclusion studies. Also included in Table I are the actual obtained frequencies of the most intense peaks, which we used for this quantification study.

Principles of Quantitative Analysis of Fluid Inclusions. According to Placzek's (*12*) polarizability theory, the area of a Raman peak (over a finite range of wavenumbers) is a function of (1) the number of molecules of a certain species in the scattering volume (absolute concentration of the species), (2) the Raman scattering cross section of the species, (3) the irradiance of the specimen, and (4) the solid angle of light collection. If two or more Raman-active species in the same phase of a fluid inclusion are analyzed either at the same time or one immediately after the other, the irradiance, the scattering volume, and the angle of collection of light are assumed to be the same for all the species. Since the approach to quantitative fluid inclusion analysis is to determine *the ratio* of two or more species, the latter unknown parameters cancel each other. The assumption has to be made that all species in a certain phase of a fluid inclusion have been identified and are Raman-active. In practice, for a two-component system, the experimental result in units of mole percentages (C_A, C_b) is the function of three ratios: one for the determined Raman peak areas (A_A, A_B), one for the relative scattering cross sections (σ_A, σ_B) of the two species, and one for the instrumental efficiencies (η_A, η_B) for Raman scattered light at specific wavelengths and polarization orientations. The σ's and η's can be combined into "Raman quantification factors" (F_A, F_B).

$$\frac{C_A}{C_B} = \frac{A_A}{A_B} \times \frac{\sigma_B}{\sigma_A} \times \frac{\eta_B}{\eta_A} = \frac{A_A}{A_B} \times \frac{F_B}{F_A} \qquad (1)$$

The relative scattering cross sections depend on, among other factors, the invariants of the derived polarizability tensor and are therefore characteristic of the Stokes-shifted vibrational Raman bands in question. There are several published sets of experimentally determined relative (to N_2) Raman scattering cross sections for volatiles of geologic interest (e.g. ref 4, 16, 17) to quantify the composition of fluid inclusions. In order to facilitate comparison among different research groups, Schrotter and Klockner (*14*) defined the "relative normalized differential Raman scattering cross sections", which are independent of the wavenumber of the exciting light. Problems related with the noncritical use of such literature values, under the assumption that they apply to a specific instrument and sample, have been discussed in detail by Wopenka and Pasteris (*18*). One of the most serious problems is the fact that different sets of relative normalized differential Raman scattering cross-section values as published by different authors do not agree with each other, even within the stated limits of accuracy (±10% relative). Thus, even if accurate instrumental efficiency correction factors (η_A, η_B) would be known (they are difficult to obtain, as discussed below), the question remains as to which set of cross-section values they should be applied.

This paper describes how we have been able to solve this problem. We improved the accuracy of quantitative LRM analysis on our instrument (RAMANOR U-1000) by the experimental determination of instrument-specific "Raman quantification factors" (F's, see eq 1) that represent both relative Raman scattering cross sections for the species of interest and relative instrumental efficiencies for Raman scattered light originating from those species. Furthermore, due to the specific experimental technique used in this work, we also were able to determine detection limits relevant to the small scattering volume in fluid inclusions. Although the actual quantification factors and detection limits that we derived are valid only for our specific instrumental setup, the techniques described can be applied to any other single- or multichannel LRM system.

EXPERIMENTAL SECTION

Apparatus. In order to facilitate the discussion on the difficulties that are encountered in the quantitative calibration of an LRM, we describe the beam path of the one used in our laboratory, which is a RAMANOR U-1000 with a Nachet microscope, manufactured by Instruments S.A. (Figure 1).

The laser light is reflected by mirrors into the microscope. Due to a specific dielectric coating on the beam splitter in the microscope, its reflectance and transmission properties are strongly

Table IV. Detection Limits for the Vibrational Bands of Geochemically Relevant Gases in 100-μm-i.d. Capillaries for a RAMANOR U-1000

species	partial pressure, atm	species	partial pressure, atm
SO_2	0.72	N_2	0.85
CO_2[a]	1.33	H_2S	0.35
O_2	0.79	CH_4	0.34
CO	0.79	H_2	1.6

[a] The detection limit is the same for both peaks.

Detection Limits. The results reported in this work only apply to our specific instrument (with a particular optical configuration) and analytical conditions. Table IV lists the detection limits, in terms of partial pressures, that were determined in cylindrical capillaries of 100-μm i.d. A comparison of Tables III and IV show that, as was expected, the species with the highest quantification factors (i.e., H_2S and CH_4) have the lowest detection limits, whereas the species with the higher detection limits generally have low quantification factors. The results for H_2, for example, show conclusively that the detection limits have a strong inverse correlation with our Raman quantification factors (for H_2 = 1.11) *but not* with the magnitude of the reported relative scattering cross-section values (for H_2 between 3.4 and 4.2, see ref 14).

Application to Fluid Inclusions. The relative abundances of volatile species in fluid inclusions may be used by geologists to calculate gas fugacities for the purpose of inferring the mineralogy and specific composition of solid phases that could have been in equilibrium with these fluids. Accuracy is therefore very important to the geological interpretation. The calibration described in this paper indeed has improved the accuracy of quantitative Raman analyses performed with our instrument. For instance, we investigated (*20*, *29*) a suite of CO_2–CH_4–H_2O fluid inclusions. Use of the uncorrected cross sections reported in the literature (*14*) of 1.21 for CO_2 and 9.1 for CH_4 yielded a Raman analysis of about 12 mol % CH_4 and 88 mol % CO_2 for the carbonic liquid in one inclusion, whereas microthermometric analysis gave a result of about 27 mol % CH_4. Use of our empirically derived quantification factors for low-pressure gases (see Table III) yielded a Raman analysis result of 21 mol % CH_4, i.e., much closer to the microthermometry result, which is believed to be very accurate.

As discussed in more detail in ref 18, 20, and 30 and references therein, Raman scattering cross sections for volatiles are sensitive to density (pressure). Although the application of our Raman quantification factors for low-density (<15 atm) gases yields more accurate Raman results, they still are recognized to be increasingly inaccurate as the pressure in the inclusions increases. An example of this inaccuracy was presented above; the discrepancy between the microthermometric and Raman results of 27 vs. 21 mol % CH_4, respectively, can be explained by the fact that the specific inclusions analyzed have about 85 atm internal pressure. High-pressure gas cells with appropiate windows or synthetic inclusions of known composition and pressure would be necessary to obtain Raman quantification factors or Raman scattering cross sections at high pressure. The fluid inclusion community of researchers is lacking data from such experiments at the present time, and the quantification factors obtained with our method are clearly superior to the application of uncorrected Raman scattering cross sections.

Of special geological significance is the use of minute sample vessels, because it has the advantage of yielding detection limits for individual gas species. This information can be very important to geologists trying to track down an ore deposit through the geochemical signature of its fluids, to those trying to infer the original depth of an ore deposit by determining the density of its (compositionally uncertain) fluid inclusions, or to those questioning if a graphite-absent mineral assemblage was in equilibrium with the fluids now trapped in some of the minerals.

The assumption behind the listing of detection limits is that they approximate the concentrations necessary for detection of the gas species in natural fluid inclusions. However, there are two complications in the determination of the actual detection limits for any given fluid inclusion. The first is that the above experiments were all done on capillary analogues. We believe that the detection limits determined in 100-μm capillaries reflect those in natural inclusions, because (1) we found good agreement with the detection limits of gases in natural samples of well-estimated vapor pressure and (2) eliminating geometry and interface considerations, we found good agreement for the detection limit of N_2 in air. The second complication is that even among fluid inclusions the detection limits will vary according to the size and shape of the inclusion, the depth of the inclusion (which furthermore affects which objective may be used), and the color of the mineral matrix. Therefore, the optical sensitivity of the LRM analysis technique as applied to fluid inclusions is such that detection limits must be considered as approximations in any given case.

The detection limits in Table IV are given in terms of partial pressure rather than mole percent, although the latter frequently is more desirable for a geologist. Partial pressure is, of course, the actual physical limitation to detection. As a geological example, with our instrument it should be possible to detect a molar CO_2 concentration of 1% in a fluid inclusion with 150 atm internal pressure, but in an inclusion with only 10 atm internal pressure, even 10 mol % CO_2 could remain undetected. Thus, in order to apply those detection limits and to assign an upper limit in molar concentration to a nondetected species, an independent estimate of the total internal pressure of a natural fluid inclusion is required. Fortunately this is possible in many cases; once the composition of the fluid has been established by LRM analysis, the homogenization temperature (at which two fluids become one) as determined by microthermometry can be used to infer the fluid pressure.

CONCLUSION

Instead of deriving an instrumental response function to modify the literature values of Raman scattering cross sections for different gas species, we defined and determined "Raman quantification factors" for the purpose of calculating concentrations of species in gas mixtures. The Raman quantification factors are calculated from count rates in experiments on calibrated gas mixtures and, thus, combine both Raman scattering cross sections and instrumental efficiencies. We have shown in the present work that our Raman quantification factors are superior to any standard lamp calibration procedure, because (1) the derivation of combined quantification factors rather than spectral response functions avoids the problem of having to decide which Raman scattering cross section values to use, and (2) the experimental derivation of quantification factors also accounts for special geometric and polarization effects that are not accounted for by use of a calibration lamp.

The LRM is an extremely useful tool when applied to geological problems. The accuracy of its data can be improved significantly by a calibration procedure like that described in this work. The resulting improvement in accuracy will be greatest for low-density, gaseous inclusions. However, for high-density fluid and liquid inclusions, our Raman quantification factors will yield more accurate results than the ones

obtained by the indiscriminate use of Raman scattering cross sections from the literature. The technique used in this work also provided for the first time insight into the detection limits of LRM spectroscopy, which is an important piece of information in the interpretation of analyses on natural fluid inclusions. Although the reported quantification factors and detection limits apply only to our specific instrument and analytical conditions, the method of calibration can be applied to any LRM. Our calibration approach solves two problems that have to be faced by every fluid inclusion researcher using quantitative LRM spectroscopy.

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Registry No. SO_2, 7446-09-5; CO_2, 124-38-9; O_2, 7782-44-7; CO, 630-08-0; H_2S, 7783-06-4; CH_4, 74-82-8; H_2, 1333-74-0; N_2, 7727-37-9.

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Preliminary Characterization of a Graphite Vapor Plasma in a Theta-Pinch Magnetic Field

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The plasma produced by the capacitive discharge vaporization of a graphite fiber bundle is compressed by an external magnetic field. The plasma is formed by the discharge of an underdamped RCL tank circuit. The plasma current also is used to generate a magnetic field in the kilogauss range in a large coil surrounding the plasma. The plasma has cylindrical symmetry, and the coaxial magnetic field results in a diamagnetic fluid drift of charged particles. The resulting azimuthal drift current couples with the magnetic field to produce a radial Lorentz force, which compresses the plasma. While the presence of the magnetic field has relatively little effect on the electrical properties of the plasma, radiative properties are significantly altered. Design features of the plasma generation device along with preliminary electrical and spectral characterization are presented.

High-temperature plasma devices are finding widespread application in analytical chemistry as sample cells for the generation of atomic vapor, as radiation sources for atomic spectroscopy, and as ion sources for mass spectrometry. The control of plasma properties including sampling characteristics, particle number densities, electron excitation temperature, and ionization temperature is of great importance in the effective utilization of these devices for analytical applications. The simple control of plasma power often is relatively ineffective in altering these properties. Internal processes in the plasma may regulate these properties by altering the plasma volume so as to keep power density relatively constant (*1*, *2*).

Several recent studies have shown that external magnetic fields can be very effective in altering plasma properties for microwave-induced plasmas (*3*), high-current capacitive discharge plasmas (*4–8*), and glow-discharge plasmas with currents in the millampere range (*9–11*). The presence of the magnetic field causes ions and electrons to precess in circular paths in the plane normal to the field direction. If the plasma contains a macroscopic electric field with a component normal to the external magnetic field, charged particles undergo a drift motion in the direction normal to the plane containing the electric and magnetic field vectors (*12*, *13*). This $E \times B$ drift motion has been used to alter the properties of high-current capacitive discharge plasmas (*4*, *5*) and improve their analytical performance (*6*, *7*). Recently, this type of plasma

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