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Moles quantification in liquid samples by Raman spectroscopy

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ABSTRACT

The mole is a unit of measurement that expresses amounts of a chemical substance. Its importance lies in that the mass and the number of molecules of a substance can be determined with this value. In this work, we suggest a mathematical expression that relates the number of moles of the sample studied with the Raman signal and the experimental parameters used. In other words, with this mathematical expression it is possible to obtain quantitative information in a simple manner from Raman spectra. We have applied this method to different samples and we have observed an excellent correlation between the experimental and expected data.

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1. Introduction

Raman spectroscopy has proved to be an excellent non-destructive tool, not only for qualitative purposes but also for quantitative analysis [1,2]. The general spectrum profile (peak position and peak intensity) provides a unique chemical fingerprint which can be used to identify a substance and distinguish it from others. In addition, the intensity of a Raman signal in a spectrum is directly proportional to the sample concentration. Typically, a calibration procedure can be used to determine the relationship between peak intensity and sample concentration.

Several quantitative Raman studies have been reported in different liquids or mixtures with two or more components. Unlike isotropic liquids, solid powder mixtures are more complicated systems. However, some studies have been conducted in this regard because of the several possible applications in the biology and pharmaceutical industries as well as in the quantitative analysis of drugs and other compounds [3–14]. The references provided of published quantitative Raman applications are by no means exhaustive.

The instrumental factors that may affect the quantitative Raman analysis include variations in laser power or wavelength, optical train variations and irreproducible sample placement. The most common solution to the problem of instrumental variation is to use a standard sample, wherein the concentration of the sample is assumed to be proportional to the ratio of the sample peak height to the standard peak height. The instrumental variation affects the signal measured from the standard sample in the same way as the problem sample signal; this method can achieve excellent quantitative results as will be shown in this work. A simple mathematical relationship to get a

quantitative value, as a first approximation for any sample studied, is proposed in this work.

2. Experiments

Raman spectra were recorded with an Almega XR dispersive Raman spectrometer. These spectra were accumulated over 25 s with a resolution of $\sim 4 \text{ cm}^{-1}$ and an excitation source of 532 nm radiation from a Nd:YVO₄ laser (frequency-doubled). All samples (ethanol—99.9%, methyl parathion—99.9%, pyridine—99% and rhodamine 6G—99%) used in this work were purchased from sigma Aldrich and used as received. The pure compounds and dilutions, prepared with triply distilled water, were stoked into well-sealed vessels.

2.1. Theoretical analysis

It is well known that a concentrated solution should be diluted to obtain another solution of lower concentration. In this case, the volume of the solvent is increased to obtain the new concentration, which can be calculated by $C_1V_1 = C_2V_2$. In a similar manner, a mathematical expression can be adjusted to monitor the amount of sample mass that is transferred to a smaller volume. In other words, we studied the following relationship: $C_iV_i \rightarrow V_H \rightarrow v_s$, where V_i is the initial volume; C_i is the initial concentration; V_H is the volume in a homogeneous configuration and v_s is the volume of the laser spot used in the Raman experiment. Whereas a Gaussian beam, we determined the volume of the laser spot as $v_s = \pi^2 d^4 / 4 \lambda$. Here, we used $d = 4 \lambda f / \pi D$ as the diameter of a cylinder and $L = \pi d^2 / \lambda$ as the height of the cylinder [15]; where the wavelength of laser was $\lambda = 532 \text{ nm}$; the focal length of lens was $f = 10 \text{ mm}$ and the laser beam diameter was $D = 1.9 \text{ mm}$.

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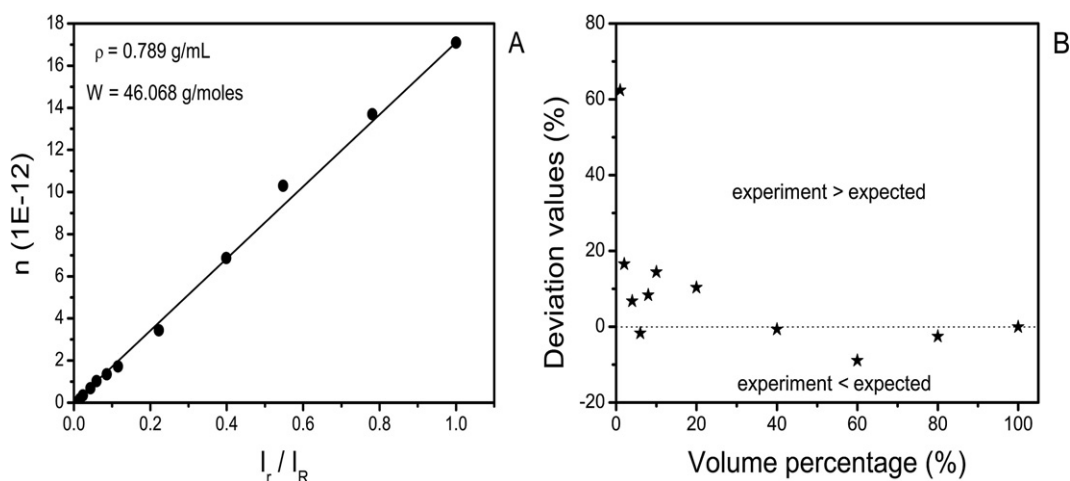


Fig. 1. Expected (line) and experimental (circles) data for the ethanol sample (A) and deviation values of data (B).

However, we noted that the number of moles “ n ” does not remain constant ($n_{initial} > n_{Homogeneous} > n_{spot}$), it changes as the volume of study decreases. Based on these considerations, a mathematical expression can be obtained for the number of moles that exist within the laser spot (volume):

$$n_s = A * C * V \quad (1)$$

where $A = v_s/V_H$ is the ratio between the volume of the laser spot and the homogeneous volume considered in the experiment. C is the concentration of the sample in Molarity and V is the volume of study in liters. If the number of moles in a system is known, the number of molecules and the sample mass can be determined with the following relationship: $N_{molecules} = n_s * N_{Avog}$ and $g = n_s * W$; where, N_{Avog} is the Avogadro's number ($6.022 \times 10^{23} \text{ mol}^{-1}$) and W is the molecular weight of the studied sample.

On the other hand, Raman intensity is proportional to the intensity of the excitation source and to the number of molecules in the sample volume being probed with the Raman instrument [16,17]. Experimentally, it is known that the intensity of a Raman spectrum is directly proportional to the concentration. In this paper, considering the previous premises and our experience, we propose that the Raman signal is proportional to the number of molecules by using the following simple correlation:

$$I_R = M * i \quad (2)$$

where M represents the number of elementary entities and i represents the Raman emission of each entities, which is representative of the material of study and under our experimental conditions. If we assume that $M = n_s$, where n_s represents the number of moles present within the laser spot (mathematical expression 1), the unitary intensity can be expressed as: $i = I_R/n_s$. Similarly, it can be assumed that it also satisfies the relationship: $I_r = n * i$, where I_r represents an arbitrary Raman signal. Therefore, the number of moles can be determined in an arbitrary Raman signal with the following equation:

$$n = I * n_s \quad (3)$$

where, $I = I_r/I_R$ is the ratio between the arbitrary and reference Raman intensity. We observed that I varies between $0 \leq I \leq 1$.

For pure and diluted substances, we have used the following mathematical expressions: $A = v_s/V_H$; $C = C_i = n_i/V_i$; $n_i = m/W$; $\rho = m/V_i$; $V = V_H$, in Eqs. (1) and (3); then, we were able to obtain two particular expressions by quantitative Raman analysis of the liquid samples, in which we know the density “ ρ ” or initial concentration “ C_i ” of the reference sample. We implemented all these expressions in an excel worksheet.

$$n = I * v_s * \left(\frac{\rho}{W}\right) \quad (4)$$

$$n = I * v_s * C_i \quad (5)$$

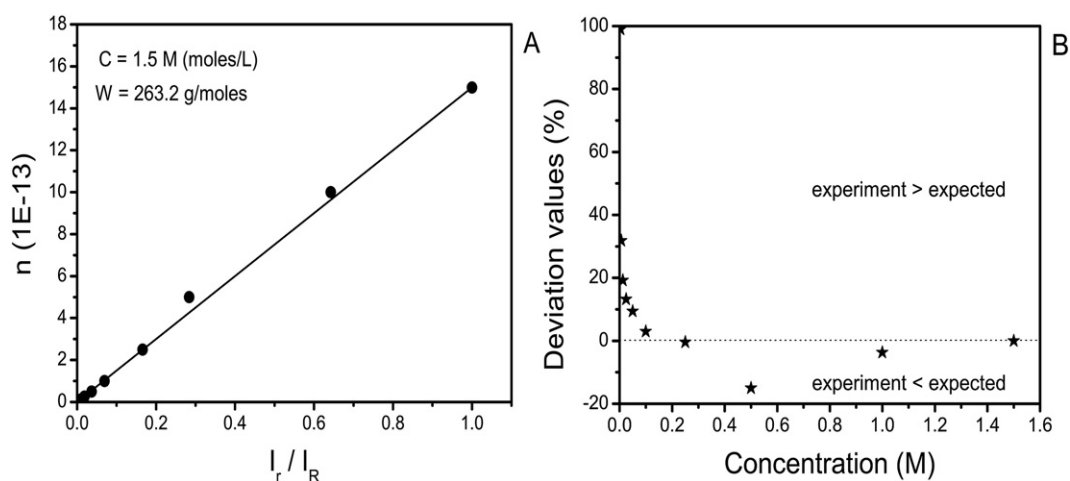


Fig. 2. Expected (line) and experimental (circles) data for the methyl parathion sample (A) and deviation values of data (B).

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