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RAMAN PROBE OF POLLUTANTS IN WATER: MEASUREMENT PROCESS

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Abstract: Raman probe can be used to detect substances dissolved in water. Here are reported and discussed some experimental and data treatment processes needed to identify species and also to determine their content in a mixture. A particular attention is paid to the treatment of Raman line intensity used in the calibration of the probe.

Keywords: Raman sensor; pollutants; water quality control; calibration.

1. INTRODUCTION

Raman spectroscopy is a well known technique to analyze various substances in different states [1-3]. Only recently this tool was used to probe species in a more or less complex mixture [4-6]. It is possible to distinguish different substances since in principle each Raman line is associated to a vibration mode into a peculiar chemical bond. Thus substances with anions such as NO_3, NO_2, PO_4, HPO_4, and SO_4… can be identified by means of Raman spectroscopy. However the use of this technique as a quantitative probe of species is not easy and requires some careful procedures including normalization of the spectra and appropriate calibration. These aspects are reported in this paper, and the sources of precision and accuracy are discussed as well. Nitrates dissolved in water are used to illustrate our purpose, but the same approach can be applied to several substances diluted in aqueous solution.

2. QUALITATIVE APPROACH

Raman probe of a substance needs at first an appropriate choice of one peculiar Raman line in the spectrum, which should be well resolved, relatively intense and changing with the substance content. The both first conditions provide in principle the identification of a substance among others, from a line position or vibration frequency. Indeed the frequencies of internal vibrations of a molecule are specific to involved chemical bonds; however they depend on the environment of the molecule, the state of the substance, and external parameters such as temperature or pressure. Raman spectrum can be complicated due to the substance structure. In aqueous solutions of phosphates, nitrates, nitrites, sulphates, it is generally admitted that the Raman spectrum consists into own stretching and bending modes of H_2O, and internal modes of the active anion, less or more perturbed by cations, and/or hydroxyl groups, the number of lines depending on the symmetry of active molecule. The motions corresponding to internal modes of NO_3 are described in figure 1 ([3]) and the associated Raman lines are observed in Figure 1. All modes but the ν_2 vibration are Raman active. The vibrations ν_3 and ν_4 are degenerate modes in the free molecule.

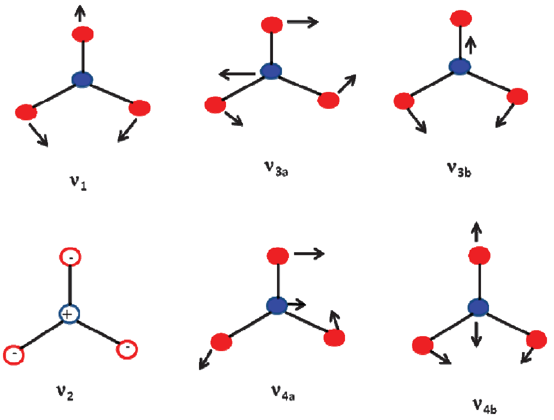

Fig. 1. Internal vibrational modes of nitrate ion.

Raman measurements were performed at room temperature using a Raman spectrometer RXN-1 from Kaiser Optical Systems, with an excitation source at 532 nm and a power at the sample of 71 mW. The Raman detector is a charge coupled device (CCD) camera of 1024 pixels cooled by liquid nitrogen to -40°C. The spectral resolution is about 2 cm^{-1}.

Figure 2 shows a typical Raman spectrum of sodium nitrate solution (1.18 mol/l or 100 g/l). A very intense and broad band between 3000 and 3800 cm^{-1} due to OH stretching is detected beside weak peaks corresponding to modes ν_3 and ν_4.

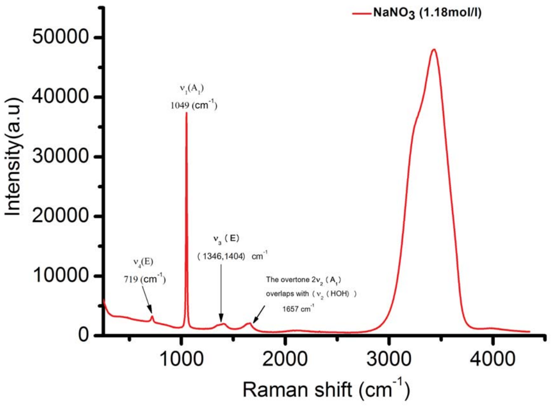

Fig.2. Raman spectrum of sodium nitrate solution.

In addition a sharp and intense peak is observed at 1049 cm^{-1} .This line corresponds to the symmetric ν_1 stretching (A_1 symmetry) mode of NO_3 molecule. This line is found to be specific to this molecule, as demonstrated in Figure 3 since its position is nearly the same (the shift is about 1 to 2 cm^{-1}) independently of the nature of cation (NH_4^+, Na^+ and K^+) and concentration of nitrate in water. This double property is of great importance in the context to use Raman spectroscopy in a sensor to probe various substances and to derive their concentration.

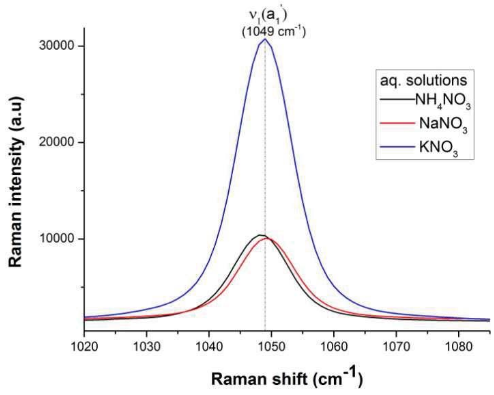

Fig.3. Raman line of ν_1 vibration mode for different nitrate aqueous solutions.

3. QUANTITATIVE PROCESS

Since the ν_1 mode is considered to be the specific and relevant signature of nitrate ion, the study as function of the concentration can be undertaken. The intensity of this peak is measured and its change with different parameters is studied. The objective of a Raman sensor [5] is to determine the content of different species in a mixture. It is based upon the fact that the Raman intensity is directly proportional to the number of active molecules N in the scattered cross section, [7] as:

$$I = K.N.\left(\frac{\partial \alpha}{\partial Q}\right)^2 .\nu_0{}^4.(n+1).I_0$$

where ν_0 is the frequency of the incident laser beam (which is much larger than the vibrational frequency), n is the Bose-Einstein (thermal population) factor, I_0 is the input laser intensity on the sample, $\partial\alpha/\partial Q$ is the polarizability derivative of the molecule (the value $\neq 0$ is required for Raman active vibration modes) and K is a proportional factor depending on experimental conditions related to the spectrometer, detector, recording time, collecting optics, scattering geometry…

The calibration can be established for each active anion as function of salt content expressed in mol/l. It is to be noted that even if in practice the content is often expressed in g/l, the calculations have to be done in mol/l. Thus, a single calibration of one kind of salt dissolved in water can be established regardless the nature of cation, according to Figure 3.

In Figure 4 is reported the dependence of ν_1 line on concentration for sodium nitrate solutions. It is observed that the position does not shift with NO_3 content and its intensity dependence is monotonous. Nevertheless this peak is not perfectly symmetric with appearance of a shoulder in the low frequency side of the peak, especially seen for small concentration range. This band is attributed to ion-pair formation [8]. Instead of the maximum intensity of the Raman peak, the integrated intensity is considered within the procedure to evaluate the content. This has two advantages: i) to involve the whole scattered signal even in the case of degeneracy lifting of molecule vibration ii) to discard the effect of spectrometer drift. Indeed a drift of 1 or 2 cm-1 with time is usual during one month, so that the maximum position can be shifted with respect to the expected value.

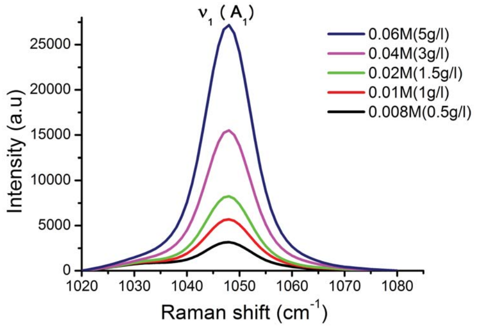

Fig.4. Evolution of the ν_1 Raman line with the concentration in nitrate aqueous solution.

Quantification requires two steps to prepare the calibration: the extraction of the true signal arising from the chosen vibrational mode, and then the normalization of the intensity of this peak. The first step consists to define the baseline in order to subtract the background from the peak signature. The question of the normalization is not easily solved. It is related to the fact that a change in the Raman intensity can arise from other sources than the active molecule content variation (see equation above).Thus the scattered intensity varies with any fluctuation in the laser source power or detector. Therefore it should lead to systematic errors in the determination of the concentration. As a consequence, a peak sensitive to these variations and independent of the substance under study has to be taken as reference in the spectrum. We can consider external and internal references. Internal standards arise either from the own OH Raman bands, or from the background. The external reference comes from the probe itself or from the Raman signal of a known substance added in the sample without any perturbation. Different solutions can be compared with their respective advantages and drawbacks. Figure 5 shows lines of an intrusive probe in sapphire which are lying beside the interesting peak associated to NO_3 molecule.

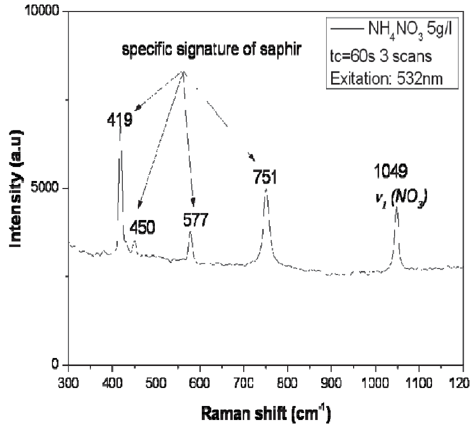

Fig.5. Sapphire peaks of the Raman probe used as external reference.

The intensity of the sapphire lines is varying with laser, detector, or recording time changes, and the normalization consists to divide the integrated intensity of the peak ν_1 by the intensity of one sapphire line. Then the proper calibration can be performed. For this, is established the dependence of the normalized integrated intensity on the nominal content of the dried salt derived from its weight measured before dilution in water. An example of this plot is reported in Figure 6.

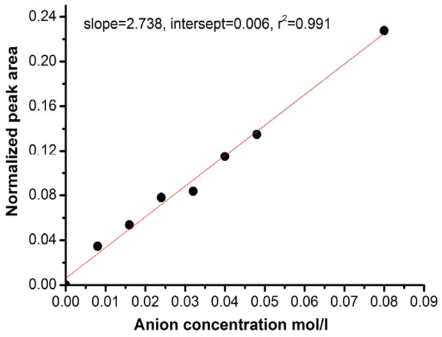

Fig.6. Normalized peak intensity vs the nitrate content.

4. ACCURACY AND PRECISION

We discuss here the different sources of error which can be considered in the intensity measurements and thus the determination of the substance content.

We can distinguish at first internal and external origins of errors. Among internal sources of error, we can consider error related to the choice of the line used as the substance signature, errors within the normalization and calibration processes, and the instrumental errors due to the instruments and experimental conditions [9]. A careful attention of conditions in the quantitative process within the data exploitation allows a reduction of some errors.

External errors are more difficult to be estimated since their sources are various. They come from physical or physico-chemical parameters influencing the signal to be treated. Thus waste water, or generally the matrix inside which the substance to be analysed is introduced, can affect the signal in the relevant frequency. Another perturbation can come from temperature change. If it is not controlled, temperature can cause a shift in the peak position, and a variation in its integrated intensity.

5. CONCLUSION

We reported on the study of Raman probe of nitrates dissolved in water. Firstly, among the different liners associated with the internal vibration modes of nitrate anion, we took one peak specific signature of the anion, which was then used for the determination of the salt content in water.

The various parameters allowing improving the resolution, the accuracy and the signal/noise were investigated. Raman probe was shown to be promising to get a simultaneous detection of several species in a mixture.

6. REFERENCES

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