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# Raman probe of chemical species diluted in water: technique reliability and estimation of uncertainty

Kawther Ben Mabrouk<sup>1,2</sup>, Thomas H. Kauffmann<sup>1,2</sup> and Marc D. Fontana<sup>1,2</sup>

<sup>1</sup>Université de Lorraine, Laboratoire Matériaux Optiques, Photonique et Systèmes, EA 4423, 2 rue E. Belin, 57070 Metz, FRANCE

<sup>2</sup>Supélec, Laboratoire Matériaux Optiques, Photonique et Systèmes, EA 4423, 2 rue E. Belin, 57070 Metz, France

marc.fontana@supelec.fr

**Abstract.** The soil and water preservation requires new sensitive techniques. Raman probe was recently shown to be an interesting alternative to electrical sensors to detect several contaminants diluted in water. Here we report on the procedure to reliably determine the substance concentration within a fairly good accuracy and a high speed.

## 1. Introduction

The access and the control of clean water is an important challenge for an always rising number of people through the world. This requires the detection of all pollutants in flow water, rivers, basins, lakes.... Nitrates, sulphates, and phosphates have to be specially sought since they are very water soluble and lead to negative incidence in the environment [1-3]. They arise generally from fertilizers used in agriculture. Their detection requires reliable and efficient techniques which are able to provide in situ and quick measurements [4]. Several techniques such as electric conductivity and calorimetric methods are used to detect nitrates and phosphates. Nevertheless despite their sensitivity, these analysis methods are off-lines and time-consuming since they need the preparation of solutions.

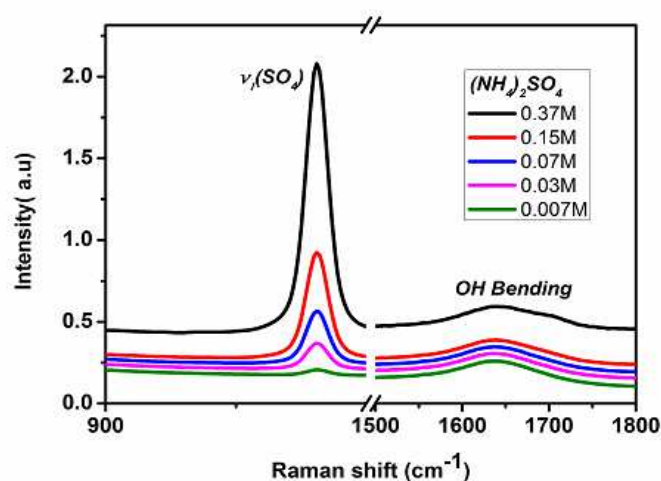
We have recently shown that Raman spectroscopy technique can detect the presence of several pollutants dissolved in water and the same probe is able to discern between nitrite and nitrate, phosphate, and di-hydrated phosphate, sulfate and sulfite [5]. Generally each detected substance has its own signature in the Raman spectrum, since it is assigned to one (or two) intense and well resolved peak [5, 6]. This ensures the great selectivity of the method compared with other techniques. Measurements were recorded at room temperature using a Raman spectrometer RXN-1 from Kaiser Optical Systems. The spectral resolution obtained with an excitation source at 532nm is about 2cm<sup>-1</sup>. The Raman detector is a charge coupled device (CCD) camera of 1024 pixels cooled by a Peltier device to -40°C. Measured power at the sample level is 71mW. The Raman light was backscattered

collected by the same specific probe, and filtered with a notch filter before being dispersed by a holographic grating.

Here we report on the procedure to render reliable this technique in order to determine the species concentration, and we discuss on the accuracy and precision.

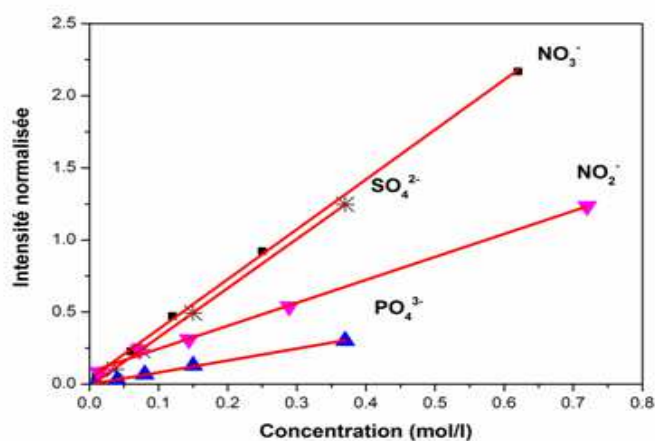
## 2. Calibration and determination of concentration

Since it is proportional to the number of active molecules of one species, the intensity of the Raman peak signature of one substance is used, after calibration, to the determination of the concentration. As shown in Figure 1, this intensity increases monotonously and generally linearly with the substance content. To avoid the effect of spectrometer drift the integrated intensity is in fact taken in the calculations. In order to achieve the reliability of the technique, the intensity has to be rendered independent of the sensor characteristics such as the laser, spectrometer and detector, and experimental parameters. For this, the peak intensity has to be normalized to internal references, i. e. lines of the spectrum which are unaffected by the sought substance, or external standards. Here the intensity is normalized to the intensity of the band corresponding to the OH bending vibration (see Figure 1). Since this band is nearly independent of the salt content, it can be applied as a trustworthy standard. Consequently the ratio noted *S* between these two integrated intensities is used, as the relevant parameter providing the calibration of the concentration



**Figure 1.** Raman spectra recorded in ammonium sulphate aqueous solution with different concentrations (in units M=mol/l)

In Figure 2 are reported the calibration achieved for different species as function of their concentration. It is to be noted that the slope reflects the sensitivity of the Raman probe to a peculiar substance.



**Figure 2.** Calibration of the normalized intensity of the Raman peak signature of different anions as function of their concentration.

### 3. Uncertainty calculation

According to the ISO GUM [7], the standard measurement uncertainty is evaluated via uncertainty of type A and type B as well. The uncertainty on the concentration determination arises from the calibration, the method and the substance titration [8]. The main source of error comes from the method i.e. the measurement of integrated intensity. In fact as explained above, we calculate the ratio  $S$  between integrated intensities of two bands (see Figure 1). and assuming a rectangular shape for these peaks we consider the uncertainty on the intensity maximum  $u(I)$  and the uncertainty  $u(w)$  on the fullwidth at half maximum (FWHM) of both bands. The relative uncertainty  $u(I)/I$  is linked to the S/N ratio and therefore increases for decreasing concentration. The quantity  $u(w)$  is mainly related to the spectrometer resolution. Applied to the determination of nitrate anion we find a standard uncertainty of 0.02 mol/l for a solution of 0.3 mol/l and 0.01 mol/l for a more diluted sample of 0.04 mol/l. External sources of error can influence the accuracy and precision of the method. Thus a change of temperature of the solution, and/or the presence of another species can affect the determination of the seek substance. Both cases are discussed and their effects are evaluated.

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