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Abilities of Raman sensor to probe pollutants in water

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Abstract. The control of water quality requires rapid and efficient monitoring techniques. A Raman sensor is shown to present interest for the analysis of chemical substances dissolved in water. The identification of chemical pollutants and the determination of their content as well are reliably obtained. The main characteristics and abilities of this multi-component Raman sensor are reported.

1. Introduction

Raman spectroscopy (RS) is a widely used technique to know the physico-chemical properties of a solid, liquid or gas, via the study of vibrational characteristics of molecules or ions [1,2,3]. Raman sensors appear only recently [4, 5]. They combine the determination of a physical parameter, as in any sensor, with the physical mechanism associated with this parameter. The position (mode frequency), the width (damping) and the intensity of a Raman line can be exploited in a Raman sensor.

The control of the water quality is a growing challenge in order to insure the access of water in healthy conditions to an always rising number of people through the world. This implies the obligation to detect all pollutants in flow water, rivers, lakes and tanks. Nitrates, sulphates, nitrites, chlorides and phosphates coming either from fertilizers used in agriculture or product manufacturing are specially pursued since they are very water soluble and have a negative incidence in the environment, leading to eutrophication and thus to asphyxia of aqueous ecosystems in rivers and lakes [6,7,8]. Electric conductivity, calorimetry, chromatography and UV spectrophotometry are used [9] to detect different species. Despite some advantages such as their cost and sensitivity, these methods are generally specific to probe one anion only. Moreover they are off-lines and therefore time-consuming techniques. Thus they do not fully respond to the need of continuous monitoring of soil and water. The question is if a Raman sensor could offer an alternative method to detect *in situ* several contaminants within fairly good accuracy and high speed. As RS is a non-destructive technique analysing only a small volume of a substance without needing any preparation, Raman sensors are in principle suitable for *in situ* and in real-time measurements. Here we demonstrate the abilities of Raman sensor to provide the detection of several chemical substances dissolved in water. In a first stage measurements are performed within laboratory conditions, in order to achieve the calibration and to check the reliability and efficiency of this technique. The characteristics of our sensor are briefly described. The main advantage compared with other techniques is its ability to probe simultaneously or successively several substances. The measurement of nitrates is given as an example, but sulphates, sulphites, phosphates, and nitrites can be detected with the same sensor [10].



2. Identification

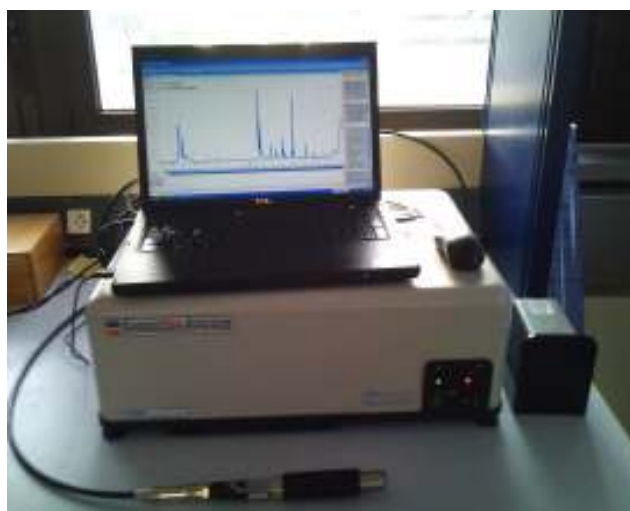


Figure 1. Raman spectrometric sensor.

Measurements were recorded at room temperature using a Raman spectrometer RXN-1 from Kaiser Optical Systems (see Figure 1). This Raman is a portable instrument designed for industrial applications. The spectral resolution obtained with an excitation source at 532nm is about 2cm^{-1} . 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 scattered light was backscattered collected by the same specific probe, and filtered with a Notch filter before being dispersed by a holographic grating. Spectra were recorded over the $150\text{-}4300\text{cm}^{-1}$ frequency range. Figure 2 shows the typical Raman spectrum of an aqueous solution of sodium nitrate compared with the spectrum obtained in pure water. A very intense and relatively sharp peak lying at about 1049cm^{-1} comes out from the nitrate spectrum. This line was shown to be the specific signature of the molecule NO_3^- , since it appears at nearly the same position in several nitrate salts.

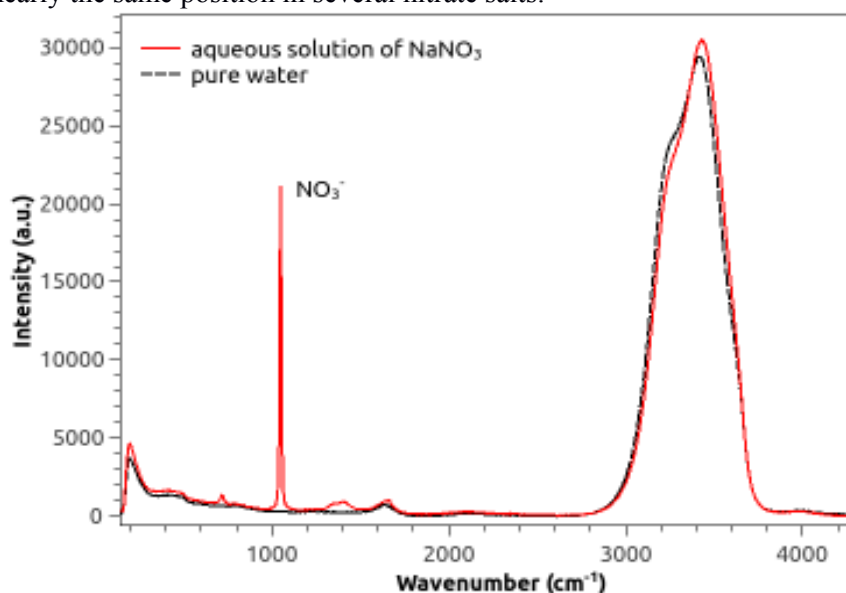


Figure 2. Raman spectra recorded in sodium nitrate aqueous solution, and in pure water.

In addition the line at 1049cm^{-1} can be clearly distinguished from the lines characterizing other salts dissolved in water, as shown in Table 1. The assignment of a Raman peak to a unique anion, consequently provides the simultaneous (or not) identification of several chemical substances in water

[10]. It proves the selectivity of the Raman sensor. Then the Raman peak taken to identify the anion NO_3^- in a mixture is used after an appropriate calibration, to determine its concentration.

Anions	SO_4^{2-}	PO_4^{3-}	HPO_4^{2-}	H_2PO_4^-
Main peak position in cm^{-1}	981	936	989	1076

Table 1. Main peak position of several anions in aqueous solution.

3. Calibration and determination of concentration

In Figure 3 is reported the main Raman peak recorded in solutions of sodium nitrates with different concentrations. It is shown that the position of this peak is unchanged whatever the salt content in water is. It is observed that this peak is not fully symmetric since a shoulder appears in the low-frequency side especially for low concentration. Therefore instead of the peak maximum, the intensity integrated over a wide wavenumber range ($1020\text{--}1070\text{cm}^{-1}$) was taken for the calibration process of NO_3^- .

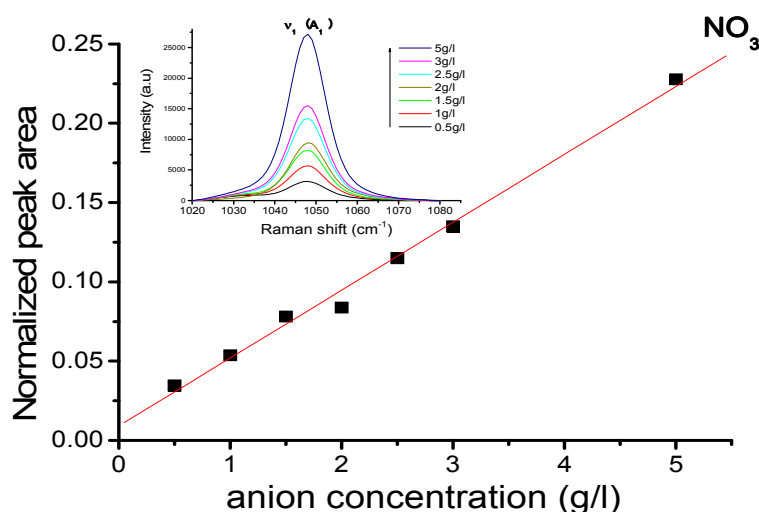


Figure 3. Calibration of the Raman intensity of the peak signature of the nitrate molecule as function of this concentration (expressed in g/l).

As in principle Raman band intensity is proportional to the number of molecules involved in the scattering process, the intensity of the peak signature of the sought substance can provide the substance content. In addition according to the Raman rules the molecule should be non-centro symmetric and highly polarisable, in order to enhance the Raman activity and sensitivity. In fact the absolute intensity is generally difficult to be reached since it needs to account in its calculation the characteristics of the spectrometer, the laser source and detector and all optical components as well. This is impossible in the *in situ* measurement conditions since the intensity depends on the external conditions as the temperature etc. Furthermore even the roughly measured intensity cannot be simply used, since it is affected by any fluctuation of the laser power, or any change in the experimental conditions. As a consequence the relative intensity of the peak normalized to the intensity of an extra band chosen as reference, is utilized in the calibration and determination of a substance concentration. The extra line denotes a peak in the Raman spectrum which is independent of the substance under study, but which is affected by any external perturbation likewise as the signature peak. Extra peak should be relatively intense and well separated from the signature peak. Two kinds of references can be considered. Internal references are provided by the solvent (here the water), or a product added in the mixture, that does not react with initial substances, and possess well known Raman lines. Sometimes external reference is given by the probe itself in the case of contact measurement, since the probe has its own Raman characteristic lines. In our study the OH band located around 1700cm^{-1} is retained, since it holds the above conditions for a suitable reference. It is to mentioned that the upper

frequency OH band around 3000cm^{-1} , even it is very intense, cannot be used as reference since affected by of the studied substance (see Figure 2, the intensity of this band changes with the presence of nitrate).

This point is particularly important in the measurement of very small substance quantities. This sometimes as demonstrated below, requires longer recording time. Fluctuations of power intensity or generally experimental perturbations during this time can lead to the same change in Raman intensity, as this induced by a small variation of substance content.

It is remarkable to note that this calibration holds for any nitrate in aqueous solution, regardless the cation. This was checked for dissolved sodium, ammonium and potassium nitrates. Then in order to reinforce the validity of the method, nitrate content in an aqueous mixture containing sulphates and phosphates as well was determined via the above calibration. The results of this blind test are reported in Table 2. They show a fairly good agreement between the expected value and the determined value issued from the calibration. However an error, of about 50mg/l (or 50ppm) arises from the detection of the sought substance (here the nitrate) in a complex mixture. The use of chemometrics techniques [11, 12] in the spectra analysis allows diminishing this error.

$[\text{NO}_3^-]$ by weight (mg/l)	200	400	600
$[\text{NO}_3^-]$ determined by our sensor (mg/l)	250	397	558

Table 2. Results of blind tests made on several nitrate solutions.

4. Experimental parameters

Here we briefly discuss on experimental conditions. The choice of the exciting wavelength of the laser in the Raman scattering process is of prime importance, since it strongly affects the sensitivity of the sensor. At first the wavelength is taken in the UV, visible (usually 532 and 633nm) or IR (generally 785 and 1064nm) to avoid the large fluorescence of the sample which can hide the Raman spectrum, and to limit the absorption. This is particularly important in the investigation of real samples since waste water which contains substances which obscure Raman signal. This leads to generally perform *in situ* measurements with an IR rather visible excitation. On contrary the use of shorter wavelength allows the enhancement of Raman intensity. In addition the choice of suitable spectrometers and detectors has to be done. A spectrometer with high resolution is necessary for the detection of narrow peaks and/or the separation between different substances in a mixture. Nevertheless, according to the aims required in terms of accuracy and precision, a spectrometer with a poor resolution, (i.e. 5cm^{-1}), and therefore cheaper, can be sufficient. CCD detector also affects the sensor efficiency the equipment. More generally the signal to noise ratio has to be improved. Finally experimental conditions can require the choice of the contact- or contactless-probe, which strongly affects the sensor ability. All these parameters affect the accuracy and precision of the sensor [13].

The main limit in the Raman sensor efficiency in the determination of substance content comes from the fact that the intensity is proportional to the number of molecules scattered by the light, and this number is obviously small if the substance content is weak. Different alternative Raman techniques can partly solve this problem- resonance Raman scattering or surface enhanced Raman scattering [14] – but they are heavier to be implanted and present other drawbacks, such as the nonlinear signal response. However the Raman intensity can be enhanced even within conventional Raman technique. One solution consists into the increase of measurement recording time. Compared with other methods Raman spectrometry has the advantage to provide signal in a few seconds, an increasing measuring time is acceptable. Figure 4 displays the time dependence of the limit of detection LOD, defined by the criterion $\text{SNR}=2$ (Signal to Noise Ratio). LOD can be pushed down by increasing recording time. It is observed that the limit of water drinkability (50ppm) can be reached by a measurement during 2min , which remains reasonable. This result is obtained with a 70mW power source. This time could be reduced if using a larger laser power, but this should induce additional random error related to the intensity instability. Thus compromise between different parameters has to be achieved in order to improve the sensor according to the requirements of the application [10].

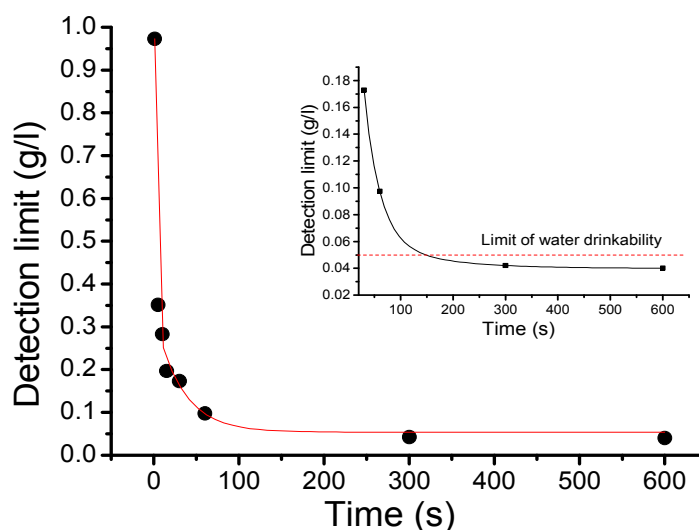


Figure 4. Recording time dependence of the limit of detection. The concentration of nitrate corresponding to the water drinkability is reported for comparison

5. Conclusion

We demonstrated the interest of Raman sensor for the detection of chemical substances dissolved in water. The assignment of well-defined and intense Raman peaks to most frequent anions was achieved, assuring the sensor selectivity. After calibration of various pure substances, the identification of one species in a complex mixture and its concentration determination proves the validity of the technique, firstly within laboratory conditions. Future investigations will concern the measurement of very small quantities by reducing the detection limit, and the application to waste water.

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