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DETECTION OF POLLUTANTS DISSOLVED IN WATER BY RAMAN SPECTROMETRY PROBE

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Abstract: The paper is devoted to the abilities of Raman probe to detect simultaneously several salts diluted in water. It has shown that this probe can be used for in situ monitoring of pollutants in waste water.

Keywords: Raman sensor, optical detection, pollutants**.**

1. INTRODUCTION

The control of the quality of water is a growing need in our modern societies in order to insure the access of water in healthy conditions to an always rising number of people through the world. This leads to the obligation to detect all pollutants in flow water, rivers, basins, lakes… [1]. This challenge requires new and efficient techniques which are able to provide in situ and quick measurements.
Nitrates, sulphates, and phosphates have to be specially purchased since they are very water soluble and lead to negative incidence in the environment. They arise generally from fertilizers used in agriculture [2,3].

Numerous techniques have been used to detect anions SO_4^{-2}, NO_3^-, and HPO_4^{2-} such as electric conductivity [4] and calorimetric methods [5,6]. Despite the performances, these methods are unable to respond to the increasing conditions needed for the soil and water preservation. Indeed, technologies allowing long-term continuous monitoring are more and more required to detect in situ several contaminants within a fairly good accuracy and a high speed. So far, the analysis methods generally used are sensitive but off-lines and time-consuming which therefore need the prelevment of solutions.

Here our aim is to show the abilities of Raman sensors to detect the presence of several pollutants dissolved in water and to determine their concentration as well. Raman scattering is a well known spectroscopy technique useful to study the vibrational properties of molecules in a material. The main advantages of the technique are the speed of measurement and the fact that it does not require any special preparation of the medium to be analysed. Moreover Raman systems involving diode lasers CCD detector and fiber-optics probes become more and more cheap, robust and portable. Only recently Raman sensors have been developed to provide some parameters linked to the change in the Raman spectrum. Thus was reported a new Raman sensor of NaCl in aqueous solution [7-9]. This probe is founded on the detection of the change of OH stretching peak which is caused by the introduction of sodium chloride in water.

2. RESULTS

Here we performed Raman measurements in various dissolved salts of nitrates, sulphates, and phosphates and the peculiar influence of anion, and cation and H_2O on the spectrum of each substance was analysed. Measurements have been done with a 532 nm exciting line using a spectrometer Kaiser RXN1 within a resolution of 2 cm^{-1}. The main question is the ability for such a sensor to discriminate between the different substances. It is seen in Figure 1 that an own signature can be detected by Raman probe for each kind of anion in different spectral ranges. This means that peculiar lines of the Raman spectrum can be used as a fingerprint-like of the presence of SO_4^{-2}, NO_3^- or HPO_4^{2-}, as a consequence, the concentration of each salt in water can be deduced from an appropriate calibration.

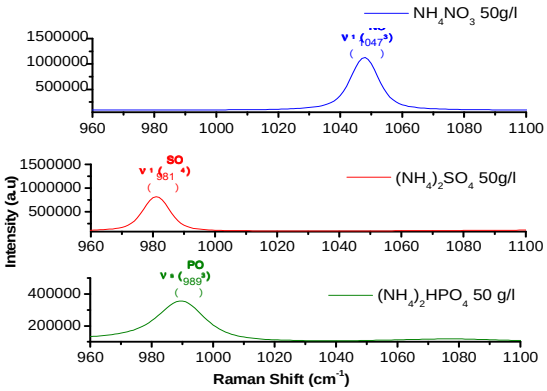

Fig. 1. Specific Raman signatures of nitrate, sulphate and phosphate anions.

Figure 2 shows the concentration dependence of the peak associated to the vibrational mode within the anion NO_3^-. The calibration of the Raman probe was achieved by recording the integrated scattered intensity of this line as a function of the concentration varying between 5 and 0.5 g/l and prepared by titration. A linear law was obtained.

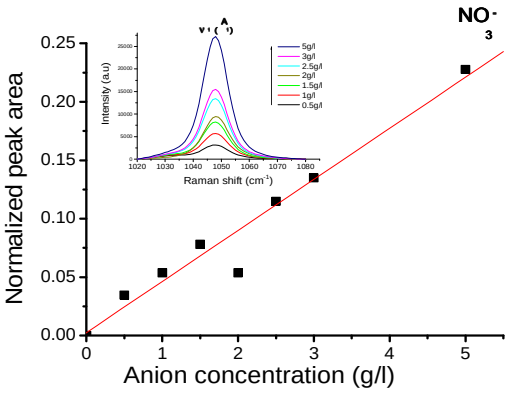

Fig 2. Nitrate content dependence of integrated Raman intensity. The insert shows the behavior of the relevant part of the Raman spectrum exhibiting the ν_1 vibrational line as a function of concentration.

In a second step the complex mixed solutions in waste water including several pollutants have been studied and analysed from the data sources obtained in the pure substances. An example of spectrum is shown in Figure 3. Although the spectrum is more complicated an assignment of main peaks could be achieved so that a separation of the signature of each pollutant is nevertheless possible.

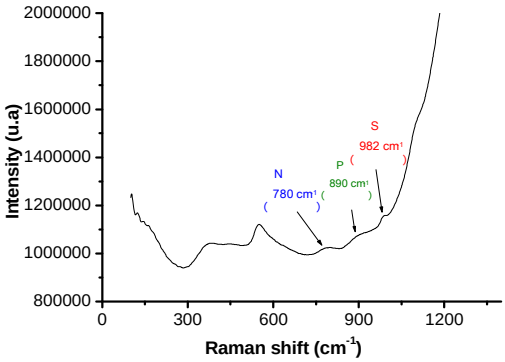

Fig. 3. Raman spectrum recorded in waste water. Arrows indicate the species N (nitrate), P (phosphate) and S (sulphate).

For each particular purchased pollutant, the influence of additional salts was studied and the sensitivity and the accuracy of our probe were evaluated. The influences of several measuring parameters such as laser source (power and wavelength) acquisition time, contact or contactless probe…were successively investigated

3. CONLUSION

We reported on the study of Raman probe of various pollutants like sulphates, phosphates, nitrates dissolved in water. Each salt was first separately and carefully investigated Then the abilities to get a poly-detection sensor was discussed. The various parameters allowing improving the resolution, the accuracy and the signal/noise were investigated. This probe was shown to be promising to get a simultaneous detection of several species in a mixture.

4. REFERENCES

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