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WATER POLLUTION DETECTION

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Abstract: Human activities are, more or less directly, responsible of the increasing pollution in running waters, making their pollution an important issue over the last decades and the ones to come. Many documents define a legal frame on the water pollutants (classifying them depending on their toxicity, environmental impacts or origin), thus underlying the importance of the surveillance of their presence in the environment. The difficulty for the surveillance of these products is the great diversity of pollutant families, leading to the necessity to use several analytical techniques. This paper shows the possibility of using Raman spectrometry for the detection/quantification of several pollutant families in an aqueous media (drugs, pesticides, or salts coming from the fertilizers).

Keywords: Raman spectroscopy, water pollution, phytosanitaries, drugs, nitrates.

1. INTRODUCTION

The increase of the pollution of water courses in many countries emphasizes the importance of its surveillance. Indeed, the environmental media, and waters more specifically, are polluted with thousands of pollutants which can have severe environmental impacts. An example of the water's pollution impact is the phenomenon of lake eutrophication provoked by the algae proliferation due to large quantities of fertilizers dissolved in water (Figure 1).

Fig. 1. Example of lake eutrophication.

More and more documents define a legal frame on the water pollutants (classifying them depending on their toxicity, environmental impacts or origin), thus underlying the importance of the surveillance of their presence in the environment. Several pollutant families are more specifically aimed by these legal documents; the drugs and the pollutants of the agricultural activities (pesticides and fertilizers) are nowadays at the top of the list.

The quantification of pollutants in a water media is mostly done by ionic chromatography followed by a measurement of the electric conductivity. Even though the combination of these techniques offers good detection limits (generally below 1 mg/L), it is not appropriate for *in situ* measurements, and can not answer to the increasing need of continuous monitoring. The use of a spectroscopic technique for the water pollution detection is nowadays under investigation [1].

The aim of this work is to investigate the possibility of using Raman spectrometry as a mean for the water pollutant detection and quantification. Indeed, this technique is known to be particularly adapted for the analysis of aqueous solutions [2], and can easily be used for *in situ* measurements thanks to portable spectrometers. For this purpose, a bibliography research permitted to identify the pollutant families that are considered as most important to survey (due to their frequency and quantity of usage and their impacts). For each family, several species were chosen as representative, and were then studied by Raman spectroscopy.

2. POLLUTANTS OF INTEREST

2.1. Drugs

The main source of drugs in the natural water courses are human urines and dejections from animal breeding areas. In France, it is estimated that 30 000 tons of drugs are not used each year, and only 13 000 tons are recovered by the drug stores. The remaining 17 000 tons of unused drugs are thrown in the garbage, and ultimately end up in natural water sources by infiltration in soils and water flows.

The surveillance of the drug rejections in the water flows is becoming an important issue, especially in France which was for a long time at the top of the drug consumers in the world. Even though France is today in the average of drug consumption, the quantity of drugs used is still in constant increase. A study performed in 2011 by the ANSES (National agency of sanitary security) thus showed that a quarter of water samples tested contained traces of drugs. Even when present in traces, these products can induce severe environmental impacts and are thought to be the origin of the decrease of aquatic fauna and of the feminisation of certain populations (due to the bio-accumulation of oestrogen). This led the French ministries of Ecology and of Health to set a national plan on residual drugs in water [3].

2.2. Pesticides

The pesticide consumption in France achieved 71 600 tons in 2006 [4]. France is hence the pesticide consumer n°1 in Europe and n°4 in the world, and 95% of the pesticides is used for agricultural purposes. Furthermore, according to certain studies, 90% of applied phytosanitaries are directly scattered in soils and waters. By taking into account that in France each year over 70 000 tons are applied, the necessity of their surveillance in the environment becomes obvious.

In order to diminish the quantities applied, a “Zerophyto” plan has been set to place in French communities with the support of local Water Agencies. The French state also presented “Ecophyto2018” plan, with the objective to diminish the use of pesticides by 50% in ten years. The development of techniques permitting their surveillance in the environment is a growing need.

2.2. Fertilizers

The fertilizers contain important quantities of nitrates or phosphates, and the agriculture presents the origin of 66% of nitrates and 23% of phosphates that can be found in water courses [5]. The pollution of waters by the nitrates and phosphates of agricultural origin is nowadays well known. These species being the nutritive elements for the aquatic vegetation, they induce their excessive development, the eutrophication, leading to asphyxia of aqueous ecosystems in rivers and lakes.

The environmental impacts of these products led to the establishment of several directives and decrees in France and throughout Europe with the aim of surveillance of their presence in the environment [6-8].

3. SPECTROSCOPIC METHOD APPLIED

Raman spectroscopy (RS) gives us an information on the vibrations of bonds that are present in the analysed material, giving an insight on the material's chemical composition and structure. In RS, the spectrum contains peaks (or “Raman lines”) whose different characteristics give different qualitative and quantitative information (Figure 2). Hence, each peak corresponds to a specific vibration of one chemical species.

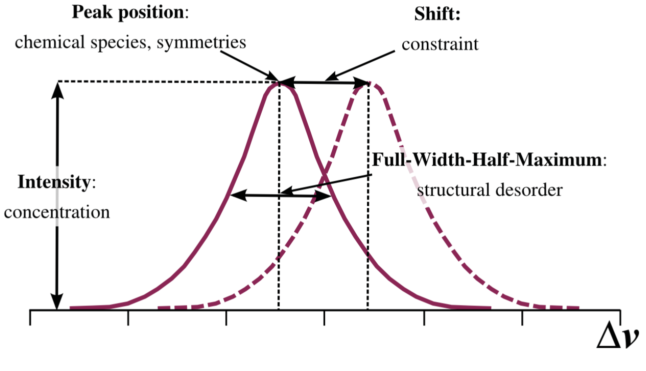

Fig. 2. Qualitative and quantitative information that can be extracted from a Raman spectrum [9].

The position of the maximum of the peak in the spectrum can permit the identification of the chemical species in question. Since one chemical species can vibrate in different ways (stretching, bending, rocking, …), it usually presents several Raman lines (different vibrational modes).

The intensity at the peak maximum, on the other hand, can be directly related to the corresponding species' concentration. Indeed, even though the intensity of a peak depends on experimental conditions such as the laser beam power or the parasite light, by using the normalized integrated intensity of Raman lines, it is possible to follow the relative changes in the integrated intensity induced by the species' concentration.

A method based on the calculation of the integrated scattered intensities of selected peaks was developed for the water pollution application. The analysis of polluted solutions of known concentrations served for the identification of each pollutant' characteristic peak(s). For each pollutant, one specific peak was chosen and then used for the establishment of a specific calibration curve for the concentration determination.

4. POLLUTANT ANALYSIS

Raman spectroscopy was used for the analysis of aqueous solutions of several pollutant families: drugs, pesticides, fertilizers. For each family, a specific pollutant was chosen according to its frequency of use in France, and used as a reference.

4.1. Pollutants analysed

Among the most critical drugs in France are the hormones coming from contraceptive pills, and the anti-inflammatory drugs. Therefore, the CÉTÉ de l'Est launched a study on the ethinylestradiol, the hormone present in the majority of contraceptive pills [10], and niflumic acid was chosen as a reference for the anti-inflammatory drugs.

For the family of pesticides, only one product was chosen as a reference pesticide, the glyphosate. This product is on top of the list of the pesticides which are most commonly used. A study conducted by IFEN on surface waters in France in 1997/1998 showed that 80% of samples contained glyphosate [11].

The last pollutant family analysed by Raman spectroscopy corresponds to the salts issued from the fertilizers used in agricultural activities. As the fertilizers used are numerous, a specific attention was devoted to the study of synthetic nitrates and phosphates [12]. These salts are the main constituents of the fertilizers and represent the main cause of the appearance of the lake eutrophication.

4.2. Spectroscopic signatures

Raman analysis was performed on dissolved pollutants with a BWTek iRaman spectrometer with a 532 nm excitation wavelength. The Raman spectra obtained for aqueous solutions reflect the complexity of the product analysed.

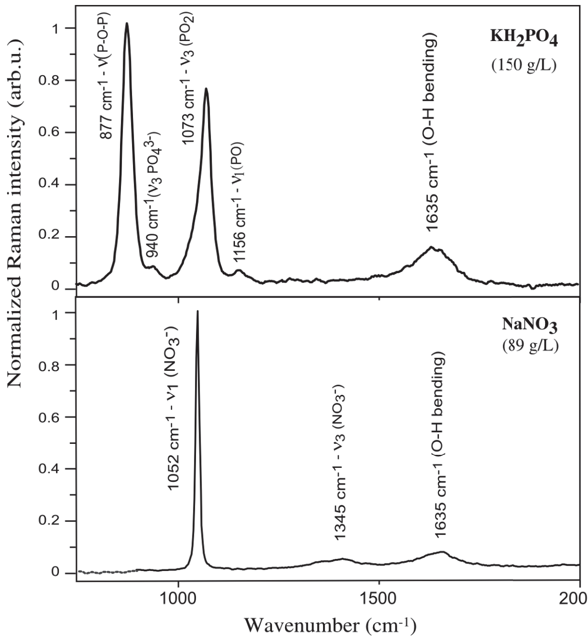

Fig. 3. Raman spectra of dissolved potassium phosphate (up) and sodium nitrate (down) obtained at room temperature (20°C).

For the case of dissolved synthetic salts (potassium phosphate and sodium nitrate – Figure 3), there is only a few characteristic peaks for each species. Hence, nitrates present two peaks in the 750 – 2000 cm^{-1} frequency zone. The phosphates, on the other hand, present more peaks, two of which are predominant. For the elaboration of the calibration curve, it is therefore possible to use either one of them.

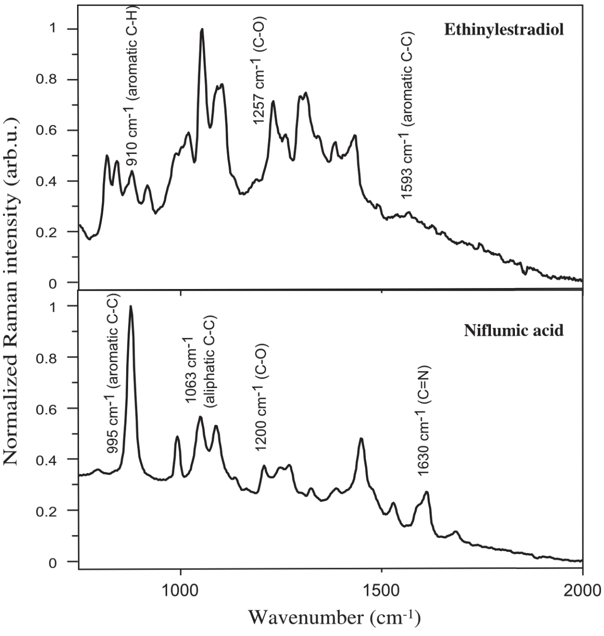

Fig. 4. Raman spectra of a dissolved contraceptive pill - ethinylestradiol (up) and a drug based on niflumic acid (down) obtained at room temperature (20°C), and the designations of their characteristic peaks.

When the study is based on more complex products, their Raman spectra are much richer. This is the case of drugs, where, besides the main molecule, there are numerous other components that are present. A further analysis of their Raman spectra is therefore necessary in order to identify the peaks that are characteristic of the main molecule and that is of interest for the definition of each pollutant's spectral marker. Raman spectra of a contraceptive pill whose main component is ethinylestradiol and a drug based on niflumic acid are presented on Figure 4. On the spectra is presented the identification of the characteristic peaks, other peaks corresponding to vibrations of other components of the analysed drugs (such as magnesium stearate or talc).

4.3. Elaboration of calibration curves

The identification of Raman specific signatures can be used for the establishment of a calibration specific for each chemical species. The calibration curves are hence obtained by focusing on the integrated scattered intensity of the specific Raman peaks. For that purpose, solutions with different concentrations of dissolved products are prepared, and each one of them is analysed by Raman spectroscopy. The plot of the spectral marker (based on the characteristic peak's scattered intensity) as a function of concentration gives the calibration curve for the analysed species.

As an example, Figure 5 presents the Raman spectra of solutions with different concentration of dissolved sodium nitrate, and the calibration curve obtained by the exploitation of the acquired data.

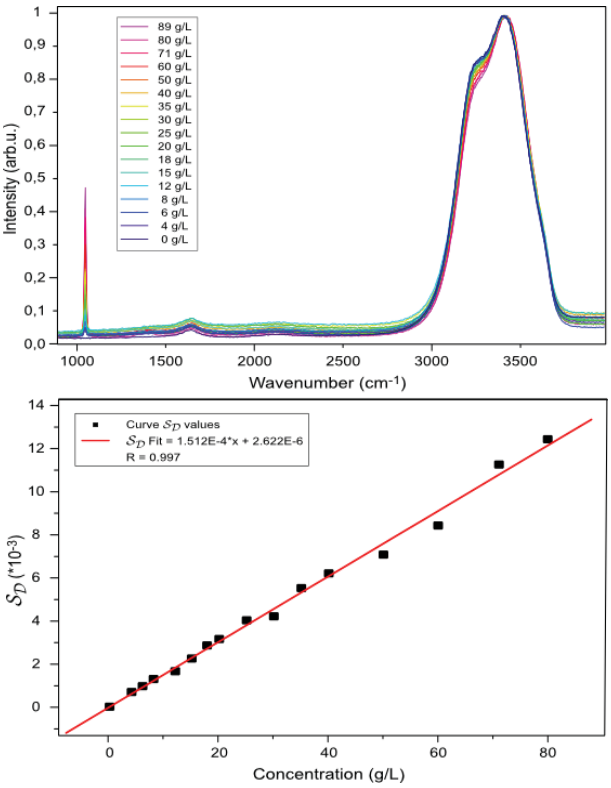

Fig. 5. Concentration influence on Raman spectra obtained for aqueous solutions of sodium nitrate at room temperature

(20°C) and standard pressure (up) and calibration curve obtained experimentally (down).

The calibration curve was obtained by the follow-up of the peak located at 1052 cm^{-1} which corresponds to the symmetric stretching of the NO_3^- species. With this approach, the minimal concentration of nitrates that can be detected in waters is close to the potability limit, which is 50 mg/L for the nitrates. For the phosphates, the limit of detection was estimated to be 100 mg/L.

The same spectroscopic approach was led on drugs and pesticides. The calibration curves obtained for niflumic acid and glyphosate are presented Figures 6 and 7. For the niflumic acid, the integrated scattered intensity of the peak at 995 cm^{-1} (corresponding to the molecule's aromatic C – C vibrations) was chosen for the definition of a specific spectral marker (Figure 6). The calibration curve for glyphosates (Figure 7) is obtained by the calculation of the integrated scattered intensity of the glyphosate's peak located at 1194cm^{-1}, corresponding to C – NH – C vibrations.

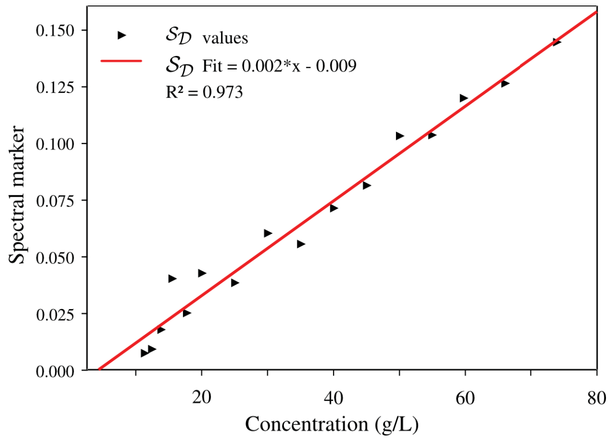

Fig. 6. Calibration curve for the niflumic acid, obtained by the calculation of a spectral marker representing the concentration impact on the integrated intensity of the 995 cm^{-1}.

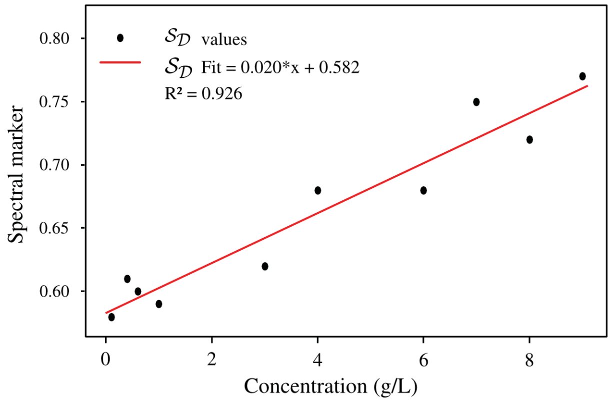

Fig. 7. Calibration curve of the glyphosate, obtained by the follow-up of the integrated intensity of one of its characteristic peaks, at 1194 cm^{-1}.

The calibration curves for the niflumic acid and glyphosate follow a linear law and permit the determination of these product's concentration down to 1g/L.

5. CONCLUSIONS

Raman spectrometry was used for the analysis of several water pollutants. The first results obtained for nitrate aqueous solutions are rather encouraging, and permit to detect the quantities that are usually found in the water courses. The limit of detection of our spectroscopic method for the nitrates is close to the potability limit (50 mg/L). The drugs, on the other hand, are usually present at concentrations of a hundred ng/L. Our technique does not permit to detect such low quantities (for the case of niflumic acid, its quantification limit is 1 g/L). However, Raman spectra of these products are rather rich and present many possibilities of data treatment. The use of chemometric can therefore permit a better spectral analysis and an improvement of the data treatment (work that is currently in progress), which could lead to significant improvement of detection limits. Raman spectroscopy is thus shown as a possible and efficient mean of water pollutant detection and quantification.

6. AKNOWLEDGMENT

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