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Water monitoring by optofluidic Raman spectroscopy for in situ applications

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A B S T R A C T

The feasibility of water monitoring by Raman spectroscopy with a portable optofluidic system for in-situ applications has been successfully demonstrated. In the proposed approach, the sample under analysis is injected into a capillary nozzle in order to produce a liquid jet that acts as an optical waveguide. This jet waveguide provides an effective strategy to excite and collect the Raman signals arising from water contaminants due to the high refractive index difference between air and water. The proposed approach avoids any necessity of liquid container or flow cell and removes any background signal coming from the sample container commonly affects Raman measurements. Furthermore, this absence is a significant advantage for in situ measurements where fouling problems can be relevant and cleaning procedures are troublesome. The extreme simplicity and efficiency of the optical scheme adopted in our approach result in highly sensitive and rapid measurements that have been performed on different representative water pollutants. The experimental results demonstrate the high potentiality of our device in water quality monitoring and analysis. In particular, nitrate and sulfate are detected below the maximum contamination level allowed for drinking water, whereas a limit of detection of 40 mg/l has been found for benzene.

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1. Introduction

The availability of global freshwater resources is diminishing due to ever increasing population, pollution and wasteful use of water. A wide range of human and natural activities affects the quality of the remaining worldwide drinkable water. The discharge of toxic chemicals from industry plays an important role in the pollution of water resources, but it is not the only responsible for the loss of freshwater resources. The presence of nutrients in waterbodies represents one of the main cause of water quality pollution.

The occurrence of ionic nutrients in waste waters as for instance phosphates, nitrates or sulfates can induce an abnormal growth of plants and phytoplankton. This anomalous development takes place at the expense of other life forms due to the consequent reduction of oxygen content dissolved in water (eutrophication) [1].

The access to safe drinking water and the preservation of the existing water resources are strongly related to the possibility to effectively detect water pollutants, often at trace level, providing, at the same time, on-site detection. Several analytical techniques

are used to detect chemical species of interest in water monitoring as for instance, UV spectrophotometry, chromatographic techniques or electroanalytical techniques [2].

In addition to mature technologies used for the detection of contaminants in water systems, in recent times, microfluidic and optofluidic approaches, are also gaining importance in water pollution detection [3–5] as also biosensors such as immunosensors [6].

Despite some advantages offered by both recent and consolidated technologies, such as their sensitivity and sometimes their cost, most of these approaches present the detrimental characteristic to be specific for the detection of a particular water contaminant. In addition, they often require off-site experimental activity. For this reason, these methods are considered too time consuming in order to provide effective and timely response to protect the public health [7]. Instead, a reliable in-situ detection of trace chemicals should be matched by a reasonable cost and by the use of a single analytical technique.

The vibrational spectrum provides rich information on the chemical composition of the sample. Then vibrational spectroscopy (VS) offers the possibility to simultaneously detect different water pollutants.

For this reason, in the past decades, VS attracted lots of interest in the scientific community because of its potentiality in water quality monitoring. Beside the wide detection range of chemical

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and microbial contaminants, VS requires minimum sample preparation and it is a fast technique [8,9].

Among VS techniques, Raman spectroscopy (RS) and infrared spectroscopy (IRS) are frequently employed as analytical techniques because of their ability to identify molecules due to the specificity of its spectrum. In some way, RS can be considered as a complementary technique with respect IR spectroscopy as the origins of Raman and IR spectra are different. In particular, a vibration is Raman-active if there is a changing in the polarizability of the molecule during the vibration, whereas a vibration is IR active if there is a change in the molecule dipole moment [10].

Due to the technical progress, in the last years, the analytical capabilities of Raman spectroscopy have significantly improved [11,12].

Today Raman spectroscopy is an analytical technique considered mature enough for the water analysis as evidenced by the literature results [7]. This is true in particular for high performance instruments in laboratory environment but less for portable Raman systems. In fact, due to the low cross sections of Raman transition, RS suffers from a low sensitivity, hence affecting the device sensitivity, especially in portable sensors where compact and low cost detectors are usually employed. This drawback is emphasized by the presence of background noise coming from the fluorescence or Raman signals arising from the solution containing walls [13].

The use of liquid core waveguide (LCW) was proposed in the 70's in order to increase the sensitivity of devices based on RS [14]. In this approach, total internal reflection (TIR) arising between the liquid material under analysis (core) and the capillary material used to contain the solution (cladding) was used to effectively collect Raman signal towards a detection system. The major progress in LCWs has been the employment of Teflon AF2400 as cladding material [15]. Having a refractive index n=1.29, this material enables the use of water solution as a liquid core material. In spite of high improvement with respect measurements performed with standard cuvettes [16], Teflon AF2400 exhibits autofluorescence at some wavelength excitation [17], hence cumbersome background subtraction could be required. Hollow core photonic crystal fibers (HCPCFs) are considered a promising approach to enhance the Raman signal. As a consequence of their photonic band gap, HCPCFs enable strong light-matter interaction which is responsible of a Raman signal increase. Unfortunately, practical reasons as reusability or slow filling process by capillary action seem to prevent, at the moment, their use in portable device [18].

Surface-enhanced Raman spectroscopy (SERS) is an emerging technique in which RS is enhanced, as much as 10^6 to 10^7, by absorbing analytes on roughened metal surfaces or colloidal metal particles.

There is growing interest about the potential use of SERS for contaminants detection [19,20] and portable Raman systems based on SERS are nowadays commercially available [7,21,22]. The main advantage of SERS in water quality monitoring is the achievable limit of detection (LOD). This value is often well below the maximum contamination level (MCL) allowed for drinking water which is set by the US Environmental Protection Agency (EPA) [7] or by the World Health Organization (WHO) [23]. However the design of a portable device based on SERS and able to detect a wide range of water pollutant could be severely limited by intrinsic factors. The SERS effect is strictly dependent on the substrate, hence this, in some case, interference with other chemicals could limit the ability to interact simultaneously with different anions [24,25].

Moreover, the reversibility of the substrates is not always obvious as also their fouling resistance. Furthermore, the implementation of SERS as a practical detection method is still limited to the lack of a method for fabricating stable and reproducible substrates. Due to the present limitations on batch fabrication, a large number of fabrication method for SERS substrates reported in literatures are considered not suitable for the environmental analysis both in lab and in field [26]. In addition, the SERS signal is not necessarily linear with respect to the sample concentration, thus complicating the sensor calibration [25].

For all these reason, despite the high potentiality in environmental monitoring, SERS, at present time, seems a technique suitable for monitoring the presence of a known SERS-active contaminant, but normal RS represents a more attractive approach for the identification of unknown contaminants in multicomponent systems [24].

In this work an efficient and reliable approach for RS is exploited for the realization of a device for in-situ measurements. In order to increase the weak sensitivity of RS, the portable device exploit water jet as liquid waveguide [27]. In some way, the proposed method reshapes the concept of LCW by replacing the cladding material with the air. This experimental solution provides collection and excitation efficiency of the sample, unattainable with similar approaches based on TIR as it will be shown in the next session. Furthermore the absence of solid walls used to contain the solution under analysis, allows to eliminate also the background signals coming from cuvettes or flow cells that usually affect Raman measurements.

At the same time, the absence of any system to contain the solution under analysis avoids time consuming cleaning actions or the use of a large number of sample container. Both this advantage are particularly attractive for in-situ activities.

2. Material and methods

2.1. Working principle and sensor design

The strategy approach to increase Raman signal detection, with respect different method based on RS, is an optofluidic water jet waveguide [28]. A liquid jet is a stream of a liquid material having approximately a columnar shape. This liquid column, exiting for instance from a capillary nozzle, will break up into droplets due to surface tension. In this breakup process, different forces will act and oppose to the action of surface tension: viscous, inertial and gravitational forces. Viscous forces are responsible of the damping in the growth of the deformations of the liquid column that lead to the jet pinch off. Inertial forces support the formation of a long liquid column as also the gravitation can contribute to elongate a falling liquid thread in opposition to the action of the surface tension.

For a specific liquid and nozzle diameter, different regimes can be observed, depending on the liquid flow rate. At slow liquid velocity, the dynamics of the fluid is dominated by a balance between surface tension and inertial forces leading to the so called "dripping regime" and no jet is observed. The droplet size is influenced by the nozzle size [29].

An additional increase of the liquid velocity, if suitably large such that the liquid surface energy is overcome by its kinetic energy, it will lead to a liquid jet formation. This threshold velocity can be expressed in terms of Weber number (We) as [30]:

$$We = (\rho r v^2)/\gamma > 4$$

Where ρ is the liquid density, r is the radius of the jet, v is the liquid velocity and γ is the liquid surface tension. The liquid jet preserves a regular cylindrical shape up to a specific length called "breakup length" , and then it breaks into droplets. There is a linear regime where, an increase of the jet velocity corresponds to an