OPTOFLUIDIC RAMAN SENSOR FOR ETHANOL DETERMINATION

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Abstract – A compact optofluidic sensor based on liquid jet waveguide has been developed and applied to detect alcohol contents in liquids. Raman spectroscopy improvement is demonstrated thanks to the waveguiding nature of a jet stream. Low detection limits of ethanol in water has been demonstrated (0.34%). The proposed method provides high excitation and collection efficiency of the sample under analysis, avoiding, at the same time, background noise that commonly affects Raman spectroscopy of liquids.

Keywords: liquid jet waveguide, Raman spectroscopy, ethanol, optofluidic waveguide.

1. INTRODUCTION

The production of alcoholic beverages represents a significant part of the present-day food industry. Quantification of ethanol content in liquids is particularly significant in food science as this determination interests both fermentation process monitoring and quality control of alcoholic beverages.

Several methods are available for the determination of ethanol in beverages. Those methods include, for instance, liquid chromatography [1] amperometric sensor [2], mass spectrometry [3], near infrared spectroscopy and Raman spectroscopy [4], fluorimetry [5] and colorimetry [6]. However, most of them make use of expensive and sophisticated instrumentation or they require time consuming procedures.

Instead, in routine analysis and process control high speed, degree of automation and cost-effectiveness are key parameters evaluable for the sensing approach.

Among the existing methods for the determination of ethanol in beverages, Raman spectroscopy offers several advantages.

For example, sample preparation is not required for Raman spectroscopy, which simplifies on-line quantitative analysis. Moreover, since the band intensities caused by OH stretching vibrations are weak in Raman spectra, a water-rich sample can be analyzed directly.

Nevertheless, Raman spectroscopy, due to the low cross sections of Raman transition, often requires the use of high performance benchtop laboratory spectrophotometer.

In this work an effective but simple approach is exploited for the realization of a compact sensor for Raman spectroscopy. The use of a jet waveguide permits an enhancement of the signal excitation and collection with respect conventional approaches for Raman spectroscopy [7].

2. OPTOFLUIDIC SENSOR

The presented optofluidic sensor relies its performances on the properties of liquid jet waveguides. Those waveguides can be easily produced by pumping a liquid into a capillary if the liquid velocity is greater than a threshold velocity. This threshold value depends on the liquid density, the nozzle diameter and the liquid surface tension [8].

If the fluid has an adequate velocity, the jet (i.e. a regular column of liquid) will be formed up to a specific length, named breakup length. Instead, beyond this breakup length, the fluid will give rise to the formation of drops.

The threshold of the fluid velocity is often expressed in terms of Weber number (We) i.e. a parameter describing the ratio of inertial forces to surface tension forces [8]:

$$We = (\rho r v^2)/\gamma > 4 \qquad (1)$$

Where r is the radius of the jet, ρ is the liquid density, v is the liquid velocity and γ is the liquid surface tension.

For fluid velocity higher than the threshold, the liquid jet preserves a regular cylindrical shape up to a specific length and then it breaks into droplets. This length is known as "breakup length". There is a linear regime where, an increase of the fluid velocity corresponds to a growth of the breakup length. This linear regime is the one considered in our measurements.

This liquid jet acts as an optical waveguide of numerical aperture NA=0.88. This high value is due to the difference of refractive index between the jet (n_{H2O}=1.33) and the surrounding air (n_{air}=1).

High NA enables an efficient excitation of the solution, exploiting the propagation along the liquid waveguide by means of total internal reflection (TIR). The same TIR mechanism allows efficient collection the Raman signal arising from the chemical compounds under analysis.

Moreover, this approach does not require the use of a sample container, hence it avoids typical background noise (fluorescence) affecting common methods for Raman spectroscopy.

2.1. Experimental setup

A stainless steel capillary is connected to a micro-pump in order to produce the liquid jet. The liquid jet (diameter d=1mm) is made to flow on the tip of an optical probe which is used to collect the fluorescence signal. The fiber optic probe is a 2 fiber probe. One fiber (diameter 200 µm and NA=0.22) is coupled with a laser source emitting at 785nm. The other fiber (diameter 600 µm and NA=0.39) is coupled with a compact size spectrometer.

Both of the capillary and the fiber probe are assembled in a self-aligned configuration using standard optomechanical cage system and no manual adjustments is required. A schematic of the jet production system and an illustration of the sensing principle are shown in figure 1 whereas the actual sensor is shown in figure 2.

For the jet production, the micro-pump provides a flow rate of 1.6 ml/s. This value ensures suitable stability of the jet as it corresponds to a breakup length around 10 cm, which is far superior to the distance between the capillary nozzle (18mm) and the optical probe i.e. the jet portion exploited as optical waveguide. Except the system for the jet production, all the other components are enclosed in a metallic chassis of compact size (28cm X 20 cm X 18 cm) as shown in figure 3.

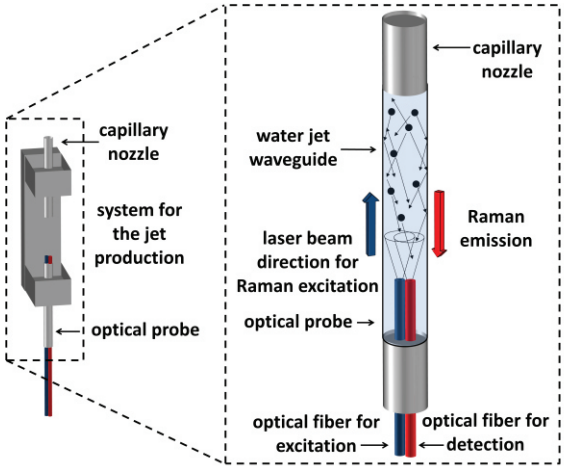

Fig. 1. Sensing principle of the optofluidic sensor.

This metal chassis contains the excitation source, the spectrophotometer and the optical fibers used to deliver optical signals, whereas an excitation filter is used to clean-up the laser output and a long-pass filter is used to filter out the Rayleigh scattering coming from the source.

More specifically, the source is a compact and low power consumption narrow-linewidth diode laser emitting at 785 nm. This wavelength choice is motivated by the well-known property that a near infrared excitation source is able to diminish sample fluorescence that commonly occurs in complex organic molecules.

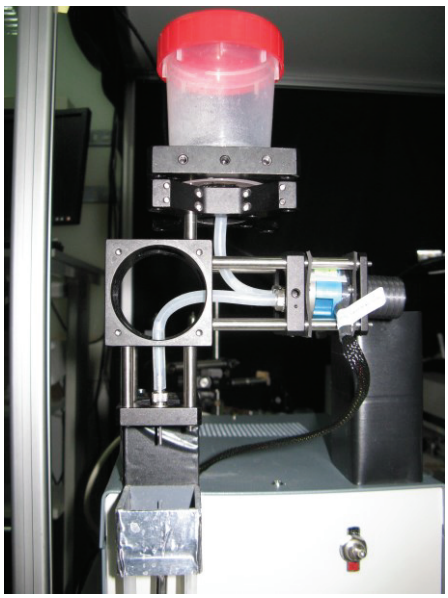

Fig. 2. Detail of the actual optofluidic sensor. The system for the jet production is shown with cover protection removed.

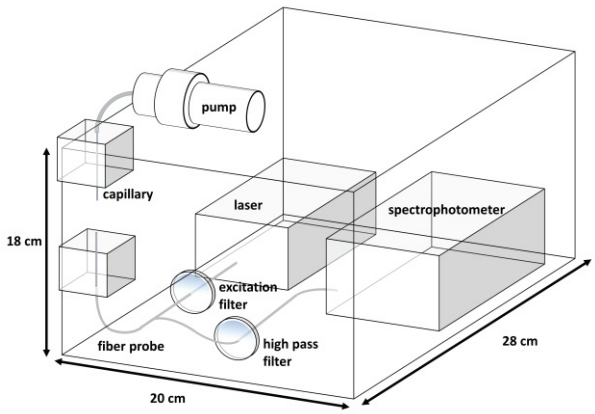

Fig. 3. Schematic of the optofluidic sensor and instruments used in the device.

The spectrophotometer is also a compact instrument. This detector is optimized for Raman measurements at an excitation wavelength of 785 nm and it is provides a NA=0.39 that perfectly matches with the collecting optical fiber.

The spectrophotometer employs a 1625 lines per mm holographic grating, a slit width of 50 µm providing a resolution of 10 cm^{-1} at 810 nm.

The detection window allowed by the spectrometer corresponds to the range 277-2025 cm^{-1}.

In order to control the laser source and the spectrophotometer, an external laptop is used.

The communication with the instruments is performed via USB cable.

The insertion of the solution is made in the container located above the pump as shown in figure 2. If necessary, a recirculation system could be easily arranged by a simple repositioning of the tubing. In this alternative method of use, a tube collecting the solution runoff from a baker can be connected to the inlet of the micro-pump.

3. EXPERIMENTAL RESULTS

The experimental measurements have been performed by considering the ethanol-water solutions in a concentration range 2 %to 20%.

The spectra have been collected by employing an integration time of 1s, whereas the output power of the laser source at the probe level has been measured as 120 mW.

For each concentration, 10 measurements have been acquired under the same experimental conditions.

In order to analyse the measurements, the area of the Raman peak centered at 888 cm^{-1} have been calculated.

The peak centered at 888 cm^{-1} corresponds to a very strong transition, which is assigned to the C-C stretching [9].

A blank measurement of pure water has been also acquired at the same experimental conditions. Some of the recorder spectra (after background subtraction) are shown in figure 4.

The Raman spectrum of ethanol displays different specific peaks in the frequency range investigated, among those, besides the peak at 883 cm^{-1} which has been exploited for the ethanol determination in our measurements, other peaks are distinctive of the ethanol.

The assignment of the most intense peaks is summarized in the following Table 1.

Table 1. Raman peak of ethanol assignment [9].

Raman peak position (cm^{-1})	Assignment	Intensity
883	C-C stretching	very strong
1054	C-O stretching	strong
1096	CH_3 rocking	strong
1454	CH_3 bending	medium
1479	CH_3 bending	very weak

From the peak area at each concentration, a linear regression has been calculated and a calibration curve for the ethanol content in water have been obtained.

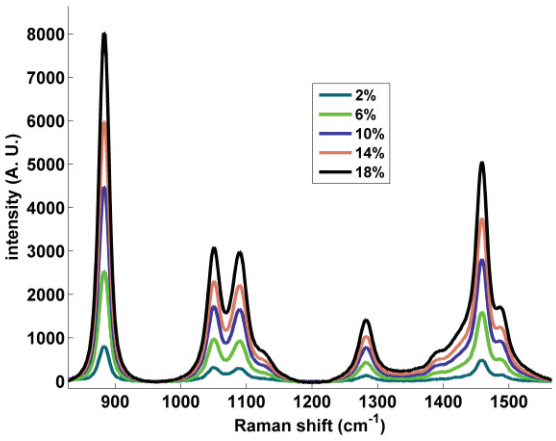

Fig. 4. Some acquired spectra of the ethanol in water, after background subtraction.

The calibration curve for ethanol-water solution and the corresponding limit of detection are reported in figure 5.

The LOD has been determined from the data linear regression as the concentration corresponding to a signal equal to the background (blank) plus three times the standard deviation of the blank. An LOD= 0.34 % (v/v) has been determined adopting the previous definition.

The use of an internal standard (as for instance acetonitrile, sulphate, etc.) in the solution to analyse is a common procedure which is adopted to compare a reference signal to obtain a better precision in the experimental results

In order to keep the experimental procedure as simple as possible, by avoiding any sample pre-treatment, the sensor characterization do not make use of any internal standard, i.e. no chemical compound is added in our solution as a reference.

This choice, in addition to being motivated by the wish to avoid time-consuming procedures, is related to the possibility to use the proposed approach for in-line monitoring, by avoiding any adulteration with the prospect to reuse the samples under analysis for food consumption.

The sensor performance appears very promising with respect different methods adopted for ethanol in water determination and more than adequate for the proposed applications.

For instance, literature results for ethanol quantification by means of absorbance measurements reports an LOD=1.5% [10] whereas amperometric approach seems to performs slightly higher values (LOD=0.4%) [2] with respect our approach.

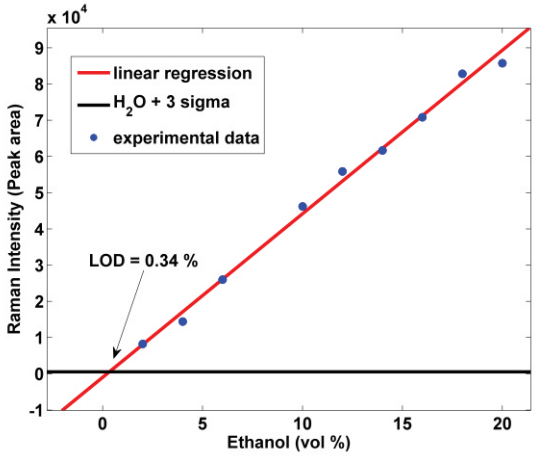

Fig. 5. Calibration curve of the sensor. The LOD determined for ethanol in water is 0.34%.

Fluorescence detection in immobilized doped sol-gel film [11] demonstrates an LOD=0.6:

Instead, specific sensors for ethanol determination in alcoholic beverages based on fluorescent probe 5,10,15,20-tetraphenyl porphyrin (TPP) performs very low LODS (0.05%) [12].

A comparison of different methods for the determination of ethanol in aqueous solutions is summarized in Table 2.

Besides the numerical comparison of the achievable performances with respect other approaches, the proposed method offers additional advantages.

The proposed method is very simple and at the same time, it avoids possible background noise coming from the sample container. Moreover it offers the possibility to perform measurements in very fast time with respect other methodologies described in the literature.

The presented results have been obtained with a spectrophotometer integration time of 1s and 10 repeated measurements corresponds to a total of measurement time T=10 s.

This is due to the high collection and excitation scheme of the jet waveguide approach.

Those characteristics are due to the numerical aperture of a water jet (NA=0.88). Thanks to this property, a suitable Raman signal is acquired in times that are faster than other approaches.

Table 2. Comparative table of different approaches for ethanol quantification.

Method	LOD (vol %)	Reference
absorbance	1.5%	[9]
amperometric sensor	0.4%	[2]
fluorescence detection in immobilized doped sol-gel films	0.6%	[10]
fluorescence sensor based on 5,10,15,20-tetra-phenyl porphyrin (TPP) doped on PVC	0.05%	[11]
jet waveguide	0.34%	This work

4. CONCLUSIONS

A compact jet waveguide optofluidic sensor on-chip has been developed and applied for the determination of ethanol content in liquids. The LOD determined with jet waveguide approach appears very promising for application in fermentation process monitoring and control of alcoholic beverages. The proposed method appears competitive with respect more complex or expensive approaches.

Moreover, this novel method not only minimizes laboratory equipment and time consumption but also provides a simplification of the experimental procedure to carry out the measurements. Due to this encouraging results, as a next step, it is planned to apply the optofluidic sensor also in alcoholic beverage adulteration by determining the methanol content in mixture of ethanol water solutions by exploiting the methanol peak centred at 1035 cm^{-1}.

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