Determination of ethanol content in wine through a porous silicon oxide microcavity

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Abstract

This paper reports on a new sensor, based on a porous silicon oxide microcavity, for the determination of the alcoholic strength of white and red wines. The shift of the cavity mode due to interaction with ethanol is monitored in continuous way by means of Fourier transform infrared (FT-IR) spectroscopy comparing the data obtained in condensation and evaporation mode. The results demonstrate the advantage of working in evaporation mode and the possibility to determine the alcoholic strength of wine with a good reproducibility and selectivity.
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1. Introduction

The rising development and the high-quality requirements of the food industry in the last years have caused an increased interest for sensor devices able to insure rapid and low-cost analysis. In this context the determination of ethanol is an important task due to its presence in many fields of the food industry either a desired or unwanted product.

The monitoring of ethyl alcohol is crucial in the liquor industry because it determines the quality of alcoholic beverages (wine, beer, liquor and spirit) since it is the main product of the alcoholic fermentation, and for some food preparations (packaging of "bakery products") since it is often added as a conserving agent due to its antibacterial properties and its ability to limit staleness.

The common methods to evaluate the ethanol concentration are chromatographic, such as gas and high performance liquid chromatography (GC and HPLC), [1–3] and sometimes require distillation followed by density or refractive index measurements. These methods necessitate professional laboratory with specialised personnel, expensive equipment and sample pre-

treatment without going to meet the increasing needs of on-line measurements and automation of the food industry. Moreover they do not allow continuous monitoring during industrial processes and are useless for fast routine analysis.

In the wine industry these aspects are extremely important since the winemakers need to monitor ethanol, in the must, throughout the process of fermentation as well as in the final product. To date only some biosensors based on enzymes such as alcohol oxidase [3–6] and alcohol dehydrogenase [3,7], or micro-organisms [3,8], like *Saccharomycies ellipsoideus* [9], that use a modified oxygen electrode to measure the oxygen consumption produced by the selective conversion of ethanol, have been proposed as an alternative to the common methods. The biosensor drawbacks' could be found in its low stability, short lifetime of the immobilized enzymes or micro-organism, and sometimes in a low selectivity.

This paper describes a new type of ethanol sensor, for wine application, based on a porous silicon oxide microcavity (PSOM) and compares its sensitivity to the official method of detection imposed by the Italian laws. The shift of the cavity mode (CM), correlated to a change of the PSOM optical properties due to physisorption/condensation of ethanol into the pores, was monitored in presence of different wines and a linear increase of the red-shift by increasing the alcohol strength has been observed. The effects of condensation/evaporation of

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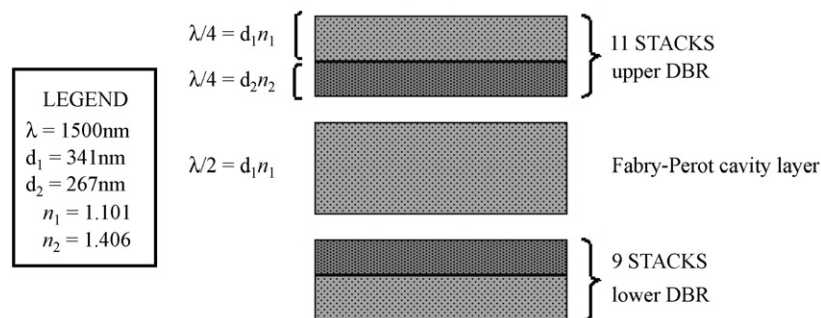
Scheme 1. Sketch of the PSOM.

reference solutions and wines on the PSOM shift will be discussed and the advantage to work in evaporation mode will be demonstrated. The PSOM stability and its selectivity to ethanol compared to other volatile compounds of wines (acetic acid) were also tested.

2. Experimental details

2.1. PSOM preparation

The PSOM, made of two distribute Bragg reflectors (DBRs) with a Fabry Perot $\lambda/2$ cavity in the middle, was produced through electrochemical etching of a single crystalline, $\langle 1\,0\,0 \rangle$ oriented, boron doped (5–15 mΩ cm) silicon wafer. The etching solution was a 1:1 mixture of hydrofluoric acid (50% in water) and ethyl alcohol (>99.9%). The DBRs were made of stacks, 11 for the upper Bragg and 9 for the lower (Scheme 1), of two alternating layers of different porosity and refractive indexes. The current densities were 550 and 200 mA/cm^2 for the high and low porosity layer, respectively. The PSOM was projected in the near infrared range with the cavity mode at 1500 nm.

The refractive indexes of the oxidized layers were estimated by means of a simulation program: SCOUT by Theiß [10]. The oxidized samples were prepared using the two current density values and oxidized with the receipt described afterward. The simulation was carried out using an effective medium approximation (EMA) based on the Bruggeman approach; the dielectric constants of vacuum and silicon dioxide were used in the EMA.

2.2. Oxidation process

All the oxidation treatment were made in an ASM oxidation furnace using the following recipe: (I) pre-oxidation at 400 °C for 1 h in O$_2$ flow, 2 l/min; (II) ramp from 400 to 850 °C in N$_2$ flow, 1 l/min; (III) oxidation at 850 °C for 30 min in O$_2$ flow, 5 l/min; (IV) ramp from 850 to 300 °C in N$_2$ flow 1 l/min.

2.3. Wine samples

Two wine sets [A, B], which include different types of Barbera d'Asti DOC, Barbera d'Alba DOC, Barolo DOCG, Nebbi-

olo DOCG, were used to test the PSOM. The alcoholic strength, measured with the official method, are summarized in Table 1.
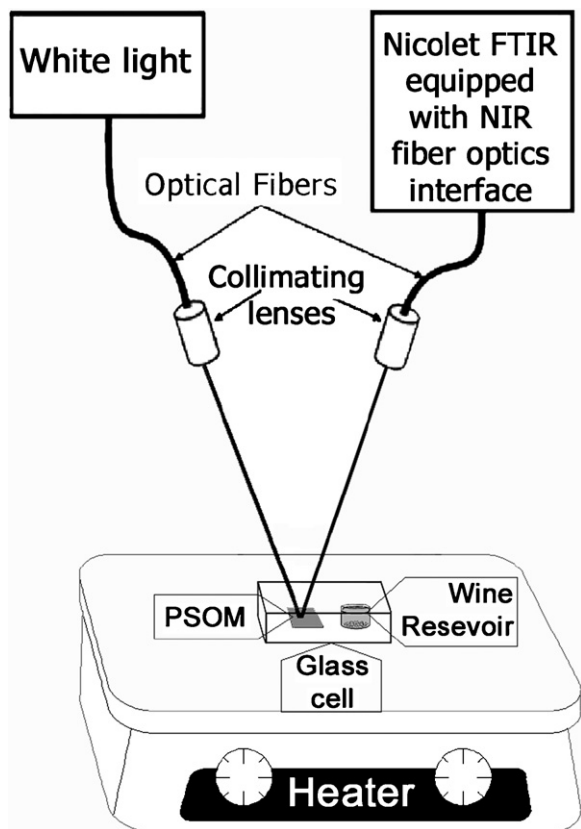
The official method is the OENO 24/2003 [11] and it implies the following steps:

- 200 ml of wine are transferred into a volumetric flask and its temperature recorded;
- the wine is transferred into a distillation flask where inert porous material (pumice) and 10 ml of calcium hydroxide 2 M are added and then distilled;
- the distillate (about three-quarters of the initial volume: 200 ml) is collected in the same volumetric flask and the flask is filled up to 200 ml with distilled water. The distillate must be keeping at a temperature within 2 °C of the initial temperature;
- the distillate density is measured by an hydrostatic balance and the alcoholic strength is furnished by international tables which convert the density in ethanol amount. Reproducibility of this method is ±0.2% vol.

Table 1
Wines list

Set A	
Red wines	
A	12.3
B	12.34
C	12.35
D	12.86
E	12.87
F	12.96
G	13.38
H	13.8
Set B	
White wines	
F1	12.25
G1	13.69
H1	14.43
A1	12.35
Red wines	
B1	12.86
C1	13.18
D1	13.8
E1	15.06

All the values are calculated with the official method OENO 24/2003.

Scheme 2. Measurements set-up.

Fig. 1. CM shift in condensation mode for reference solutions and wines (set A) as a function of the alcoholic strength (ethanol, vol.%).

2.4. Measurement set-up

A Nicolet Fourier transform infrared (FT-IR) spectrometer, model Nexus, equipped with a near infrared fiber optics interface was used to monitor the shift of the CM. The fiber optic bringing the light from the internal source (white light) of the spectrometer as well as the one collecting the reflected light were equipped with a collimating lens and tilted of less than 10° respect the surface normal. Two millilitres for each wine were poured in a small reservoir and positioned with the PSOM on a heater and covered with a closed glass cell; both were kept at fixed temperature: 35 °C. The measurements set-up is depicted in Scheme 2.

3. Results and discussions

Fig. 1 shows the red-shift of the CM obtained with reference solutions, prepared with pure ethanol and water, and with the wines of set A as a function of the alcoholic strength; the inset reports an enlargement of the 9–16% range. The shift is monitored in condensation mode: the CM position, measured after the system wine/PSOM has reached the equilibrium (≈10 min), is subtracted to the starting position; each samples is tested three times.

The CM shift increases linearly with the amount of ethanol in the reference solutions, while a random shift is observed when the alcohol strength of the wines increases. Moreover, removing the wine, the emptying of the PSOM (monitored by collecting
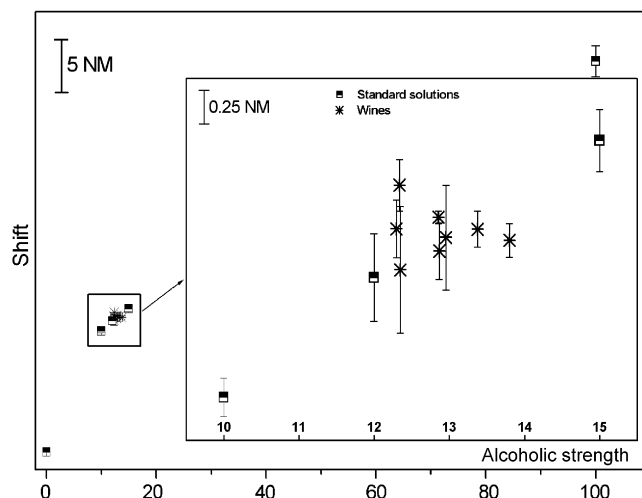
FTIR spectra each 0.2 s, data not shown) follows a two steps behaviour:

1. *Rapid step*: The CM blue shifts close to the starting position without recovering it (difference estimated in a couple of nanometers).
2. *Slow step*: The CM recovers its original position after several minutes.

This behaviour is different for the reference solutions, where the emptying follows a single step and the original position is quickly recovered. The random shift can be explain taking into account the wine composition, in which several volatile compounds coexist and contribute to the overall shift; moreover, these compounds could also be responsible for the two steps behaviour since they could interact stronger than ethanol with the oxidized surface increasing the emptying time. To verify this assumption the emptying dynamic of three solutions, ethanol (20% in water), acetic acid (1% in water) and pure water (Fig. 2), were monitored by registering FTIR spectra each 0.2 s. The acetic acid was chosen as representative of the whole volatile compounds since it is the major component of the wines vapour phase along with ethanol and the two concentrations of 20 and 1%, for ethanol and acetic acid, respectively, since they could roughly represent the highest values of these compounds in wines.

The curves in Fig. 2, which are normalized for comparison, clearly show that the CM recovers its original position in a shorter time for water and ethanol compared to acetic acid. The evaporation of water require seconds (≈20 s), ethanol minute (≈1 min) and acetic acid, which interacts strongly with the oxidized surface, several minutes (≈6–7 min): this evidence supports the assumption made on the two steps behaviour. On this basis it should be possible to considerably limit the contribution of acetic acid and hence the wine random shift by monitoring the evaporation.
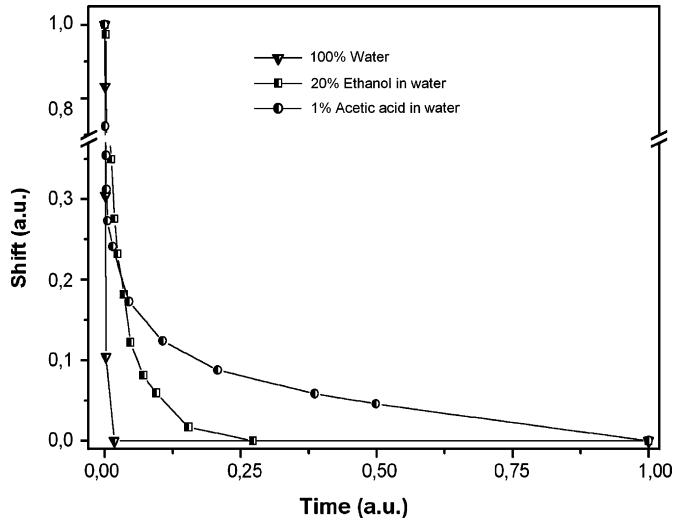
Fig. 2. Dynamic of the CM shift in evaporation for three reference solutions: 100% water; 1% acetic acid in water; 20% ethanol in water. The data are normalized for comparison.

The data obtained subtracting the CM position after 1 min from the emptying (time estimated sufficient for the complete evaporation of ethanol, Fig. 2) to the position at equilibrium are reported in Fig. 3. The same reference solutions and wines of the condensation test are used for comparison.

The wine shift follows the same linear behaviour of the reference solutions except for the lower overall shift that can be explained considering the different physical properties, such as surface tension, viscosity and density of wine.

The comparison of the two modes clearly shows that evaporation significantly improves the PSOM ability to discriminate alcohol percentage in wine (Fig. 4).

After the optimisation of the PSOM response, wine C (set A, alcoholic degree 12.35%) was tested three times during one month, days 0–15–30, to verify the shift reproducibility and to test the sensor stability (Table 2). During this time, in order
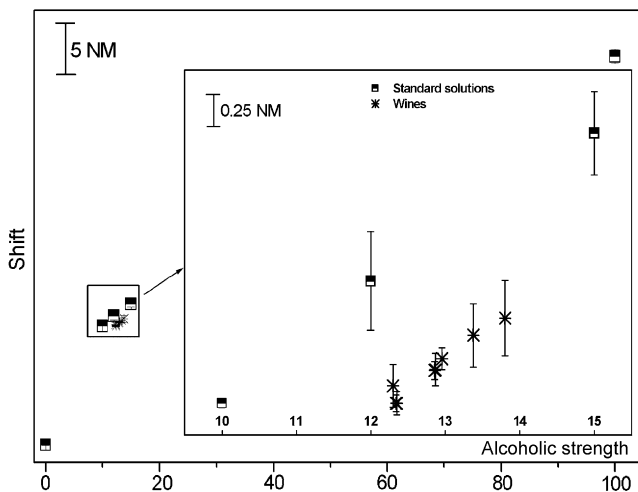
Table 2
CM shift in evaporation mode for wine C (set A) during 30 days

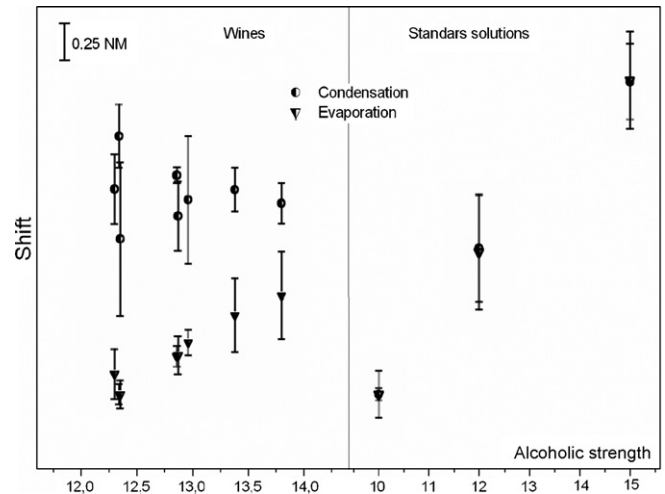| Wine C	Shift (nm)
Day 0	24.447[a]
Day 15	24.529[a]
Day 30	24.462[a]

[a] Mean of 10 measures.

Fig. 4. Comparison of the CM shift in condensation and evaporation mode for wines (set A) as a function of the alcoholic strength (ethanol, vol.%).

to preserve the wine characteristics, sample C was stored in a refrigerator in a sealed bottle avoiding air contact.

The data of Table 2 demonstrate that the PSOM response, in evaporation, is stable and reproducible during the 30 days of measurements. To extrapolate a calibration curve and to verify the PSOM response, not only with red but also with white wines, a second set of samples (set B) was investigated (Fig. 5).

The linear response observed in Fig. 5 confirms the PSOM ability to determine the alcoholic strength independently from

Fig. 3. CM shift in evaporation mode for reference solutions and wines (set A) as a function of the alcoholic strength (ethanol, vol.%).
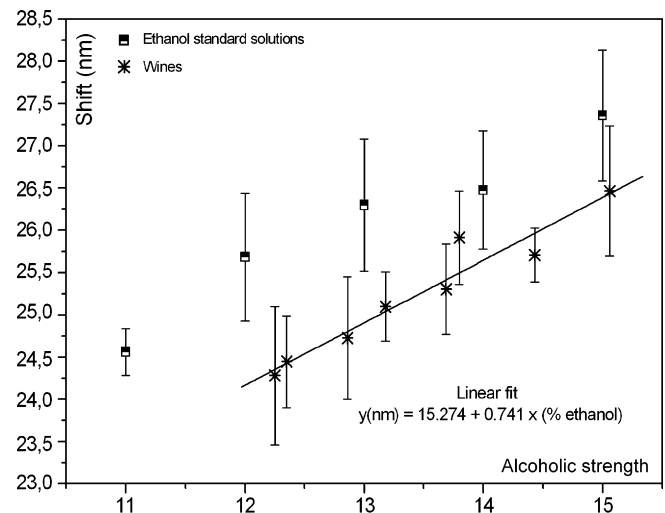

Fig. 5. CM shift in evaporation mode for reference solutions and wines (set B) as a function of the alcoholic strength (ethanol, vol.%).

Table 3
Comparison of the alcoholic degree of three red wines calculated with the official method OENO24/2003 and with the PSOM

Samples	Official methods			PSOM		
	A	B	C	A	B	C
Set C						
CM shift (nm)				24.89 ± 0.17407	24.81 ± 0.153	24.43 ± 0.1953
Alcoholic degree	12.75	12.56	12.23	12.97	12.86	12.35

the wines. The following equation:

$$y \, (nm) = 15.274 + 0.741x \, (\% \text{ of ethanol}) \tag{1}$$

obtained from the linear fit of the data in Fig. 5, was used to estimate the unknown alcoholic strength of three red wines (Table 3). The CM shift reported in Table 3 were calculated mediating ten measurements for each wine.

The alcohol percentage calculated with Eq. (1) are in good agreement to those determined with the official method and within the 0.5%. This limit is imposed by the Italian law to the wine producers and it represents the highest difference allowed between the alcohol concentration declared in the bottle tag along with the real value.

4. Conclusion

In conclusion the PSOM, working in evaporation mode, is able to determine selectively and in a reproducible way the alcoholic strength with a good approximation and can be extremely useful for fast routine analysis. The wide error bars of the shift measurements do not influence the capacity of the sensor because they are comparable for wines and reference solutions and depend on the measurement set-up, which will be extensively improved in the future. The new method (evaporation mode) developed represents an important step and also a new route to exploit the PSOM as well as porous silicon microcavity in sensor application. Moreover the use of the PSOM as ethanol sensor could be important not only in the wineries but also in the industries that produce ethanol, such as brewery and distilleries, or transform ethanol, such as vinegar industry.

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