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Ethanol Sensing in Wine with a Porous Silicon Oxide Microcavity

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Abstract: A porous silicon oxide microcavity (PSOM) has been used for the accurate determination of the alcoholic volume content of wines. The shift of the microcavity reflectivity spectrum, induced by the presence of the wine vapor phase into the PSOM pores, is monitored continuously in the infrared wavelength range. The time-resolved characterizations of the evaporation dynamics allow a selective and high reproducible determination of the ethanol volume percentage. The design of an integrated optical sensor in a lab-on-chip is also presented.

Keywords: Porous Silicon Oxide Microcavity, Ethanol Sensing, Wine

INTRODUCTION

Ethyl alcohol is largely employed in the food industry and its monitoring is of extreme importance not only for the drink industries, since it determines the quality of alcoholic beverages (such as wines, beers, liquors and spirits) being the main product of alcoholic fermentation, but also for the bakery industry, where it is often used for its antimicrobial properties.

Nowadays the standard methods to determine the ethanol concentration suffer some drawbacks since they should be applied in a professional laboratory requiring specialised personnel, expensive equipment and sometimes sample pre-treatment. These procedures do not meet the increasing demand of on-line measurements and automation of the drink industry because these methods do not allow continuous monitoring during industrial processes and are useless for fast routine analysis.

In this paper a new type of ethanol sensor, based on a PSOM, for the determination of the alcoholic volume content (AVC) in white and red wines is proposed. A comparison of the AVC values of some wines measured both by means of the PSOM and following the official method (imposed by the Italians' laws) will prove the good performances of this new sensor **[REF LEX].**

Moreover, by merging the porous silicon and the anodic bonding technologies, we have designed an integrated silicon-glass opto-chemical sensor for lab-on-chip applications which can be directly used in the proposed application. Due to the industrial interest of the proposed research, both the devices have been recently patented [2,3].

EXPERIMENTAL

The PSOM, made of two distributed Bragg reflectors (DBRs) with a Fabry Perot $\lambda/2$ cavity in the middle, was projected to be resonant in the near infrared range with the cavity mode centred at 1500nm and was prepared through electrochemical etching of a p type silicon wafer, <100> oriented, heavily doped. The upper and lower DBRs were made of unpaired periods, 11 and 9 respectively, of alternating layers with different porosities and hence different refractive indexes obtained by etching the crystalline silicon with two current density values: 550 and 200 mA/cm^2.

The oxidation process was carried out in ASM oxidation furnace with the following recipe: *I.* pre-oxidation at 400°C for 1h in O_2 flow, 2l/min; *II.* ramp from 400°C to 850°C in N_2 flow, 1l/min; *III.* oxidation at 850°C for 30min in O_2 flow, 5l/min; *IV.* ramp from 850°C to 300°C in N_2 flow 1l/min.

The refractive indexes of the oxidized layers were calculated by means of the simulation program SCOUT by W. Theiß [4] using an effective medium approximation (EMA) based on the Bruggeman approach. The dielectric constants of vacuum and silicon dioxide were used in the EMA.

The PSOM was positioned in a closed glass cell with the different wines (two milliliters for each wine) and both were kept on a heater at 35°C during the measurements. The shift was monitored using a Nicolet spectrometer equipped with a near infrared fiber optics interface.

A set of 8 wines (table 1), white and reds, were used to calibrate the PSOM shift and then the AVC of 3 red wines were estimated by means of this calibration. The wines include different qualities of Barbera d'Asti DOC, Barbera d'Alba DOC, Barolo DOCG, Nebbiolo DOCG, Arneis DOCG and Favorita DOC.

	Alcoholic Volume Content (%)				
White Wines	12.25	13.69	14.43		
Red Wines	12.35	12.86	13.18	13.8	15.06

Table 1. The alcoholic degree was measured according to the standard method imposed by the Italians law.

RESULTS

Figure 1 reports the shift of the PSOM as a function of the AVC of the wines of table 1; each experimental point is the average of 20 independent measurements by exposing the PSOM to the same amount of wine. The shift is calculated from the position of the PSOM at the equilibrium to the position after 90 seconds since the removal of the wine. Time-resolved characterizations have shown that after 90 seconds we can measure only the ethanol contribution to the overall shift of the PSOM, avoiding the interference of the other volatile compounds of wine which could strongly interact with the oxidized surface.

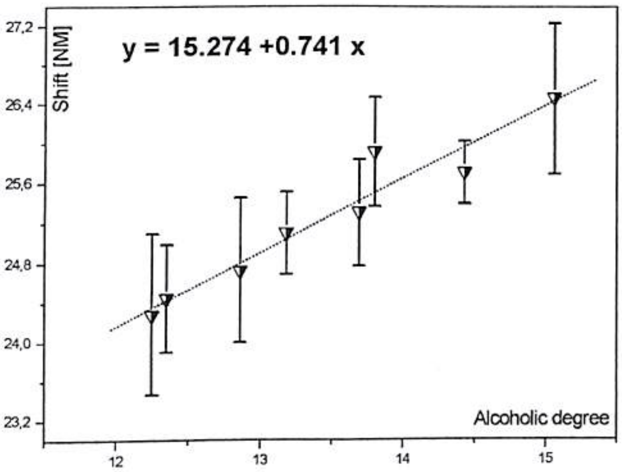

Figure 1. Shift of the PSOM as a function of the alcoholic degree. Dotted line: linear fit.

The equation in the inset of Fig. 1 has been obtained from the linear fit of the experimental points and has be used as a calibration for the PSOM.

To verify the PSOM precision and accuracy, a set of three wines of unknown alcoholic degree were measured. Table 2 shows the mean values of the shifts obtained mediating 20 measurements for each wine.

WINES	A	B	C
Shift [NM]	24,43	24,80	24,89

Table 2. Shift of the PSOM for 3 unknown wines.

The ethanol amount was calculated using the shift of table 2 by means of the calibration equation and a comparison between the AVC obtained with the PSOM and with the official method are reported in table 3.

The PSOM is able to determine the AVC with a good approximation and the values obtained are in good agreement to those determined with the official method and within the 0.5%. This limit is imposed by the Italian legislation to the wine producers and it represents the highest difference allowed between the alcoholic degree declared in the bottle tag respect to the real value.

	Alcoholic Volume Content (%)		
	A	B	C
Official Methods	12.23	12.56	12.75
PSOM	12.35	12.85	12.97

Table 3. Comparison of the alcoholic degree measured with the official method (imposed by the Italians law) and calculated with the PSOM.

In order to limit the wide error bars and the time necessary for the PSOM to reach the equilibrium with the wine (by limiting the volume) an integration in a single chip of the PSOM and the wine reservoir is proposed.

INTEGRATION

The compatibility of the porous silicon technology with the standard integrated circuit fabrication procedures allows the design of complex microsystems in which the porous silicon optical device is the transduction element. In Figure 2, we report a rough and somehow intuitive design of the patented micro-alcoholic-sensor. Each single element has already been realized.

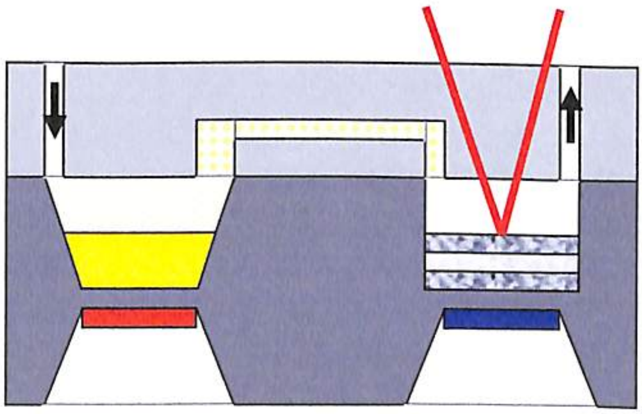

Figure 2. The PSOM can be integrated in a lab-on-chip consisting of two μ-chamber temperature-controlled by heathing integrated elements and sealed by a cover glass after anodic bonding.

REFERENCES

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