Sulfite Detection in Food Liquids (Beverages) with a Microdisk Array Sensor

J. Gobet, Ch. Provent, Ph. Rychen

The use of a microdisk array sensor for amperometric determination of free and total sulfite in beverages was evaluated. Model solutions resulted in good sensitivity (~1 ppm) and linearity (0-120 ppm) for free SO_2. In must, wine or vinegars a non-negligible residual current was observed but a good correlation between sensor response and added sulfite was obtained. Preliminary results indicate that the direct measurement of bound sulfite without alkaline hydrolysis should be possible.

The antioxidant properties and universal antiseptic action (inhibitor of enzymatic or microbial activity) of SO_2 together with its very low cost make it a widespread additive for food and beverage preservation, SO_2 is in particular very important in wine-making due to its suppression of yeast and bacterial action, and its anti-oxidant properties. Process control and legislation conformity require the use of a sensitive detection method. Iodometric titration using either colorimetric or potentiometric end point detection is commonly used for SO_2 determination:

$$HSO_3^- + I_2 + H_2O \rightarrow SO_4^{--} + 2I^- + 3\,H^+$$

In natural products sulfite is present as "free" SO_2 (HSO_3^- in neutral or slightly acidic pH) and as "bound" sulfite (sulfonates). Total sulfite is measured after 10 minutes hydrolysis of bound sulfites in alkalinized solution followed by quick re-acidification.

The iodometric method is not very accurate and requires equipment that is not easily used in production sites. A simpler and faster method would be highly desirable for on-site use. Microdisk array sensors (Figure 1) have been successfully employed for the determination of several oxidation [1],[2] and reduction agents, their possible use as sensors for the direct amperometric determination of sulfite was therefore evaluated.

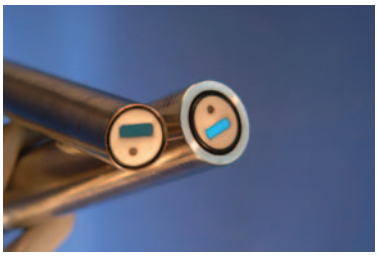

Figure 1: View of two microdisk array sensor heads with 12 mm and 16 mm diameter housings.

In acidified or neutral water solutions, microdisk arrays give a well defined SO_2 oxidation plateau between -0.6V and 1.0V (see Figure 2). The plateau current corresponds to a sensitivity close to the theoretical value. Detection limits below 1 ppm and linear responses between 0-120 ppm were readily obtained in this medium.

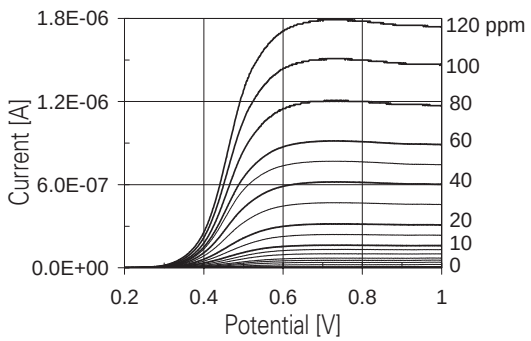

Figure 2: Potential scans in 0.005 N H_2SO_4 - 0.01 M Na_2SO_4 solution showing the effect of successive SO3 additions.

Likewise, SO_2 additions in food products including must, wines and vinegar resulted in a linear response on a microelectrode sensor, as shown in the example of Figure 3. As expected, in such complex media, the baseline value is increased at the measuring potential due to interferences by easily oxidized compounds such ascorbic acids or tannins. A lower sensitivity was also observed and it was found necessary to clean the electrodes in an acidic solution between measurements.

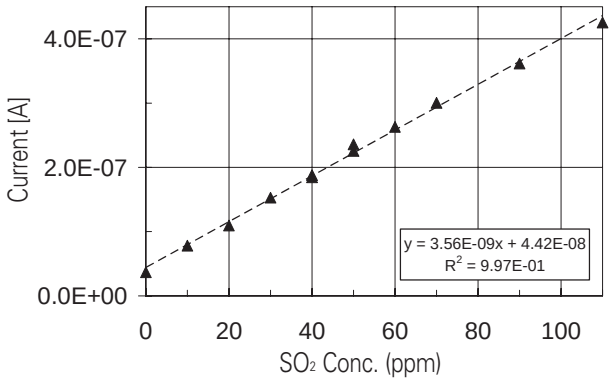

Figure 3: Linear correlation obtained between the microdisk array response and the concentration of sulfite added in a white wine.

Experiments in model solutions further indicated that free sulfite is selectively detected at a measuring potential of 0.6V while sulfites bound to aldheydes are not oxidized. Direct oxidation of bound sulfites could be observed at a more anodic potential, thus suggesting the possibility to measure total sulfite concentrations without previous alkaline hydrolysis.

In conclusion, promising preliminary results have been obtained for the detection of free and bound sulfite in beverages. The development of a sulfite microdisk array amperometric sensor will be further pursued. In particular a more detailed evaluation of matrix effects in food products and their influence on detection limit and reproducibility will be carried out.

The support of OFES is gratefully acknowledged.

[1] J. Gobet, Ph. Rychen, F.Cardot, E.Santoli, "Microelectrode Array Sensor for Water Quality Monitoring", Water Sci. Techn. 47(2003) 127

[2] Ch. Provent, W. Haenni, E. Santoli, Ph.Rychen, "Boron-doped Diamond Electrodes and Microelectrode-Arrays for the Measurement of Sulfate and Peroxodisulfate", Electrochimica Acta, 49 (2004) 3737