



Low cost and compact analytical microsystem for carbon dioxide determination in production processes of wine and beer



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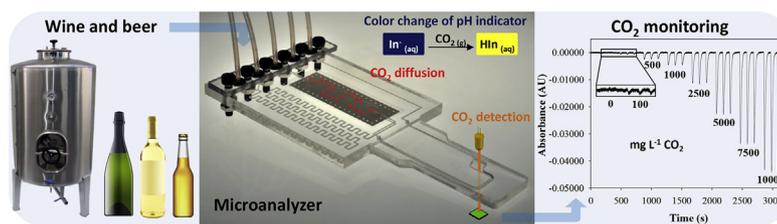
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HIGHLIGHTS

- Low cost and compact polymeric analytical microsystem.
- Carbon dioxide determination using a gas diffusion step and optical detection.
- Real wine and beer samples were successfully analyzed.
- Automatic measurements to monitor production processes of wine and beer could be performed.

GRAPHICAL ABSTRACT



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ABSTRACT

The design, construction and evaluation of a low cost, cyclic olefin copolymer (COC)-based continuous flow microanalyzer, with optical detection, to monitor carbon dioxide in bottled wines and beers as well as in fermentation processes, is presented. The microsystem, constructed by computer numerically controlled (CNC) micromilling and using a multilayer approach, integrates microfluidics, gas-diffusion module and an optical flow-cell in a single polymeric substrate. Its size is slightly bigger than a credit card, exactly $45 \times 60 \times 4$ mm in the microfluidic and diffusion module zone and $22.5 \times 40 \times 3$ mm in the flow-cell zone. The gas-diffusion module is based on a hydrophobic polyvinylidene fluoride (PVDF) membrane, which allows the transfer of the carbon dioxide present in the sample to a bromothymol blue (BTB) pH-sensitive acceptor solution, where the color change is measured optically. The detection system consisted of a LED with an emission peak at 607 nm and a photodiode integrated in a printed circuit board (PCB). The obtained analytical features after the optimization of the microfluidic platform and hydrodynamic variables are a linear range from 255 to 10000 mg L⁻¹ of CO₂ and a detection limit of 83 mg L⁻¹ with a sampling rate of 30 samples h⁻¹.

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1. Introduction

The amount of carbon dioxide (CO₂) is an important parameter in the monitoring of fermentation process in wines and beers [1]

and it is also a factor that affects their organoleptic properties [2,3]. For these reasons, CO₂ is routinely controlled in the production processes of these beverages in wineries and breweries.

There were traditionally three different official methods to determine CO₂ in these samples: the manometric, the enzymatic and the titrimetric, being the last one selected as first option due to its advantages over the others methods [4,5]. This procedure consisted in a titration with sulfuric acid between pH 8.6 and 4.0 of the

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alkalinized CO₂, using a pH electrode. Despite of its advantages, the titrimetric method shows some difficulties. In order to overcome them, direct measurements of dissolved carbon dioxide, especially those based on electrochemical methods, have also been proposed [6]. However, those methods based on Severinghaus principle show a long response time and sometimes low reproducibility and, in general, they are often expensive, not miniaturized and not easily automatable. As another alternative, automated systems based on continuous flow methodologies with spectrophotometric detection and with gas-diffusion separation step, have been used [7–9]. In this way, different quality parameters such as the analysis time, the sample and reagent consumption and the reproducibility of the measures without the need of skilled laboratory personal, were improved. In these systems, the process to determine CO₂ usually starts when the sample is injected into a carrier solution which is mixed with an acidic donor solution. At that moment, all the inorganic carbon species are converted to CO₂, which diffuses through a gas-diffusion membrane. Then, a pH-sensitive acceptor stream collects the CO₂ causing a change in the pH which is detected by a change in the absorbance of the acid-base indicator. Nevertheless, these systems present a narrow working range that hinders the determination of CO₂ in beers (about 5000 mg L⁻¹) and wines (from about 1000 mg L⁻¹ in slightly sparkling up to 12000 mg L⁻¹ in very highly sparkling wines) [1,8]. In addition, sample and reagent consumption are still too high and the size of the experimental set-up makes them not portable, limiting their use in both discrete in-situ sample analysis and on-line monitoring of fermentation process.

To overcome these drawbacks, the miniaturization of analytical systems can be applied to obtain the so-called micro Total Analysis Systems (μTAS) [10,11]. Among all the different materials that have been used to fabricate these miniaturized analyzers, such as glass, silicon or ceramics [12], polymers offer great advantages over the others. They allow a fast and easy fabrication using inexpensive facilities providing low cost, small and compact microanalyzers. In addition, depending on the polymer employed, they have a good transparency in the UV–Vis range, good mechanical resistance, high chemical inertia against most acids and alkalis and high biocompatibility [13–16]. Furthermore, polymers technology allows the fabrication of microsystems using a multilayer approach in order to obtain tridimensional structures through the use of adhesives between layers in the bonding process. However, when adhesives are used, the obstruction of the microchannels can occur and there may be leaking of liquids or delamination between layers. To overcome these drawbacks, cyclic olefin co-polymer (COC) arises to provide a thermolamination process using the same material substrate as a sealing agent. Thus, taking advantage from the different glass transition temperatures in which COC can be formulated, a hermetic bonding of tridimensional structures can be achieved through the interlink of polymer chains on the surfaces of the layers when they are put together under a certain pressure and temperature [17,18]. This technology allows also the monolithic integration of other elements such as hydrophobic/hydrophilic polymeric membranes and conductive paths or electrodes into the multilayer COC devices, which permits to integrate different steps of the analytical procedure such as sample dosage, sample pre-treatment and separation, mixing, reaction, detection, among others [13,19,20].

Finally, the advances in optoelectronics, which have let the appearance of new small light sources such as light-emitting diodes (LEDs) [21–25] and small detectors such as photodiodes [21–24], allow the possibility to reduce the size of the experimental set-up for optical measurements compared to the conventional equipments, making them easily miniaturized [18].

Herein, we propose a low-cost, COC-based microsystem with a

gas-diffusion step integrated for the spectrophotometric detection of CO₂ using bromothymol blue (BTB) as pH-sensitive acceptor solution. The microanalyzer integrates microfluidics, gas-diffusion separation step and an optical detection cell. These features, joined to the simplicity of the detection setup, make the entire system easily portable, with a reduced consumption of sample and reagents and a wider linear working range. To demonstrate its applicability, different wine and beer samples have been analyzed.

2. Experimental

2.1. Reagents and materials

The microanalyzer was fabricated with plaques and foils of COC purchased from Topas Advanced Polymers (Florence, KY, USA) in different grades and thicknesses: Topas 5013 plaques of 500 μm and 1 mm thickness, and Topas 8007 foils of 25 μm and 50 μm thickness.

A hydrophobic membrane made of polyvinylidene fluoride (PVDF) with 150 μm thickness and 0.45 μm pore diameter (Millipore) was used to separate the analyte from its sample matrix by gas diffusion.

All reagents employed in this work were of analytical grade. All solutions were prepared in Milli-Q water. Carbon dioxide standard solutions were prepared daily by successive dilutions of a 50000 mg L⁻¹ stock of Na₂CO₃ (Panreac) and degassed. As a donor solution, a 0.2 M H₂SO₄ acidic solution (Sigma-Aldrich), containing 60 mg L⁻¹ of H₂O₂ (Panreac) in order to avoid the SO₂ interference by oxidizing it to sulfate [7], was used to convert all inorganic carbon species into carbon dioxide. As an acceptor solution, a 12 mM NaH₂PO₄/Na₂HPO₄ (Panreac) buffer solution (pH 7.6), containing 0.06 mM of BTB (Sigma Aldrich), was used.

2.2. Fabrication of the microanalyzer

The fabrication process of COC-based microsystems used, which is based in the lamination of different COC layers with different glass transition temperatures (T_g), is described in detail elsewhere [19,20]. Topas 6013 plaques with T_g = 130 °C were used as fluidic structural layers for the mechanization of all motifs of the design (microchannels and flow cell) and Topas 8007 foils with T_g = 75 °C were used between them as sealing layers. The fabrication process consists of four main steps: prototype design, fluidic motifs machining, integration of additional non-COC elements (such as electrodes and gas-diffusion membrane) and final lamination. The prototype design was performed with a CAD software (Fig. 1) taking into account previous experimental results obtained by our research group and described elsewhere [20]. The microsystem was constructed using five structural layers that, once overlapped, provide the three-dimensional structure required for this application (Fig. 1A). The dimensions of the microanalyzer were 45 × 60 × 4 mm in the microfluidic and diffusion module zone and 22.5 × 40 × 3 mm in the flow-cell zone which is inserted into the detection system based on a lock-and-key concept [18] described in the 2.3 *Experimental setup* section. The microfluidics inside the microsystem included three liquid inlets (Fig. 3). Two of them converge in a T-shape confluence point. At this point the carrier solution, where the sample is injected, and the H₂SO₄ solution are mixed to obtain carbon dioxide from all inorganic carbon species present in the sample following the next chemical reactions: CO₃²⁻(aq) + H⁺ ⇌ HCO₃⁻(aq), HCO₃⁻(aq) + H⁺ ⇌ H₂CO₃(aq), H₂CO₃(aq) ⇌ CO₂(aq) + H₂O, CO₂(aq) ⇌ CO₂(g). The mixed stream is carried to the diffusion membrane unit where, along a meander microchannel, the carbon dioxide diffuses through the PVDF membrane towards the acceptor solution. The BTB pH-indicator

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