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Amperometric Detection of Ethanol Vapors by Screen Printed Electrodes Modified by Paper Crowns Soaked with Room Temperature Ionic Liquids

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Abstract: A convenient assembly recently proposed for screen printed gold electrodes (SPEs) suitable for measurements in gaseous samples is here tested for the analysis of the ethanol content in alcoholic drinks. This assembly involves the use of a circular crown of filter paper, soaked in the room temperature ionic liquid (RTIL) 1-butyl-3-methylimidazolium hydrogen sulfate, which is simply placed upon a disposable screen printed cell, so as to contact the outer edge of the gold disc working electrode, as well as peripheral counter and reference electrodes. The electrical contact between the paper crown soaked in RTIL and the SPE electrode is assured by a gasket and all components are installed in a polylactic acid holder. This assembly provides a portable and disposable electrochemical platform, assembled by the easy immobilization onto a porous and inexpensive supporting material such as paper of a RTIL characterized by profitable electrical conductivity and negligible vapor pressure. The electroanalytical performance of this device was assayed for the flow injection analysis of the ethanol concentration in some real samples of wine and beer and the results obtained are compared with the alcoholic degree reported in the relevant bottle-labels, thus highlighting a substantially satisfactory agreement. Repeatable sharp peaks (RSD = 6–8 %) were detected for ethanol over a wide linear range (1–20 % v/v in water) and a detection and quantitation limit of 0.55 % v/v and 1.60 % v/v were inferred for a signal-to-noise ratio of 3 and 10, respectively.

Keywords: Room Temperature Ionic Liquids (RTILs) · Ethanol in wines and beers · Flow Injection Analysis · Gas sensors · Screen Printed E lectrodes

1 Introduction

Ethanol is an ingredient frequently encountered in food, not only in alcoholic drinks, but also in some brandied fruits or candies, and even some plum puddings and fruit cakes can contain ethanol if distilled spirits are used for their flavouring and preserving [1–3].

Its detection is usually performed by resorting to gas chromatography that offers high selectivity, but this method is time-consuming, difficult to be automatized, unsuitable for on-line and in situ monitoring and, moreover, it requires trained personnel [4–7]. Consequently, the development of easier methods for ethanol determination based on low cost and user-friendly devices is mandatory. In particular, approaches based on headspace analysis should be desirable, so as to profit from its volatility to prevent at the best possible interferences from other species present in analyzed samples.

Electroanalytical sensors based on current measurements seem to be particularly attractive for tackling the problem of analyte detection even at low concentration levels, thanks to both their inherent high sensitivity and good selectivity [8]. Moreover, they can be performed by simple portable and low-cost instrumentation. However, common electroanalytical approaches cannot be applied to gaseous samples where no supporting electrolyte is present, and none can be added [9].

To overcome this drawback, in the last three decades amperometric gas sensors of last generation have been developed which allow electroanalytical measurements to be performed in gas phase without suffering from defects typical of conventional gas-permeable membrane electrodes (i.e. rather low sensitivity and long response times) [10,11]. Electroanalytical gas sensors based on the use of moist perfluorinated ion-exchange membranes were first proposed [10,12–15] where on their side facing the analyzed gas phase a thin layer of conducting material is

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deposited, acting as the working electrode, while the other side is contacted by an electrolyte solution containing both the counter and reference electrodes. Despite their good performance, the solvent of the supporting electrolyte is prone to dry up and cannot survive high enough temperature changes.

Instead, this last defect is not displayed by electroanalytical gas sensors based on the use of room temperature ionic liquids (RTILs) or deep eutectic solvents (DESs) which were developed more recently [16–21]. They are sensitive and fast-responding membrane-free amperometric gas sensors consisting frequently of three conductive wires piercing through a Teflon rod, whose exposed end is coated with a steadily adhesive film of RTIL or DES assuring the necessary ionic conductivity between the electrodes [22]. Alternatively, they consist of small filter paper foils soaked in a RTIL or DES, upon which three electrodes are screen printed by carbon ink, profiting by suitable masks [17]. The negligible vapor pressure of the immobilized RTIL or DES layer makes possible to eliminate the need for the use of membranes, thus avoiding that a slow limiting step such as analyte permeation is involved [23,24].

RTILs and DESs display not only a negligible volatility, but also a considerable dissolution capacity for a large variety of compounds. These are the reasons why they met with an extensive use in chemical research [25–27], for the extraction of different species [28–30], organic synthesis, electrochemistry and biocatalysis [31–33].

Recently, the assembly of RTIL-based electroanalytical gas-sensors was made significantly easier by suggesting a very simple modification of low-cost disposable devices such as screen printed electrodes (SPEs) [34,35]. This modification involves the simple application on the surface of three-electrode screen-printed devices of a conveniently shaped paper sheet soaked with a suitable RTIL [36]. This device was only tested for the reduction of oxygen, chosen as proof of concept, but no real application was so far reported.

We report here the performance offered by SPEs, equipped with a gold working electrode, and modified by coating their probe-surface with paper crowns soaked with two different RTILs, for the flow injection amperometric detection of ethanol vapors in some real samples, such as wines and beers.

2 Experimental

2.1 Chemicals and Instrumentation

All chemicals used were of analytical reagent grade quality and were employed without further purification. Ultrapure ethanol and the acid RTIL 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM][HSO_4]) were purchased from Sigma-Aldrich (St Louis, MO, USA), while the basic RTIL 1-butyl-3-methylimidazolium hydroxyde ([BMIM][OH]) was synthesized according to the literature [37]. A water content of 5 ± 1 % was determined in [BMIM][OH] by Karl Fischer titration, while the water content in [BMIM][HSO_4] turned out to be of 1.1 ± 0.2 %. Also in consideration of the fact that the device proposed here is intended for applications outside laboratories, where the humidity degree is not easily controllable, these RTILs were not dried. However, as a precaution, they were preserved in a dryer until use.

High-purity deionized water (purified by an Elgastat UHQ-PS system, Elga, High Wycombe, UK) was used as solvent and for all washing operations.

Stock solutions of ethanol were prepared by dissolving controlled volumes of this analyte in known volumes of the corresponding solvent (water, [BMIM][OH] or [BMIM][HSO_4]). Controlled amounts of these stock solutions were diluted to the desired concentration prior to each experiment.

Filter paper used for supporting RTILs was purchased from Labor (Cordenons, Italy) as 50 cm × 50 cm foils, 67 g/m^2. Circular crowns (Ø = 8 mm outside and Ø = 3 mm inside) were cut from these foils using hammer blades from KS Tools (Milan, Italy).

Disposable gold screen-printed electrodes (SPEs) type DRP-220AT were purchased from DropSens-Metrohm (Metrohm Italiana s.r.l., Varese, Italy). They were equipped with a central 4 mm diameter Au working electrode surrounded by a gold counter electrode and a silver pseudo reference electrode, all deposited on a ceramic substrate whose dimensions were $3.4\times1.0\times0.05$ cm (length × width × height).

Flow injection analyses were performed by using ultrapure nitrogen as carrier gas, whose flow rate was controlled in the range 20–200 mL min^{-1} by a micrometric valve (Viton SS-22RS2).

Real samples analyzed were two white wines and one beer purchased from local supermarkets, which were used without any preliminary treatment. In addition, a "model wine" was assayed, which consisted of a water solution containing ethanol (12 %) and 30 mM tartaric acid, whose pH was adjusted at 3.2 by NaOH addition.

A Bio-Logic BiStat pontentiostat/galvanostat (Bio-Logic Science Instruments, Seyssinet-Pariset, France), managed by the relevant 10.37 version EC-lab software, was used to perform all voltammetric and amperometric measurements which were always conducted at room temperature.

2.2 SPEs Modified by Coating their Probe-surface with Paper Crowns Soaked with RTILs

Modified SPEs were assembled as reported elsewhere [36], by profiting from a polylactic holder constructed on purpose by the fused deposition modeling technology using a FLSUN Cube 3D printer Ultimaker 2 (Ultimaker B.V., The Netherlands) loaded with a commercially available polylactic filament (FacilanTM Ortho Natural Elogiam, Filoprint, IT). This holder consisted of an upper and a lower portion, as shown in Figure 1A.

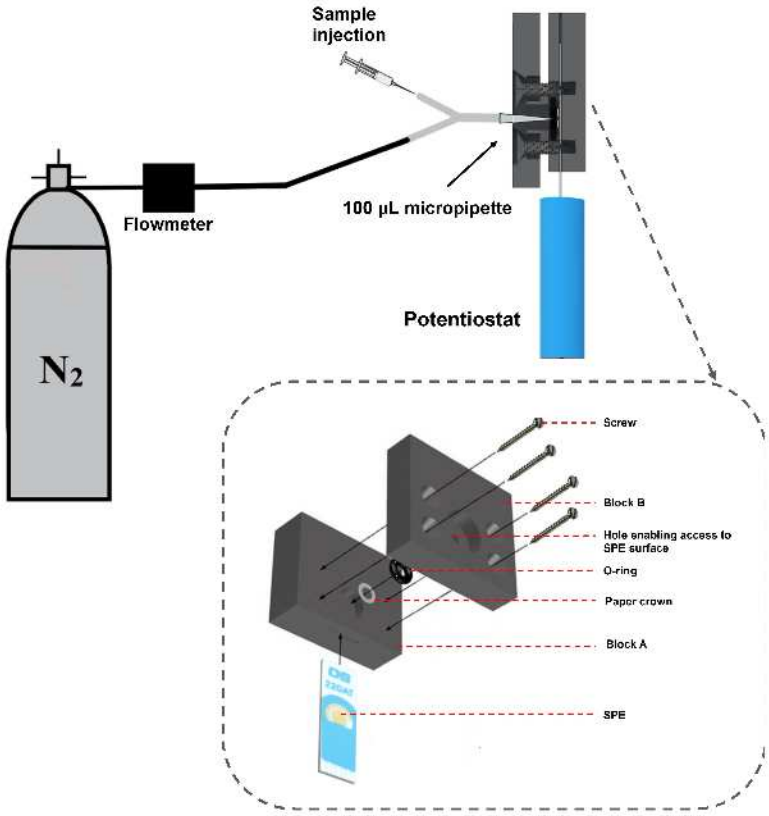

Fig. 1. Sketch of the flow system adopted to perform FIA measurements of ethanol vapors, together with the exploded view of the whole assembly of the modified SPE. A lateral slot is present in the lower portion (Block A) of the 3D-printed holder for the insertion of the ceramic plate lodging the SPE electrode, while a hole is present in the upper portion (Block B) of this holder leaving access to the three electrode circuit.

Briefly, SPEs were housed in the lower portion of the holder and paper crowns were RTIL soaked by dipping them in [BMIM][OH] or [BMIM][HSO_4] for 30 min, followed by the removal of the excess of electrolyte by sorption on filter paper. A soaked paper crown was then applied to the surface of the SPE probe, so as to contact counter and reference electrodes, as well as the outer edge of the gold working electrode. A Viton O-ring (6 mm in diameter and a ring thickness of 2 mm) was set over the paper crown and the upper portion of the 3D printed holder was joined to the lower portion thanks to 4 closure screws, so as to block the circular paper crown on the SPE probe surface. The whole assembly is reported in Figure 1, which also shows the presence in the lower holder portion of a lateral slot for the insertion of the SPE and in the upper portion of a hole for the passage of electrical cables connected to the SPE.

To perform FIA measurements of ethanol vapors, these modified SPEs were inserted in the flow equipment sketched in its turn in Figure 1.

2.3 Voltammetric Measurements at Unmodified and RTIL Modified SPEs

Voltammetric measurements were conducted in both liquid and gaseous phase. Voltammetric tests in liquid phase were performed at unmodified SPEs by dropcasting on their surface 20 µL of [BMIM][HSO_4] or [BMIM][OH], containing or not controlled concentrations of ethanol, thus covering the entire probe surface and assuring in this way the electrolytic contact among the three electrodes. These SPEs were introduced into a closed glass cell plugged with drilled stoppers through which connection cables were tightly inserted.

Voltammetric measurements in gas phase were instead performed at SPEs modified by paper crowns soaked with [BMIM][HSO_4] or [BMIM][OH]. With this purpose, they were introduced into 80 mL PET containers (about 6 cm external diameter; 8 cm in height) plugged in their turn with drilled stoppers through which connection cables were tightly inserted. They were provided with an inlet and an outlet port, the first connected to the outlet of a bubbler containing ethanol and fed with nitrogen flowing for 10 min to assure saturation of the atmosphere inside the PET container. When the nitrogen flow was stopped, both inlet and outlet port were closed.

2.4 Flow Injection Amperometric (FIA) Measurements

FIA measurements were performed with the flow equipment described above, suitably slightly modified by inserting near the end of the polyethylene tube carrying nitrogen a rubber stopper that served as sample injection port. Controlled amounts of ethanol (or ethanol dissolved in water at known concentration) were injected through this port with gas-tight microsyringes, as shown in Figure 1B. Moreover, a 100 µL micropipette was inserted at the end of the outlet polyethylene tube with its tip positioned in front of the SPE in a wall-jet configuration, at a distance of 1 mm from its surface. Sample injections were performed after stabilization of the base signal at the potential applied as the detection potential. Current signals were sampled with a time resolution of 0.05 s.

3 Results and Discussion

3.1 Voltammetric Behavior of Ethanol in [BMIM][HSO_4] and [BMIM][OH]

In this research a gold working electrode was adopted since at this surface the electrochemical oxidation of ethanol occurs in a potential region where reactive metal atoms undergo oxidation to provide a regular monolayer oxide (or OH_{ads}) that mediate analyte oxidations, thus playing an important role in many electrocatalytic reactions [38].

With the aim of individuating the best conditions for the detection of ethanol, the voltammetric behavior of both [BMIM][HSO_4] and [BMIM][OH] media was preliminarily assayed at unmodified SPEs before and after addition of C_2H_5OH (1—3 M).

As expected, a wider anodic range was found to be available in the acid RTIL ([BMIM][HSO_4]) where the discharge of the gold-solvent interphase started at about 1 V, while this discharge already started at about 0.6 V in the basic RTIL ([BMIM][OH]).

The voltammetric profiles recorded in the presence of ethanol, which are reported in Figure 2, where they are superimposed to the background profiles, pointed out that ethanol underwent oxidation in both media, but displaying quite different behaviors.

In the acid medium two well distinct oxidation processes were detected (Figure 2A). The height of the second peak, located at about 0.84 V, increased linearly with the ethanol concentration, thus suggesting that it was diffusion controlled. On the contrary, the first process, giving rise to a quite low anodic wave at about 0.5 V, displayed a very scarce dependence on the ethanol concentration, thus suggesting that the process involved was conceivably due to the ethanol oxidation mediated by the mentioned monolayer of gold oxide [38].

In the basic medium a single oxidation process was instead detected which was located at a potential of about 0.52 V, quite close to the oxidation limit enabled by the corresponding electrode-medium interphase, brought about either the gold oxidation or the solvent discharge (Figure 2B).

The voltammetric behavior found at unmodified SPEs for ethanol dissolved in the two RTILs here considered was then compared with that displayed by ethanol vapors at SPEs modified by paper crowns soaked with the same RTILs. With this purpose, SPEs modified as shown in Figure 1 were lodged in PET containers where ethanol vapors from a bubbler were fed by a nitrogen flow, as described above.

Voltammetric measurements thus performed for ethanol vapors at SPE electrodes modified by applying on their surface paper crowns soaked with either [BMIM][HSO_4] or [BMIM][OH] typically gave rise to the responses shown in Figure 3. These responses showed a good agreement with those recorded for ethanol in RTIL solutions, even though quite lower currents were found at these modified electrodes, despite voltammetric measurements were also in this case performed by using atmospheres saturated with ethanol. This fact can easily be explained on considering that the effective electrode area available at these modified SPE electrodes was not that of the entire gold working electrode. In fact, it corresponded only to the outer edge of this electrode intimately contacted by the soaking electrolyte present in the boundary zone of the paper crown, where ethanol vapors undergo charge transfer as soon as they reach the relevant interphase [36].

On the basis of these preliminary results, we chose to perform our investigations, aimed at evaluating the performance provided by paper-crown modified SPE electrodes for the FIA analysis of ethanol vapors, by adopting the sole acid RTIL [BMIM][HSO_4]. This choice was made in view not only of the fact that the ethanol oxidation occurs in this medium at potentials quite different from the solvent discharge, but also because a better repeatability was displayed by the relevant voltammetric profiles.

3.2 Flow Injection Analysis of Ethanol Vapors

FIA measurements were carried out by the home-made flow apparatus described in the Experimental Section 2.4, where modified SPEs were placed as wall-jet amperometric detectors at 1 mm from the outlet of the polyethylene tube (see Figure 1).

Preliminary tests were performed for optimizing both the nitrogen gas carrier flow rate and the detection potential. At first, a potential of 0.8 V, surely suitable for assuring the occurrence of the ethanol oxidation, was imposed to the working electrode and the effect of the flow rate in the range 20–60 mL min^{-1} was evaluated. In these tests 200 µL of headspace in equilibrium with pure ethanol at 20 °C were repeatedly injected (corresponding to 1.15 µmol as inferred from its vapor pressure at the indicated temperature [39]). At this potential, sharp readouts were recorded, characterized by a very short response time (about 2 s), whose height increased until

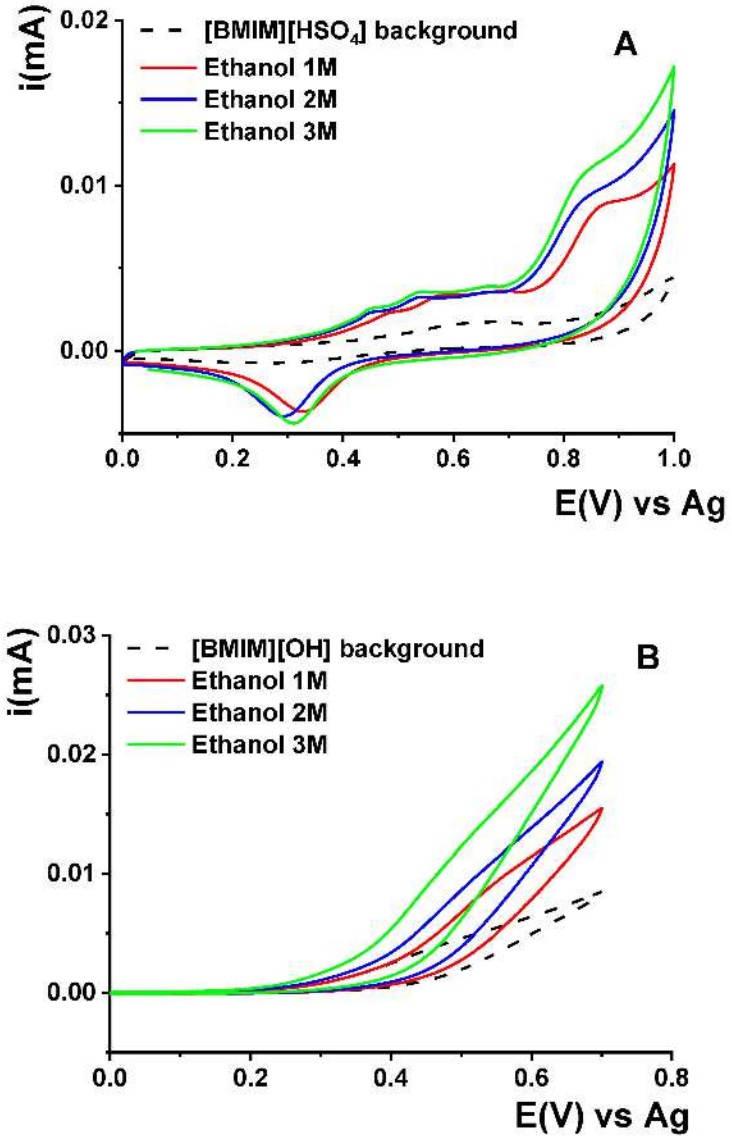

Fig. 2. Voltammetric profiles recorded with a scan rate of 20 mVs^{-1} at a gold unmodified SPE electrode in [BMIM][HSO_4] (A) and in [BMIM][OH] (B) containing the indicated ethanol concentrations and compared with the corresponding background profiles.

the flow rate reached approximately 40 mL min^{-1}, while no appreciable increase was observed for higher flow rates. Subsequently, by adopting a carrier gas flow rate of just 40 mL min^{-1}, FIA responses were recorded for the injection of 200 µL of headspace in equilibrium with a sample of pure ethanol at 20 °C and imposing to the working electrode different potentials as reported in Figure 4 (0.6–0.8 V). The results shown in this Figure pointed out that the higher sensitivity was achieved at a working potential of just 0.8 V. The rather low sensitivities observed at lower potentials confirmed conceivably that a surface-mediated process is involved in the potential region where only the first oxidation wave was present.

The injection of different volumes (in the range 50–1000 µL, equivalent to 0.29–5.75 µmol) of head-space in equilibrium with a sample of pure ethanol at 20 °C allowed us to ascertain that the corresponding FIA responses increased linearly only in the range extending up to 1.2 µmol (about 200 µL). The injection of higher amounts of ethanol led instead to a progressive curving trend.

In order to have at our disposal a calibration plot in which FIA current signals were related to ethanol concentrations expressed as ethanol/water v/v concentrations (as usual for alcoholic beverages), flow injections of 200 µL of head-space in equilibrium with aqueous solutions containing known concentrations (expressed as v/v) of ethanol were performed. FIA responses recorded under the optimized conditions mentioned above (nitrogen flow rate 40 mL min^{-1} and electrode potential of 0.8 V) for aqueous solutions of ethanol in the range 1–60 % were characterized by a very flat baseline with a noise of about 28 nA. These responses allowed us to infer

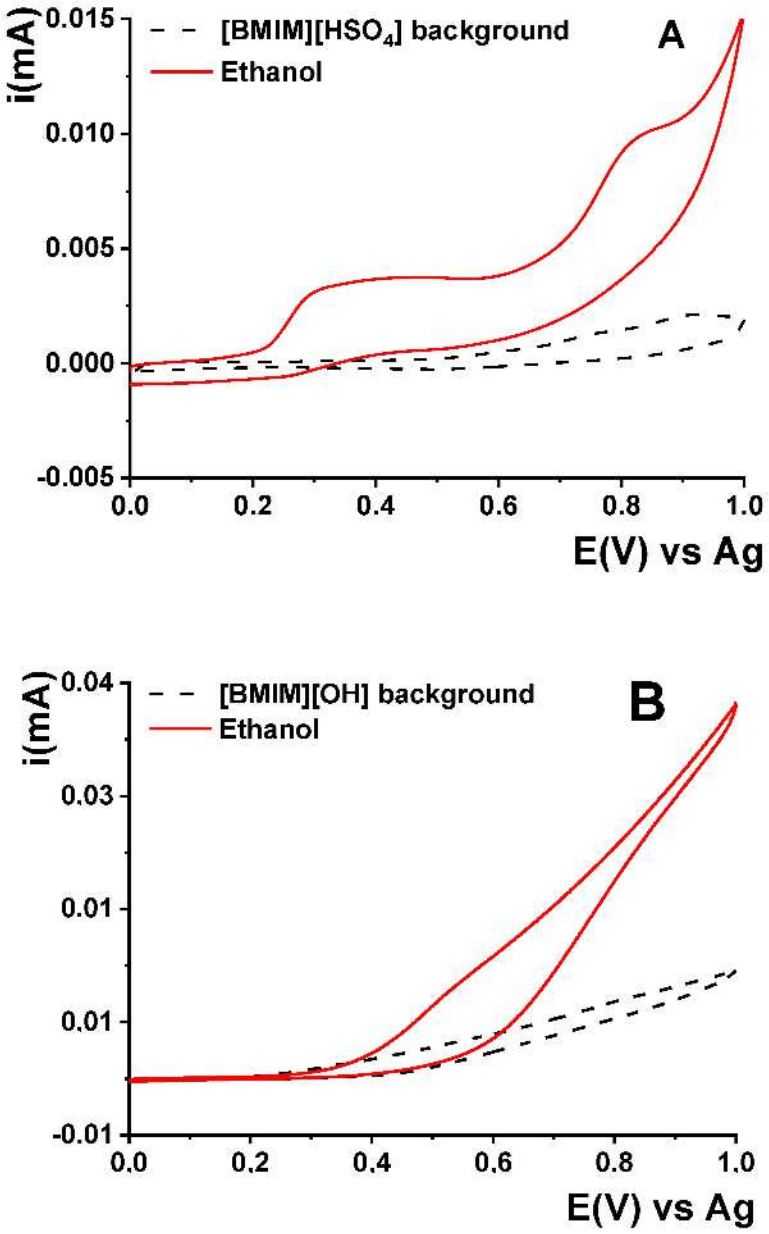

Fig. 3. Voltammograms displayed by ethanol vapors at gold SPE electrodes modified with paper crowns soaked with [BMIM][HSO_4] (A) and [BMIM][OH] (B), compared with the corresponding background profiles. Scan rate 20 mVs^{-1}.

the desired calibration plot ($i(\mu A) = 0.0176 \times C_{EtOH}$ (%v/v) + 0.0291), which is reported in Figure 5, together with some of the corresponding FIA peaks. Also in this case, a linear increase was found only for fairly low ethanol concentrations (≤ 12 % v/v), while a progressive curving trend was observed at higher contents, in agreement with the results reported above for the injection of increasing amounts of pure ethanol. From these responses, also the relevant correlation coefficient R^2 (0.994), detection limit (0.55 % v/v), evaluated for a signal-to-noise ratio of 3, and quantitation limit (1.60 % v/v), evaluated for a signal to noise ratio of 10 could be inferred. All these results were the average of values obtained for three different modified SPEs, all assembled as described above, with the aim of also estimating the inter-device reproducibility. The results obtained in these tests indicate that the modification procedure here suggested for SPE electrodes is characterized by a good reproducibility (within about 7 %).

The response time of these devices, evaluated as the difference between the time corresponding to the recording of the peak maximum and the injection time, was very short (about 2 s), thus highlighting that the assembly adopted acts as a fast-responding electroanalytical sensors Most of the credit for this short response time is likely to be attributed to the ability of these modified SPEs to respond as devices capable of providing signals coming from the establishment of a three-phase contact. In fact,

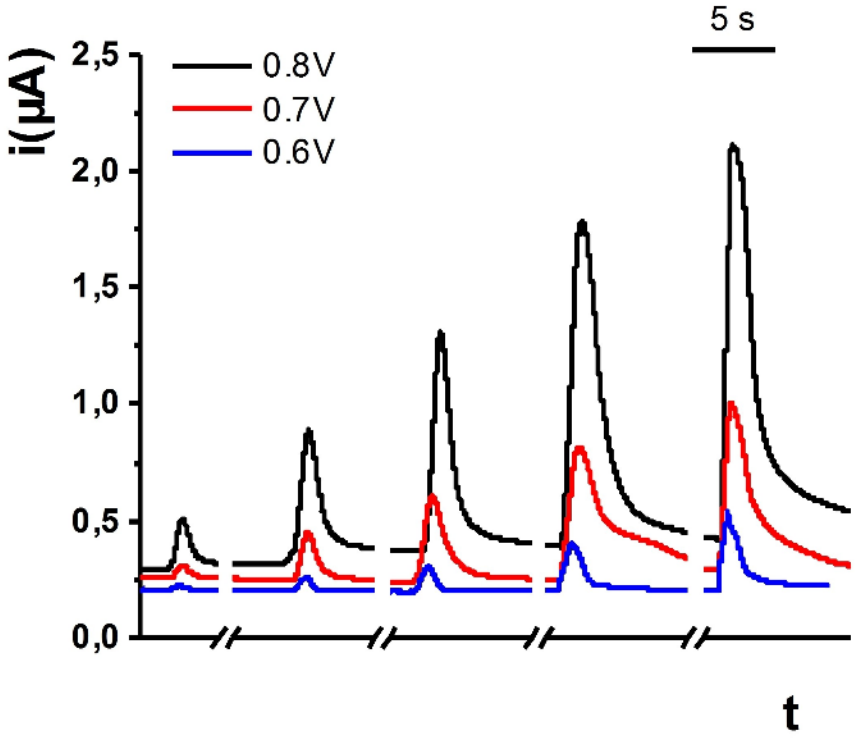

Fig. 4. FIA peaks recorded at a SPE electrode modified with paper crowns soaked with [BMIM][HSO_4] at the increasing potentials indicated. Carrier flow rate 40 mL min^{-1}. Sample injected : 1, 50 μL; 2, 125 μL; 3, 250 μL; 4, 500 μL; 5, 1000 μL.

no diffusion/permeation step is involved because the flowing analyte can approach directly the active interphase where the working gold disc electrode was contacted by the paper-soaking electrolyte.

Finally, the repeatability turned out to range from 5 to 7 % and also the long-term stability was found to be quite satisfactory. In fact, modified SPEs could operate at room temperature for several days (up to 14), performing some hundreds of ethanol injections, without any significant response change. Moreover, after replacing in modified SPEs the soaked paper crown with a new one, in its turn soaked following the same procedure, the responses obtained for ethanol injections did not differ by more than 6–8 % (comparable with repeatability) from those initially found.

The whole of these results is summarized in Table 1.

Table 1. Performance displayed by SPEs modified by applying on their surface a paper crown soaked with [BMIM][HSO_4] in FIA measurements carried out on head space in equilibrium with aqueous ethanol solutions at different concentrations (number of replicates = 6).

Parameter	Performance
Sensitivity [i(μA)/C_{EtOH}(% v/v)]	0.0176 (RSD % = 5.76)
R^2	0.994
Linear range (% v/v)	1–12
LOD (% v/v)	0.55
LOQ (% v/v)	1.60
Repeatability (%)	5.94
Reproducibility (%)	6.91
Baseline noise (μA)	0.028

3.3 FIA Analysis of Ethanol in Real Samples

Real samples, consisting of two white wines and one beer purchased from local supermarkets, as well as a "model wine" suitably prepared as described in the Experimental Section 2.1, were analyzed by following the same procedure adopted for inferring the calibration plot.

In principle, the detection of ethanol in real alcoholic drinks could be interfered by the presence of at least two electroactive species such as SO_2 and methanol [40]. Consequently, we performed some tests to estimate their possible interference. With this purpose, the voltammetric behavior displayed in gas phase by these two species was preliminarily investigated, thus inferring that SO_2 does not underwent oxidation in the potential range employed for the ethanol detection. On the contrary, the oxidation of methanol occurs just at the same potentials of ethanol, as shown in Figure 6 where the voltammetric profiles recorded for saturated atmospheres of these two alcoholic species are compared. Even though the current recorded for methanol was enough comparable with that recorded for ethanol, (it was only slightly lower), such interference does not seem to be a real problem, since the methanol content in alcoholic drinks is usually very low with respect to ethanol (usually no more than 0.02 % [41]). In fact, when FIA peaks were recorded for the injection of aqueous solutions of ethanol in the range 1–12 % v/v after

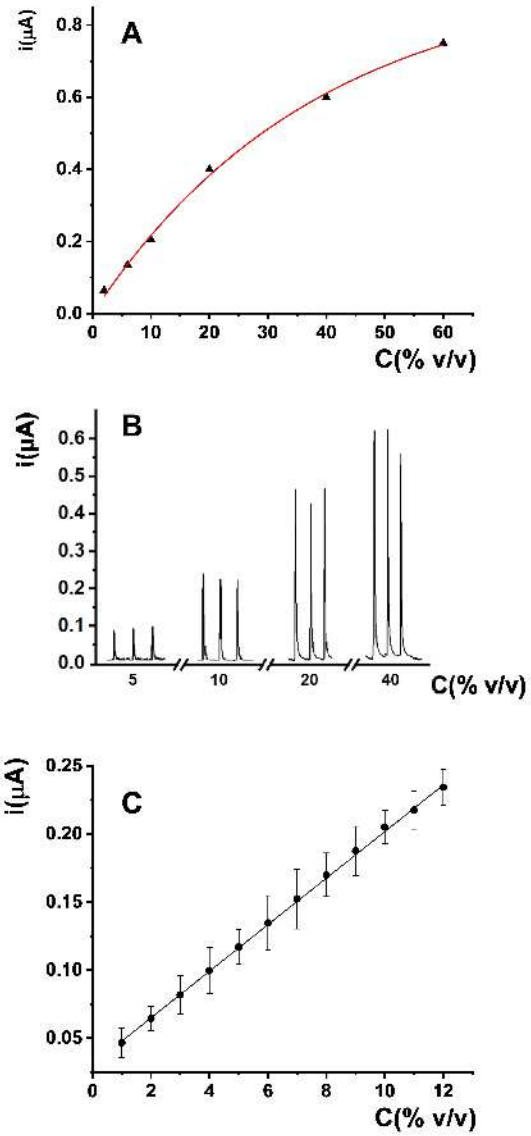

Fig. 5. **(A)** Calibration plot for FIA measurements conducted on head-space in equilibrium with aqueous solutions containing known concentrations of ethanol in the range 1–60 % v/v. (B) FIA peaks recorded for some of these measurements. (C) Calibration plot constructed in the concentration range where a satisfactory linear increase was indeed found.

the addition of 0.05 % of methanol, no appreciable difference was observed.

The results obtained for the real samples considered are summarized in Table 2, where they are compared with the alcoholic degree reported on the labels present in their bottles. Of course, in the case of the "model wine", such a comparison was made with the known amount of ethanol added to this aqueous solution.

The good agreement of the values found with those expected shown in this Table gives evidence in favor of the reliability of responses provided by the proposed sensor.

4 Conclusions

The performance provided by the SPE electrode modified as described in this paper points out that this type of sensor is actually suitable for monitoring ethanol vapors released from alcoholic beverages. This sensor offers some advantages over other approaches, mainly because it allows the rapid detection of ethanol in drinks, but also in food, by disposable, cost effective and real time instrumentation, also suitable for untrained operators and easy to be transported.

In particular, as to real time measurements, it must be underlined that the shape and location adopted for the paper support makes possible a truly intimate contact between the RTIL soaking electrolyte present in the inner edge of the paper crown and the working gold electrode, so that electroactive gaseous analytes can undergo charge transfer as soon as they reach the corresponding interphase. Therefore, these modified SPEs behave as fast responding membrane-free electrodes since no diffusion or permeation step is involved.

Finally, it must be considered that this type of sensor is simply based on the use of both SPEs, easily commercially available at low enough prices, and circular crowns of paper (a low cost material) soaked with a suitable RTIL which belongs to a class of compounds always displaying very low volatility, high intrinsic conductivity, wide electrostability and the ability to dissolve several organic and inorganic species.

Acknowledgements

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Table 2. Comparison of the ethanol content determined in real samples with the content reported in the labels present on their bottles (with the corresponding relative standard deviations in parenthesis, found in 6 replicate mesurements).

Sample	Ethanol found (%)	Alcoholic degree reported on the label (%)	Ethanol added (%)
Beer	4.6 (±0.2)	4.9	–
White wine 1	10.6 (±0.3)	10.5	–
White wine 2	12.8 (±0.1)	12.5	–
Model wine	11.6 (±0.2)	–	12.0

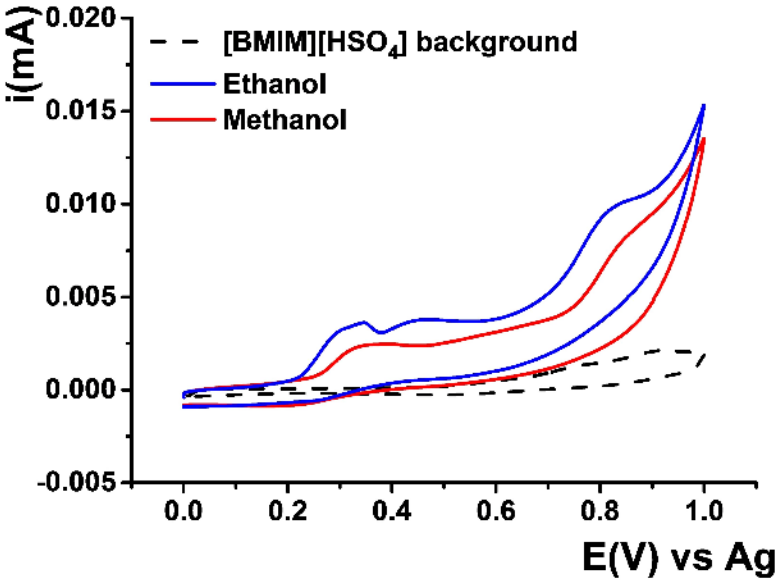

Fig. 6. Comparison of voltammetric profiles displayed at gold SPE electrodes modified with paper crowns soaked with [BMIM][HSO_4] by nitrogen atmospheres saturated with ethanol and methanol.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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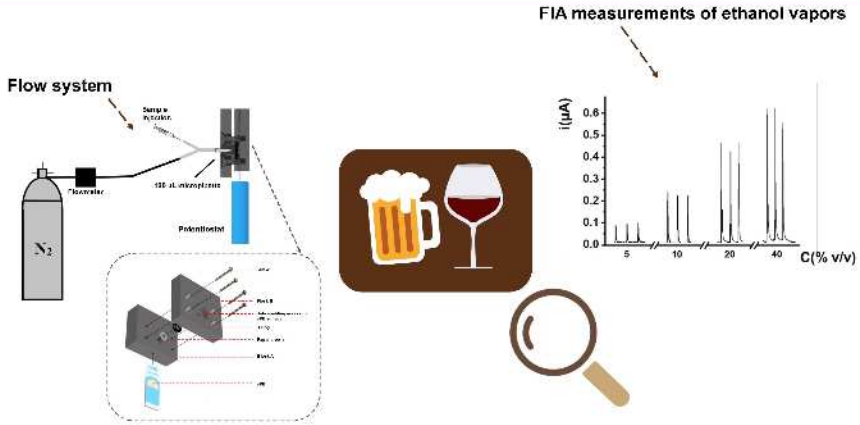

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