



Simultaneous quantification of 4-ethylphenol and ethanethiol in wines by headspace amperometric measurements

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ABSTRACT

Simultaneous analysis of 4-ethylphenol and ethanethiol has been carried out since they often coexist in wine samples producing significant organoleptic defects. Dual working screen-printed electrodes have been used for this aim. An activated fullerene C₆₀ modified screen-printed carbon electrode (AC₆₀/SPCE₁) was used for the determination of 4-ethylphenol, while a cobalt (II) phthalocyanine modified SPCE (CoPh/SPCE₂) was employed for ethanethiol detection. Headspace amperometric measurements were performed applying different potentials to the electrode system, which were coated by a commercial polyamide membrane immersed in supporting electrolyte, for the simultaneous and selective detection of both species in a single run. The constructed sensing dual system presented an exceptional detection performance with a capacity of detection of 2.7 mg/L and 0.2 mg/L for 4-ethylphenol and ethanethiol, respectively. The developed method was successfully applied for the simultaneous detection of both compounds in wine samples where it demonstrated a high degree of trueness and suitable efficiency.

1. Introduction

Aroma is one of the most important characteristics associated to the quality of a wine, which contains around a thousand components, some of which considerably affect this feature. Accordingly, it is well known the negative effects of 4-ethylphenol on wines affected by yeast belonging to the genus *Brettanomyces/Dekkera*. This compound contributes to the aromatic complexity of a wine at low concentration, although provokes unpleasant olfactory perceptions, described as “animal smell” or “horse sweat”, at certain concentration values [1,2]. Likewise, wine contains a substantial amount of volatile sulfur compounds, including ethanethiol, being responsible for “rotten egg” or “cooked cabbage” off-odors, also exerting an enormous influence on its aroma [3,4]. Since the appearance of these described unpleasant odors is a major concern for the wine industry, many research works have been devoted to both understanding the formation of these compounds and developing analytical methods for their quantification. Due to their volatility, the preferred analysis technique for their determination has been gas chromatography [5,6]. In order to solve problems related to the low concentration of analyte and to reduce the impact of the matrix effect on the final analytical result, different pretreatment, isolation and extraction steps have been performed in wine samples before

chromatographic analysis, making these methods quite tedious and difficult to apply in routine analysis [1–21]. Electrochemical techniques, with sensitivity and selectivity similar to chromatographic techniques, but with greater simplicity, lower cost and portability options, are presented as an interesting alternative for *in situ* analysis [22]. Despite these advantages, only a few works have achieved the successful electrochemical determination of ethanethiol [23–25] and 4-ethylphenol [26–29] in wine. Most of these works describe sensors based on the use of disposable screen-printed carbon electrodes (SPCEs) as transducers, which present important advantages related to low-cost mass production, design flexibility and small size. This last feature allows their use with portable devices that can be easily handled for the *in situ* analysis of low sample volumes [30]. Moreover, SPCEs can be easily modified with different types of substances to improve their characteristics or to solve a specific analytical problem, like the achievement of sensitive and selective sensors for the analysis of different components in wine. In this way, the incorporation of fullerene C₆₀ (C₆₀) to the SPCE surface has resulted highly effective in the development of sensitive electrochemical sensors for different analytes, including 4-ethylphenol [28,31,32]. This molecule presents unique electrochemical properties, being reduced C₆₀ films successful electron transfer mediators, which not only promote the decrease of peak potential but also the increase of

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peak current, thus enhancing the sensitivity of the electrochemical sensor [33,34]. Macrocyclic organic molecules such as metallophthalocyanines have also been used in combination with SPCEs for the analysis of different compounds, being cobalt (II) phthalocyanine (CoPh) one of the most selected as a redox mediator in the development of electrochemical sensors due to its low cost and high chemical and thermal stability [25,35–37]. Selectivity can even be increased by using electrochemical methods based on the determination of the analyte content present in the headspace in equilibrium with the liquid sample [25,28,38,39]. This selective procedure has allowed the analysis of 4-ethylphenol [28] and ethanethiol [25] in wine eliminating any interference from non-volatile components of the sample. The simultaneous analysis of both components may result utmost importance in the routine and rapid determination of these compounds. Thus, this work describes the development of sensitive and selective electrochemical sensors for the simultaneous headspace analysis of 4-ethylphenol and ethanethiol, responsible for the appearance of undesirable organoleptic defects in wine, using disposable SPCEs. The placement of the required supporting electrolyte in electrochemical measurements has also been studied. The problem of lack of wettability of the dual electrode system when using the simple adsorption of aqueous supporting electrolyte has been overcome by using commercial polyamide membranes.

2. Experimental

2.1. Chemicals and instrumentation

All chemicals used were of analytical grade. Solutions were prepared in Milli-Q water (Milli-pore, Bedford, MA, USA). Solutions of Britton Robinson buffer (BR), consisting of 0.04 M phosphoric acid (Panreac, Barcelona, Spain), acetic acid 0.04 M (VWR Chemical, Fontenay, France), boric acid 0.04 M (Panreac, Barcelona, Spain), and potassium chloride 0.1 M (Merck, Darmstadt, Germany) were used as supporting electrolyte. A 1 M NaOH solution (Ecros, Barcelona, Spain) was used to adjust the pH. Stock standard solutions were prepared from 4-ethylphenol (Alfa Aesar, Haverhill, Massachusetts, USA) and ethanethiol reagents (VWR Chemicals, Rosny-sous-Bois, France) dissolved in Milli-Q water.

A potentiostat PalmSens4 (Palmses, BV, Houten, The Netherlands) was used for the electrochemical measurements, together with dual SPCEs (DRP-X1110, Metrohm, DropSens, Oviedo, Spain) with two elliptical carbon working electrodes, one carbon counter electrode and a silver reference electrode. These dual SPCEs were individually modified using two different solutions: C_{60} (Acros Organics, Geel, Belgium) dissolved in dichloromethane (Panreac, Barcelona, Spain) and CoPh (Alfa Aesar, Karlsruhe, Germany) dissolved in ethanol (VWR Chemicals, Rosny-sous-Bois, France). Solutions 1.0 M of potassium hydroxide (Carlo Erba, Val de Reuil, France) were used to activate C_{60} . Polyamide membranes for SPCEs (DRP-MEMB, Metrohm, DropSens, Oviedo, Spain) were placed over the electrode system.

A cylindrical resin cell, with a 9 mm radius and a 30 mm height, was 3D printed using a Selective Deposition Lamination-3D-Printing machine (Anycubic: Photon Mono SE, AnyCubic, Shenzhen, China) and an Anycubic Grey Colored UV resin. The cell was designed with a small side hole, which allows the introduction of samples, and a lid that, in addition to sealing it, allows the dual SPCEs to be placed through a rectangular slot (10 mm \times 1 mm).

2.2. Headspace amperometric measurements using AC_{60} and CoPh modified dual SPCEs

Both working electrodes were modified at first in order to get a selective oxidation current for 4-ethylphenol and ethanethiol. In the case of the first working electrode, a volume of 40 μ L of a solution of C_{60} (0.1 mg/mL) in dichloromethane was deposited on the SPCE surface, dried at room temperature and electrochemically activated in a 1 M KOH



Fig. 1. AC_{60} and CoPh modified dual SPCEs, coated with a commercial polyamide membrane, for the simultaneous detection of 4-ethylphenol and ethanethiol.

solution by cycling the potential between 0 to -1.5 V at 10 mV/s ($AC_{60}/SPCE_1$) [28,40]. The modification of the second working electrode with CoPh was performed by drop-casting. A volume of 10 μ L of a 5 % solution of CoPh in ethanol was placed onto the surface of the electrode and left to dry at room temperature ($CoPh/SPCE_2$) [25]. Finally, a commercial polyamide membrane was placed over the electrode system, which was subsequently immersed in supporting electrolyte pH 5 for 10 min, improving in this way its wettability (Fig. 1). This dual device was then placed at the top of a homemade cell containing 1 mL of BR pH 5 (Fig. 2). Headspace amperometric measurements were performed by applying a potential of +0.86 V to $AC_{60}/SPCE_1$ and +0.8 V to $CoPh/SPCE_2$. Once constant intensities were recorded, a determined volume of the sample solution was directly added to the cell through its side hole. 4-ethylphenol and ethanethiol in the headspace in equilibrium with the liquid phase are subsequently oxidized on the surface of the corresponding electrode leading to an increase in current.

3. Results

$AC_{60}/SPCEs$ and $CoPh/SPCEs$ have already been used for the individual electrochemical detection of 4-ethylphenol and ethanethiol in gas phase [25,28], but not yet simultaneously in wine samples. The key point in this type of headspace electrochemical measurements is that electrodes must be immersed in a non-reactive electrolyte. Up to now, a two-step procedure in which the voltammetric measurements are carried out in solution after an incubation process in gas phase have been followed for 4-ethylphenol detection [28]. In the case of ethanethiol, headspace amperometric measurements have been carried out at +0.8 V in a sealed cell containing $CoPh/SPCEs$ in which the supporting electrolyte was preloaded by adsorption [25]. The latter approach was followed to perform the simultaneous determination of both analytes using AC_{60} and CoPh modified dual SPCEs in this work, but no successful results were achieved, as the aqueous supporting electrolyte was not properly adsorbed a time enough to record a whole amperogram. To improve the operational lifetime of these devices, it was decided to modify their surface with a commercial membrane that would improve the wettability of the dual electrode system, as it has been above-described.

The redox processes of 4-ethylphenol and ethanethiol on the surface of the $AC_{60}/SPCE_1$ and $CoPh/SPCE_2$ were due to an oxidation process in the ortho position of the molecule, giving rise to the corresponding quinone [28], and to a Co(II) mediated oxidation [25], respectively. Obviously, a single supporting electrolyte has to be used to immerse the electrodes, so several BR pH values were tested between 2 and 5 with the aim of recording selective oxidation currents in each working electrode. It was taken pH 5 as optimum one, since oxidation signals were selectively obtained only for 4-ethylphenol at $AC_{60}/SPCE_1$, applying a potential of +0.86 V, and for ethanethiol at $CoPh/SPCE_2$ with a potential of +0.8 V. As it can be seen in Fig. 2, oxidation amperometric currents were only recorded at $AC_{60}/SPCE_1$ and $CoPh/SPCE_2$ when 4-ethylphenol and

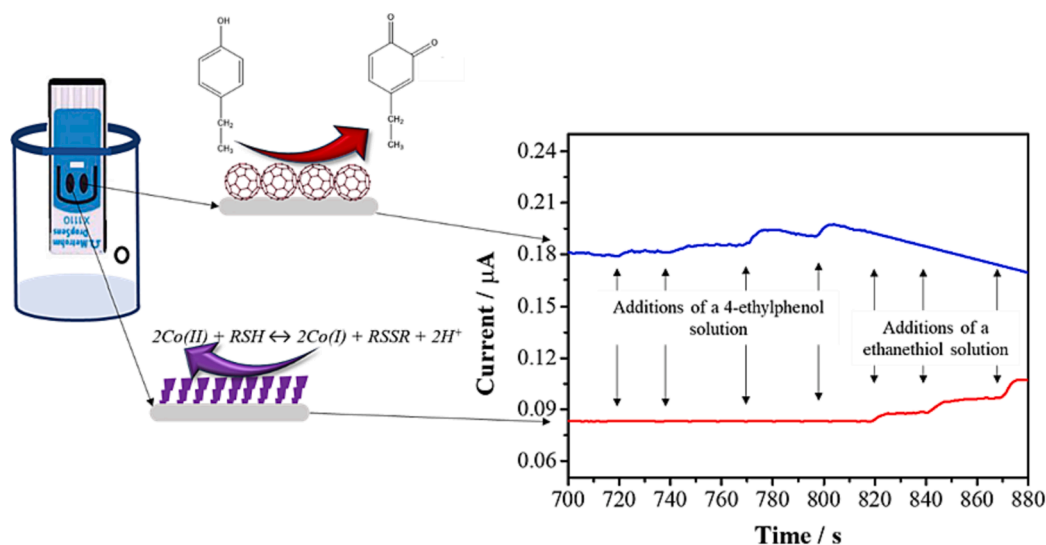


Fig. 2. Headspace amperometric measurements performed for the detection of 4-ethylphenol and ethanethiol in BR pH 5 using a dual $AC_{60}/SPCE_1$ (Applied potential, +0.86 V) and $CoPh/SPCE_2$ (Applied potential, +0.8 V) device coated with a commercial polyamide membrane.

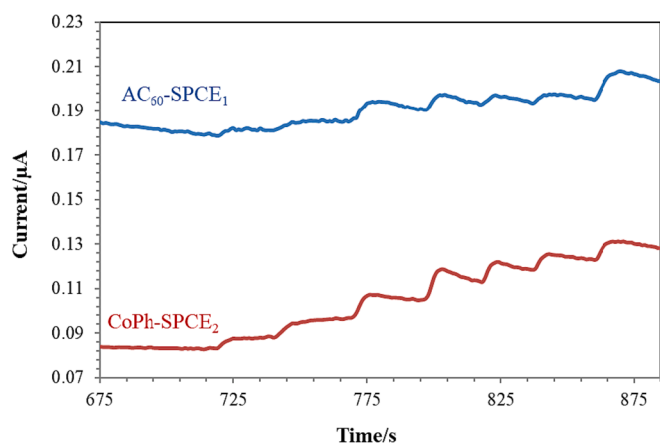


Fig. 3. Headspace amperometric measurements performed for the detection of 4-ethylphenol and ethanethiol in BR pH 5 using a dual $AC_{60}/SPCE_1$ (Applied potential, +0.86 V) and $CoPh/SPCE_2$ (Applied potential, +0.8 V) device coated with a commercial polyamide membrane. Each addition corresponds to 20 μL of a 138 mg/L of 4-ethylphenol and a 13 mg/L of ethanethiol solution.

ethanethiol solutions were respectively added into the cell. Therefore, AC_{60} and $CoPh$ modified dual SPCEs, coated with a commercial polyamide membrane, have been used for the simultaneous headspace

detection of 4-ethylphenol and ethanethiol under these experimental conditions.

This method was next validated considering parameters such as accuracy and capability of detection. Several calibration curves were recorded under the optimum conditions of the experimental variables by adding 20 μL of a single solution containing 138 mg/L of 4-ethylphenol and a 13 mg/L of ethanethiol to the electrochemical cell (Fig. 3). Accuracy measures the degree of agreement between the analytical results obtained in terms of repeatability and reproducibility, where repeatability occurs when measurements are made using the same dual device and reproducibility when using different dual devices. Accuracy was thus studied in terms of residual standard deviation (RSD) of the slopes of the calibration curves registered in the concentration range of 2.7 to 12.5 mg/L of 4-ethylphenol and 0.2 to 1.1 mg/L for ethanethiol. Anomalous points with a Studentized residual greater than 2.5, in absolute value, were removed in order to provide a correct evaluation of the calibration parameters [41]. Regarding reproducibility, an RSD of 4.2% ($n = 3$) was obtained for $AC_{60}/SPCE_1$ and 1.1% ($n = 3$) in the case of $CoPh/SPCE_2$ (Fig. 4). However, when the same device was used, a loss in sensitivity was observed when performing successive calibration curves for 4-ethylphenol and ethanethiol. This fact was not considered a major drawback in view of the simple and reproducible manufacturing of these devices.

The decision limit (CC_{α}) and the capacity of detection (CC_{β}) were also calculated from these validated calibrations, using the DETARCHI

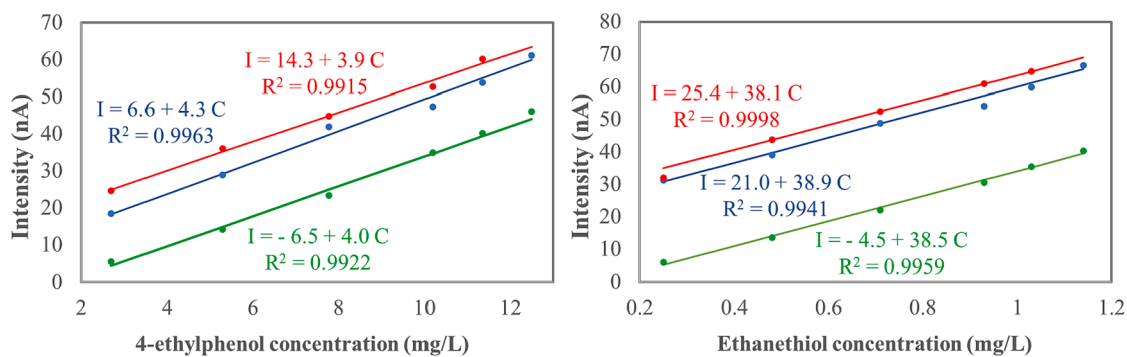


Fig. 4. Experimental points and calibration plots obtained under optimized experimental conditions for the detection of 4-ethylphenol and ethanethiol in BR pH 5 using three different dual $AC_{60}/SPCE_1$ (Applied potential, +0.86 V) and $CoPh/SPCE_2$ (Applied potential, +0.8 V) devices coated with a commercial polyamide membrane.

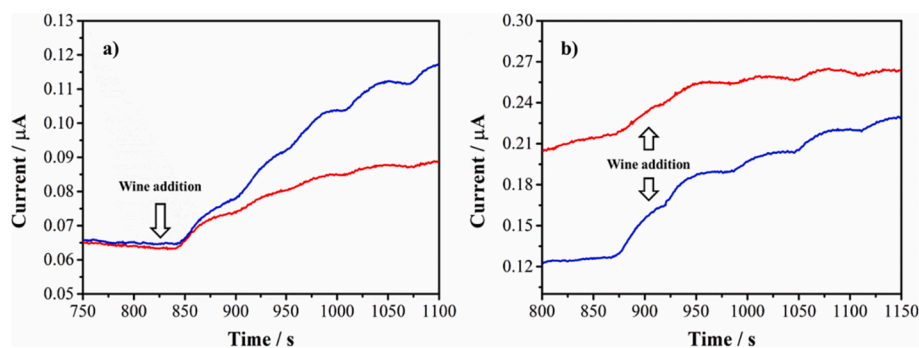


Fig. 5. Headspace amperometric measurements performed for the detection of 4-ethylphenol and ethanethiol in wine samples, both in (a) its original state and in (b) fortified samples, using a dual AC₆₀/SPCE₁ (Applied potential, +0.86 V) and CoPh/SPCE₂ (Applied potential, +0.8 V) device coated with a commercial polyamide membrane. The first addition corresponds to the wine sample or the fortified wine sample and the following ones to 20 µL of a 262 mg/L of 4-ethylphenol and a 24 mg/L of ethanethiol solution.

Table 1

Determination of 4-ethylphenol and ethanethiol in different wine samples by headspace amperometric measurements AC₆₀ and CoPh modified dual SPCEs coated with a commercial polyamide membrane.

Grape variety	Analyte	Conc. added (mg/L)	Conc. found (mg/L)	Recovery (%)	
Airen-Verdejo	4-ethylphenol	–	Not found		
		12.5	13.4 ± 0.3	107.1	
		10.1	9.5 ± 0.9	93.9	
	Ethanethiol	–	Not found		
		1.1	1.1 ± 0.1	98.1	
		0.9	0.9 ± 0.04	97	
	Tempranillo	4-ethylphenol	–	Not found	
			12.5	12.4 ± 0.8	99.1
			10.1	10.0 ± 0.9	98.8
Ethanethiol		–	Not found		
		1.1	1.3 ± 0.1	110.5	
		0.9	1.0 ± 0.1	110.3	
Chardonnay		4-ethylphenol	–	Not found	
			12.5	13.0 ± 1.0	104.4
			10.1	10.4 ± 0.8	103.3
	Ethanethiol	–	Not found		
		1.1	5.7 ± 0.4	110.5	
		0.9	1.2 ± 0.1	113.0	
	Tempranillo-Syrah	4-ethylphenol	–	Not found	
			12.5	12.5 ± 1.0	100.4
			10.1	10.2 ± 0.9	101.6
Ethanethiol		–	Not found		
		1.1	5.4 ± 0.4	105.9	
		0.9	1.2 ± 0.1	107.2	
			0.9 ± 0.1	96.6	
		0.5	0.5 ± 0.04	101.1	

program [42,43]. CC_α, defined as the minimum concentration of the analyte of interest that the method can determine with a probability of 1 – α, was 1.2 mg/L for 4-ethylphenol and 19 µg/L for ethanethiol, with a probability of false positive (α) of 0.05. CC_β, that is, the minimum concentration of the analyte that the method is able to detect with a probability of 1 – β, being β the probability of false negative, was under the concentration of the first standard for α = β = 0.05. So, 2.7 mg/L and 0.2 mg/L were the values taken for CC_β in the case of 4-ethylphenol and ethanethiol, respectively, from an analytical point of view [44]. Even these values are slightly higher than those obtained using the individual sensors, 700 µg/L for 4-ethylphenol [28] and 12.5 µg/L [25] for ethanethiol, it is noteworthy that the AC₆₀ and CoPh modified dual SPCEs coated with commercial polyamide membranes allows the simultaneous

headspace detection of both analytes, considerably reducing the time of analysis.

Finally, trueness was determined considering spiking/recovering, according to the methodology proposed by IUPAC [45]. Different red and white commercial wine samples were analysed by the method under validation both in its original state (Fig. 5a) and after the addition (spiking) of a known concentration of 4-ethylphenol and ethanethiol (Fig. 5b). At first, wine samples in its original state did not show any signal related to the presence of these analytes (Fig. 5a and Table 1). Successful results were obtained in terms of recovery, ranging from 94 to 118 %, for different concentration levels of each spiked wine (Table 1), which indicates a nice applicability of the developed analytical method.

4. Conclusions

Dual screen-printed electrochemical devices have been used for the development of amperometric sensors to simultaneously detect 4-ethylphenol and ethanethiol at gas phase. The combination of an AC₆₀/SPCE₁ and a CoPh/SPCE₂ resulted adequate for the joint determination of both species in the concentration range of 2.7 to 12.5 mg/L and of 0.2 to 1.1 mg/L for 4-ethylphenol and ethanethiol, respectively. The headspace amperometric measurements performed have also demonstrated a practical analytical efficacy in the selective and reproducible analysis of wine samples, obtaining excellent recoveries values, ranging from 94 to 118 % without any sample pretreatment. Thus, the developed method may be used as an excellent alternative to more expensive and complex methods for the simultaneous determination of compounds related to organoleptic defects in real samples.

CRediT authorship contribution statement

Paula Portugal-Gómez: Formal analysis, Validation. **Olga Domínguez-Renedo:** Investigation, Supervision, Validation, Writing – review & editing. **M. Asunción Alonso-Lomillo:** Conceptualization, Investigation, Supervision, Writing – original draft.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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