



Headspace detection of ethanethiol in wine by cobalt phthalocyanine modified screen-printed carbon electrodes

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ABSTRACT

The formation of thiols has a notable and detrimental sensory impact, especially in the aroma of bottled wines. Their detection in wine is of great interest to avoid important economic and image losses for wineries. This work reports the study of different cobalt phthalocyanine/nanomaterials-based sensors for the headspace detection of volatile thiols. The amperometric procedure based on the use of carbon sensors simply modified with cobalt phthalocyanine showed the best performance. Under the optimum conditions of applied potential, +0.8 V, and pH of the supporting electrolyte, 2.6, this procedure shows a reproducibility of 7% ($n = 5$) in terms of relative standard deviation of the slopes of calibration curves built in the concentration range from 9.9 to 82.6 $\mu\text{g/L}$, a capability of detection of 12.5 $\mu\text{g/L}$ and a decision limit of 6.5 $\mu\text{g/L}$ ($\alpha = \beta = 0.05$). The use of this electrocatalytic material and the headspace measurements reduce interferents, increasing the selectivity of the procedure, which allows the easy and successful quantification of ethanethiol in white and red wines.

1. Introduction

The current wine market requires obtaining products of high quality with a harmonious composition, lacking of organoleptic defects, which allows them to preserve the flavour and positive aromas of fruitiness and varietal character [1]. This aroma results from the large number of its components, their concentration, their olfactory thresholds and their synergistic effects [2]. Sulphur compounds, formed mainly during the fermentation process, are also fixed components of the typical aroma of each wine. When some of them are produced in greater than ordinary quantities, alterations of smell and flavour originate that are decisively rejected by the consumer. For example, H_2S , dimethyl sulphide and thioacetic acid esters, which are essential in the fermentation stage, can produce the simplest organosulphur compounds, being ethanethiol (EtSH) a significant member of this group, by reaction with ethanol or ethanal, reduction by yeasts or hydrolysis, respectively [1–3]. The formation of EtSH has a notable and detrimental sensory impact, especially in the aroma of bottled wines [4,5]. They contribute to the olfactory defect that more or less reminiscent of rotten egg, onion, burnt rubber, cooked garlic smells. This defect, well-known to winegrowers and consumers, is the most frequent cause of complaints and entails significant economic and image losses for the producing winery [1,3]. Therefore, its detection is of great interest with the aim of making early diagnoses of

preventive nature, with the minimum cost if possible.

The analysis of these compounds has generally been approached by chromatographic techniques associated with preconcentration or extraction steps, including solid phase extraction [6–10], liquid-liquid extraction [11] or headspace extraction [12,13], due to their low concentration in wine samples. Electrochemical techniques, which are also characterized by reaching good capabilities of detection, are more versatile for this purpose, bearing in mind the considerably lower cost of the electrochemical equipment and its portable arrangement, ideal for *in situ* analysis. However, they have not been widely used for the determination of thiols, which can undergo electrochemical oxidation or reduction in the available working electrode [5,14–28]. So far, only hanging drop mercury electrodes [5], gold nanoparticles modified glassy carbon or screen-printed carbon electrodes (SPCEs) [27] and molecularly imprinted polypyrrole modified glassy carbon electrodes [28] have been used for the determination of EtSH, representing thiols, in wines. In this complex matrix, not only thiols are key redox-active species, but also phenolics, sulphites, ascorbic acid, glutathione, ethanol, oxygen, quinones, metal ions, etc. [29]. In this context, the use of nanomaterials and cobalt phthalocyanine (CoPh) based sensors would be advantageous, since these electrocatalytic materials allow that thiols can be monitored at considerably low potentials [15,16,19,30]. The oxidation of thiols arises from the following reactions [15,16,19]:

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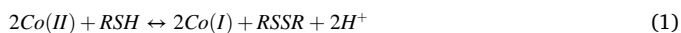
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Moreover, headspace measurements, which avoids direct contact of the electrochemical devices with the sample, can also be of great importance in continuous analysis during the different stages of wine-making, since the product is not altered. In addition, the number of interfering species is considerably reduced, since only volatile species can exert some kind of influence on the analytical signal [31]. Thus, the present work has been devoted to the development of sensitive and selective electrochemical CoPh based sensors for headspace detection of the organoleptic defect associated with the presence of volatile thiols in wines.

2. Experimental

2.1. Materials and equipment

All reagents used were of analytical-reagent grade. All the solutions were prepared in Milli-Q water (Millipore, Bedford, MA, USA). 0.1 M KCl, prepared from KCl (Merck, Darmstadt, Germany), and Britton Robinson buffer solutions, containing 0.04 M phosphoric acid (Panreac, Barcelona, Spain), 0.04 M acetic acid (VWR Chemical, Fontenay, France) and 0.04 M boric acid (Panreac, Barcelona, Spain), were used as supporting electrolyte for the electrochemical measurements. 1 M NaOH solutions, prepared from NaOH (Ecros, Barcelona, Spain), were used to adjust the pH value of the buffer solutions.

Fullerene C₆₀ (C₆₀) solutions (Acros Organics, Geel, Belgium) were prepared using dichloromethane (Panreac, Barcelona, Spain) as solvent. Cobalt phthalocyanine (CoPh) solutions were prepared by dissolving the amount of cobalt (II) phthalocyanine (Alfa Aesar, Karlsruhe, Germany) in ethanol (VWR Chemicals, Rosny-sous-Bois, France) as solvent. Solutions of EtSH (Alfa Aesar, Karlsruhe, Germany) were prepared by dissolving the adequate amount in Milli-Q water.

2.2. Voltammetric device

Electrochemical measurements were carried out using a PalmSens⁴ potentiostat (PalmSens BV, Houten, The Netherlands) using SPCEs with different modifications of the working electrode surface.

Screen-printed electrodes supplied by Dropsens (Metrohm DropSens, Oviedo, Spain) were used to carry out the electroanalysis of EtSH: screen printed carbon electrodes (SPCEs) with working (4 mm diameter) and auxiliary electrodes made of carbon and reference electrode of Ag/AgCl (DRP-C11L) and carboxyl functionalized multi-walled carbon nanotubes modified SPCEs (DRP-110CNT), graphene oxide modified SPCEs (DRP-110GPHOX), reduce graphene oxide modified SPCEs (DRP-110RGPHOX) as well as core-shell quantum dots ZnS/CdSe modified SPCEs (110CSQD) with carbon auxiliary and silver reference electrodes.

Data analysis was achieved with Statgraphics software package [32], for the experimental design and the robust regressions, and Detarchi for the capability of detection [33].

2.3. Preparation of activated fullerene modified SPCEs

A volume of 40 µL of 0.1 mg/mL solution of C₆₀ in dichloromethane was pipetted onto the carbon working electrode surface of SPCEs (DRP-C11L) for coating and left to dry at room temperature, according to a previous reported method [34]. It has been established that these immobilized C₆₀ layers can be partially reduced electrochemically in aqueous solutions containing potassium ions, forming conductive films [35–37]. Thus, 50 µL of a 1.0 M KOH solution were deposited on the C60 modified SPCE and a cyclic voltammogram from 0 to –1.5 V, at 10 mV/s, was registered. In this way, activated C₆₀ modified SPCEs (AC₆₀/SPCEs) were ready to use.

2.4. Working electrode modification with CoPh

The modification of the working electrode of different SPCEs with CoPh was performed by drop-casting. A volume of 10 µL of a 4.8% solution of CoPh in ethanol was placed onto the surface of the electrode, except for the optimization process, and left to dry at room temperature.

2.5. Electrochemical headspace measurements

Before using the devices, SPCEs were dipped in the corresponding supporting electrolyte, in such a way that is pre-loaded by adsorption. Amperometric measurements were then performed at the headspace of a sealed cell (Metrohm DropSens, Oviedo, Spain) containing 1 mL of supporting electrolyte pH 2.6, applying a constant potential of +0.8 V, except for the optimization process, under stirring conditions (500 rpm) (Fig. 1). Once a constant current was registered, a set volume of the corresponding analyte solution was added into the cell, recording the corresponding increment in the current due to the oxidation process that takes place at the electrode surface.

3. Results and discussion

Electrocatalytic responses of EtSH have been first studied using different modified screen-printed working electrodes: carbon (DRP-C11L), activated C₆₀, carboxyl functionalized multi-walled carbon nanotubes (DRP-110CNT), graphene oxide (DRP-110GPHOX), reduced graphene oxide (DRP-110RGPHOX), core-shell quantum dots ZnS/CdSe (DRP-110CSQD) and all of them modified as well with CoPh. A noisy current of scarce analytical utility was found in most of the recorded amperograms, except when the carbon working electrode was modified by CoPh (CoPh/SPCE) and by CoPh and AC₆₀ (CoPh/AC₆₀/SPCE). Fig. 2 shows the enhanced oxidation current specially registered when using CoPh/SPCE, so it was decided to continue working with this device for the EtSH quantification.

In amperometry, the selectivity is related to the choice of proper redox potential for the analyte of interest. In addition to the applied potential, pH of the supporting electrolyte and concentration of the CoPh solution used to modify the electrode, in percentage, are experimental variables that greatly influences the oxidation current registered as analytical response. Thus, a 2³ central composite design was carried out to determine the relationship, in form of mathematical model, between these variables and the oxidation current of a 98 µg/L EtSH solution, taken as response (Fig. 3) [32,38,39]. Results were evaluated using the Statgraphics program [32], obtaining the following regression

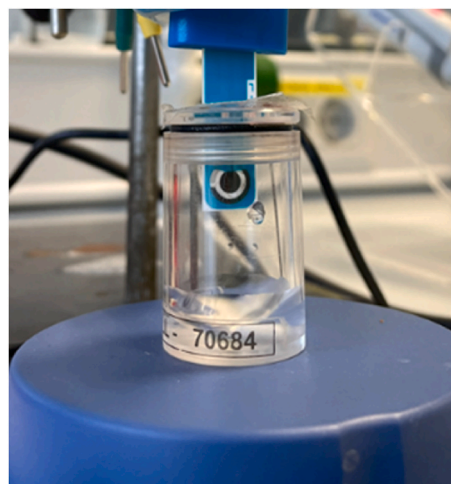


Fig. 1. Electrochemical cell used for the headspace amperometric measurements performed for the detection of mercaptans.

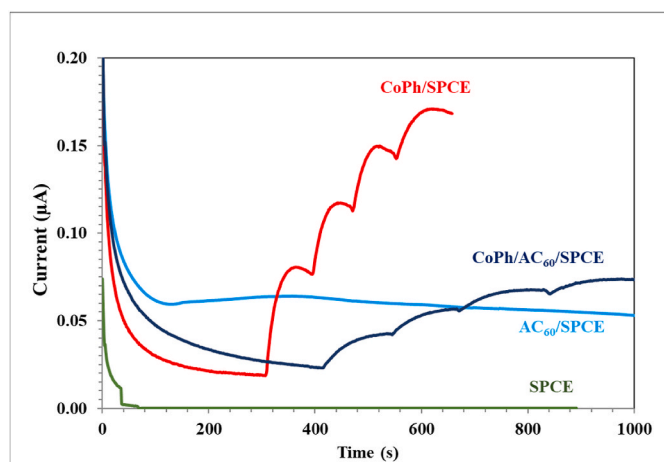


Fig. 2. Amperograms registered at +0.5 V using a SPCE, a CoPh/SPCE, an AC₆₀/SPCE and a CoPh/AC₆₀/SPCE for successive additions of 50 µL of a 100 mg/L EtSH solution in 1 mL of supporting electrolyte pH 4.

equation of the fitted model:

$$EtSH \text{ oxidation current} = -2.63662 - 0.572209 \times pH - 0.269556 \times CoPh \text{ concentration} + 37.3274 \times Applied \text{ potential} + 0.0709905 pH^2 + 0.026476 \times pH \times CoPh \text{ concentration} - 2.75445 \times pH \times Applied \text{ potential} + 0.00390899 \times CoPh \text{ concentration}^2 - 0.266385 \times CoPh \text{ concentration} \times Applied \text{ potential} - 8.94781 \times Applied \text{ potential}^2$$

From this equation, the combination of factor levels which maximized the EtSH oxidation current over the indicated region was pH of the supporting electrolyte = 2.6, applied potential = +0.8 V and concentration of the CoPh solution = 4.8%. Under these experimental conditions, a well-defined amperometric response was observed due to

the oxidation of EtSH at the electrode surface (Fig. 4).

The measured current response at the working electrode surface is dependent on the concentration of EtSH. Thus, different calibration curves were constructed under the optimum conditions of the experimental variables, in the EtSH concentration range from 9.9 to 82.6 µg/L, to validate the analytical method in terms of precision and capability of detection. Outlier 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 [32]. It was observed that these anomalous points generally coincided with those of higher concentration (Fig. 5). Precision, usually specified in terms of relative standard deviation (RSD), often varies with analyte concentration [40], so considering the slopes of such regressions avoids this drawback since different concentration levels are evaluated simultaneously [41]. An RSD of 7% (n = 5) was obtained for reproducibility, which highlights the agreement between the results registered when using different CoPh/SPCEs. In the case of using a single CoPh/SPCE to record several calibration curves of EtSH under the optimum conditions of the experimental variables, it was observed a lack of sensitivity in the successive amperograms, probably related to the loss of the mediator of the working electrode surface (Fig. 6). Bearing in mind the simplicity of manufacturing new sensors and the reproducibility achieved with them, this lack of precision under repeatability conditions was considered unimportant. A capability of detection (CC_β) of 12.5 µg/L, the smallest concentration that can be detected with an error probability of β = 0.05 (probability of not detecting analyte when it is in the sample) and a decision limit (CC_α) of 6.5 µg/L, limit at and above which it can be concluded with an error probability of α = 0.05 (probability of detecting analyte when it is not in the sample) that a sample is non-compliant, were found [33,42,43]. These parameters have been calculated based on a linear regression model using the Detarchi program [33], according to the ISO 11843 approach [42].

The selectivity in the determination of EtSH using the developed procedure was also studied, considering the possibility that other thiols, such as 4-mercaptobenzoic acid, or phenolic compounds, such as 4-

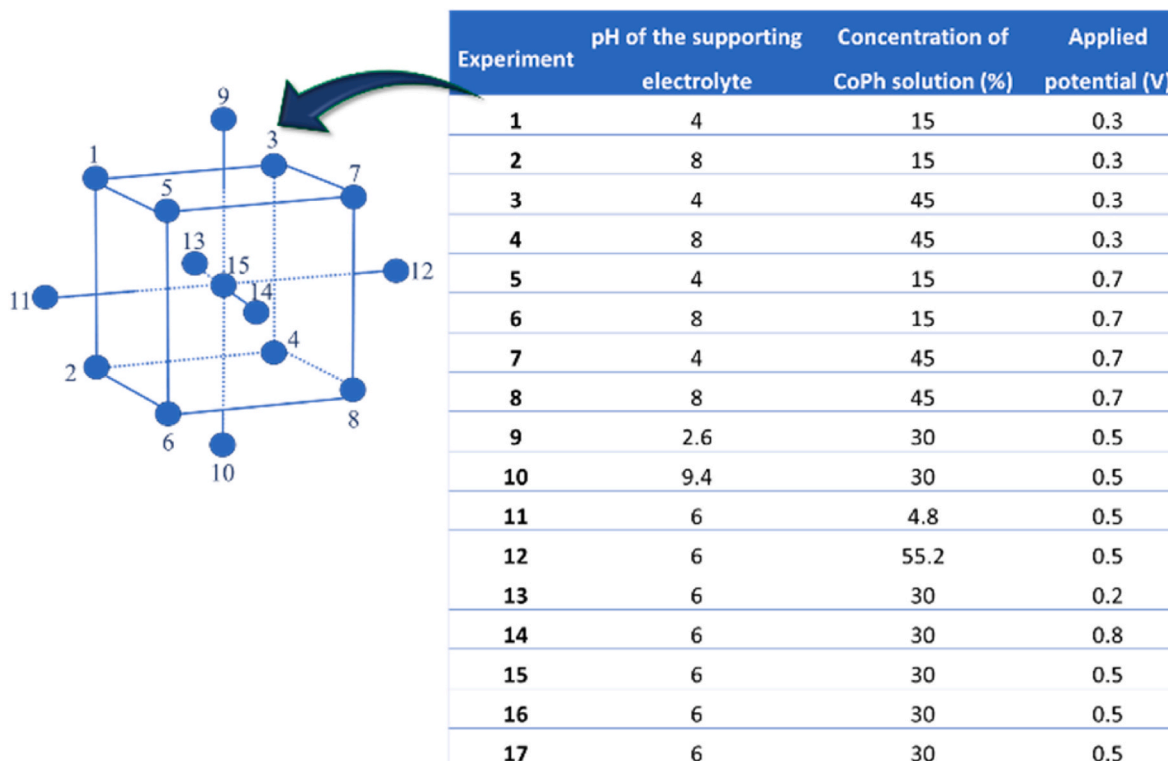


Fig. 3. Experiments carried out to maximize the EtSH oxidation current registered by amperometry using a CoPh/SPCE.

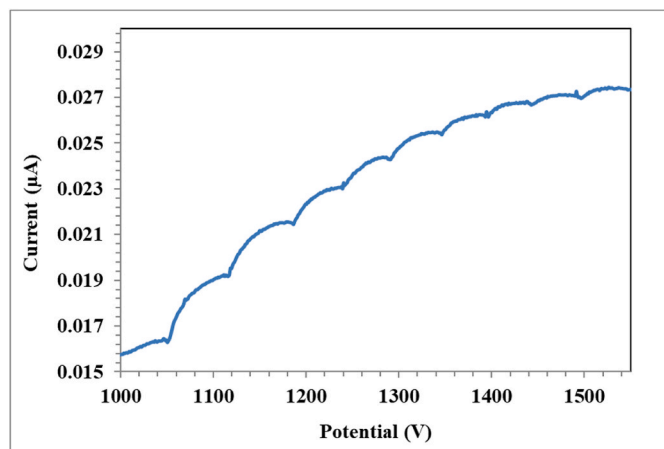


Fig. 4. Amperogram registered at +0.8 V using a CoPh/SPCE for successive additions of 10 µL of a 1 mg/L EtSH solution in 1 mL of supporting electrolyte pH 2.6.

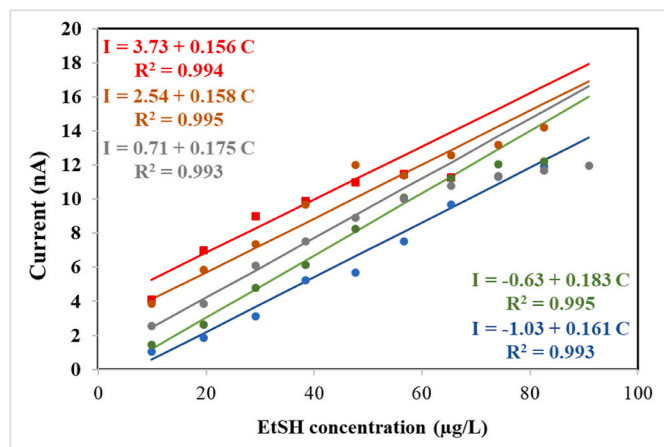


Fig. 5. Experimental points and linear regressions for the EtSH calibration curves built by amperometry at +0.8 V using different CoPh/SPCEs.

ethylphenol or 4-ethylguayacol, interfered in the measurements. Under the optimum conditions of the experimental variables for EtSH detection, no alteration of the recorded amperometric signal was detected due to the presence of these compounds, even at concentrations higher than 1 mg/L, so they were not considered interfering.

Finally, the applicability of the developed method was validated by trueness experiments, in which wines were analysed both in its original state and after the addition of a known mass of the analyte to a test portion (Spiked sample) [40]. Thus, two white and two red wine samples were analysed, under the above-described optimized amperometric conditions, by applying the method of additions of a EtSH stock solution to an aliquot of each wine sample (Standard addition method) [40]. As it can be seen in Table 1, it was not found the presence of the EtSH in any of them. Recovery experiments were then performed by the analysis of two levels of spiked wine samples, obtaining good values ranging from 97 to 106%. These values demonstrate the high selectivity of the method that, combining the CoPh/SPCE sensor and the headspace measurements, is capable of avoiding interferences in samples as complex as wine samples. Moreover, the fact that the sensor measures avoiding the contact with the wine sample, in the headspace, facilitates its use in routine analysis in wineries.

4. Conclusions

The amperometric detection of EtSH, representing volatile thiols in wine, has been achieved by using CoPh/SPCEs. Under the optimum conditions of the experimental variables, pH of the supporting electrolyte = 2.6, applied potential = +0.8 V and concentration of the CoPh solution = 4.8%, a well-defined amperometric response has been observed due to the oxidation of EtSH in the concentration range from 9.9 to 82.6 µg/L. The pre-load of the corresponding supporting electrolyte in the devices by adsorption has allowed the performance of headspace measurements at a sealed cell, which reduces the number of interferences and avoid the direct contact of the electrochemical device and the analysed sample. The performance of these sensors has been

Table 1
Determination of ethanethiol in different wine samples by DPV using CoPh/SPCEs.

Sample	Concentration Added (ppb)	Concentration Found (ppb)	Recovery (%)
White wine 1	–	No detected	–
	9.8	9.9 ± 0.3	101.4%
White wine 2	–	No detected	–
	9.8	9.6 ± 0.2	97.9%
Red wine 1	–	No detected	–
	9.8	10.1 ± 1.0	103.1%
Red wine 2	–	No detected	–
	9.8	9.5 ± 0.8	96.8%
	19.2	19.3 ± 0.4	100.2%
	19.2	19.5 ± 0.3	101.4%
	19.2	19.4 ± 0.5	100.9%
	19.2	19.7 ± 0.5	102.6%

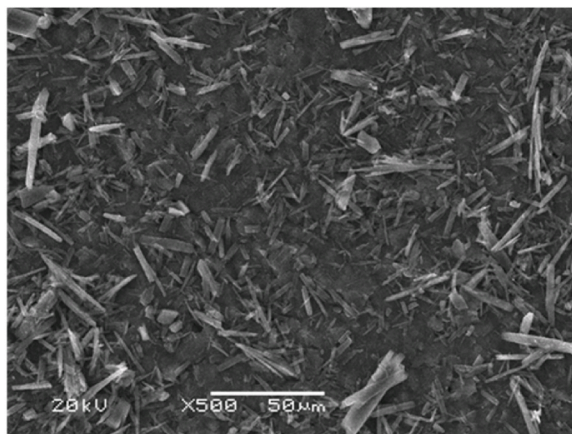
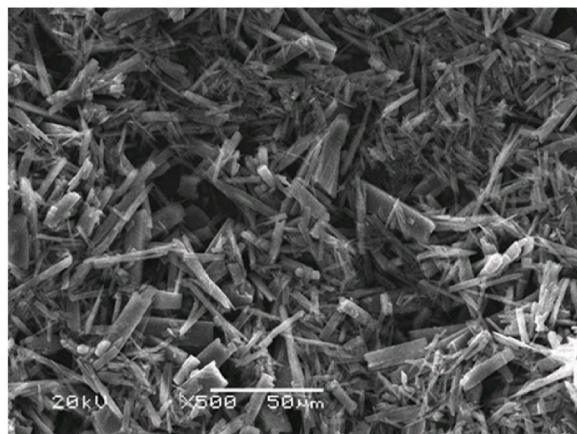


Fig. 6. SEM images of a CoPh/SPCE before (left) and after (right) registering a calibration curve in the EtSH concentration range from 9.9 to 82.6 µg/L at +0.8 V.

good enough to be used for the analysis of volatile thiols in white and red wines, with successful recoveries ranging from 97 to 103%.

Credit author statement

Paula Portugal-Gómez: Investigation, Validation, Writing - Original Draft. Olga Domínguez-Renedo: Conceptualization, Validation, Writing - Review & Editing, Funding acquisition. M. Asunción Alonso-Lomillo: Conceptualization, Validation, Writing - Original Draft, Funding acquisition.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: M. Asunción Alonso Lomillo and Olga Domínguez-Renedo report financial support was provided by Agencia Estatal de Investigación. M. Asunción Alonso Lomillo, Olga Domínguez-Renedo and Paula Portugal-Gómez have patent pending to P202231013. Nothing to declare.

Data availability

Data will be made available on request.

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