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Molecularly imprinted polypyrrole based electrochemical sensor for selective determination of ethanethiol

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ABSTRACT

This work describes a molecularly imprinted (MIP) sensor, based on the electropolymerization of pyrrole on a glassy carbon electrode (GCE), for the determination of ethanethiol. Ethanethiol was used as a template molecule for the formation of cavities in the imprinted polymer. The effect of molar ratios template molecules/functional monomers and time needed to remove the template were optimized. The developed MIP/GCE sensor presented a linear range from 6.1 to 32.4 mg L^{-1} with capability detection and reproducibility values of 7.2 mg L^{-1} and 10.4%, respectively. The sensitivity of the developed sensor was enhanced by the incorporation of gold nanoparticles (AuNPs). The AuNPs/MIP/GCE showed a capability of detection and reproducibility values of 0.4 mg L^{-1} and 4.1%, respectively (calibration range from 0.3 to 3.1 mg L^{-1}). The sensor was successfully applied to the determination of ethanethiol in spiked wine samples with recoveries ranging from 99% to 107%.

1. Introduction

The production of alcoholic beverages includes the generation of by-products, such as ethanethiol in wine, which can be formed during the fermentation process or through different chemical reactions during the aging of wine. This small anomaly in the biochemistry of fermentation may produce a notable and detrimental sensory impact, since ethanethiol can alter the aroma of bottled wines (perception threshold 1 µg L^{-1}) [1]. Consequently, these undesirable changes in the organoleptic and chemical properties can produce a lack of quality of the final product, causing important problems in the wine industry worldwide [2].

The determination of volatile mercaptans, such as ethanethiol, has been frequently carried out by gas chromatography associated with different types of detectors, such as flame photometric, sulfur chemiluminescence and conductivity [3–5]. These chromatographic methods involve novel preparatory techniques related to derivatization, isolation, separation and derivatization, for example, by 2,3,4,5,6-pentafluorobenzyl bromide, in order to stabilize unstable mercaptans during workup procedures [3,6]. These preliminary pretreatment steps increase the cost of chromatographic determinations and make them time-consuming, error-prone, and difficult to use for on-site analysis.

Electrochemical techniques can avoid these problems since, together with their high sensitivity, they present a high selectivity that makes the

use of previous stages of sample pretreatment unnecessary [2]. Moreover, they have a wide range of low-cost instrumentation that is easy to miniaturize and therefore useful for real in situ applications. However, the electrochemical behavior of ethanethiol has so far been attempted by only a few different procedures using non-enzymatic sensors. In this way, the oxidation of ethanethiol was analysed using a nickel oxide electrode, obtaining a poor sensitivity with a limit of detection of 2.9 mg L^{-1} [7]. Better results were obtained when using screen-printed carbon electrodes (SPCEs) modified with cobalt phthalocyanine [8], a hanging drop mercury electrode (HDME) [2], a glassy carbon electrode (GCE) modified with gold nanoparticles (AuNPs) [9] and SPCEs modified with AuNPs [9]. However, only two of these works describe the successfully electrochemical determination of ethanethiol in wine, since this complex matrix presents various components that make the selective analysis of this species difficult [2,9]. The work described by Guarda et al. [2] achieves the sensitive determination of ethanethiol following a reduction process of this compound at HDME surface in acid solution, once metals that could be present in the samples were removed using a strong cation exchange resin. Moreover, the use of a mercury electrode should be avoided considering its toxicity. These inconvenient were avoided in our previous work, based on the use of AuNPs/SPCEs and AuNPs/GCEs, taking into account the strong S–Au covalent bond that is easily formed between sulfur and gold atoms [9]. In order to improve even more the selectivity of this type of sensors, the modification of the

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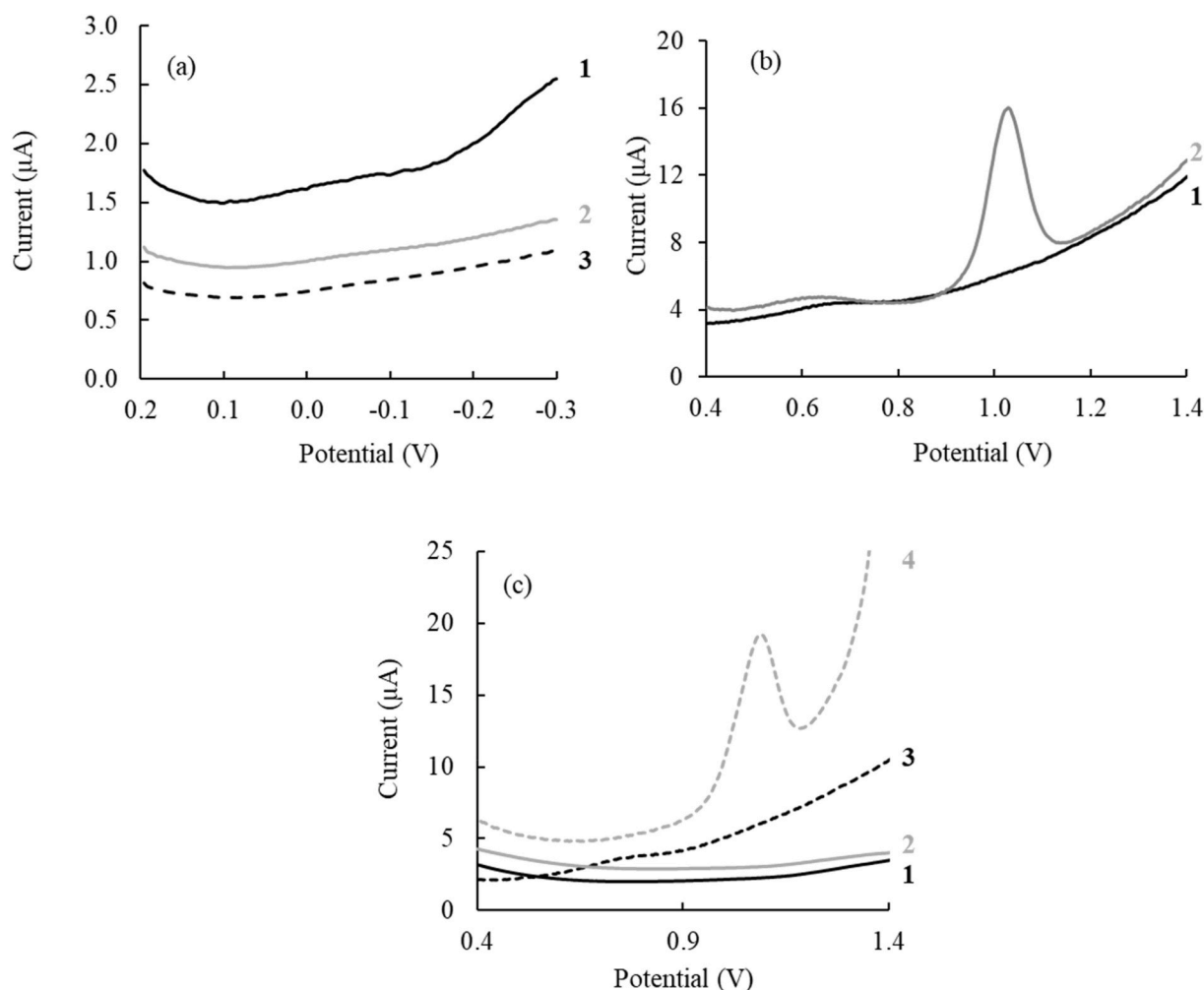
Fig. 1. Differential pulse voltammograms obtained in Britton-Robinson pH 2 using different electrodes. Reduction response in a GCE: (1a) blank solution; (2a) [ethanethiol], 10 mg L^{-1} (3a) [ethanethiol], 20 mg L^{-1}. Oxidation response in a GCE: (1 b) blank solution; (2 b) [ethanethiol], 50 mg L^{-1}. Oxidation response in a NIP/GCE: (1c) blank solution; (2c) [ethanethiol], 50 mg L^{-1}. Oxidation response in a MIP/GCE: (3c) blank solution; (4c) [ethanethiol], 50 mg L^{-1}. Scan rate, 100 mV s^{-1}; potential step, 100 mV; potential pulse, 20 mV; time pulse, 200 ms.

working electrode with molecularly imprinted polymers (MIPs) has previously been highlighted [10–12]. These electrochemical sensors present the above-described advantages of electrochemical techniques and, in addition, MIPs can be generated by easy and low-cost processes, presenting high mechanical, physical and chemical stability [10,11,14]. The generation of MIPs by electropolymerization represents the simplest method, also allowing control of the thickness and morphology of the film formed that remains strongly adhered to the surface of the electrode. The use of polypyrrole in the generation of MIPs has important advantages compared to other conducting polymers, that include stability, good biocompatibility, easier polymerization, low susceptibility to interferences and fouling caused by electroactive anions and high conductivity, which can be still increased by incorporating nanomaterials to the surface of the working electrode [10,13–15]. Nanomaterials such as AuNPs have been shown to improve the performance of different electrochemical sensors, thanks to their excellent remarkable catalytic effect and electroconductivity that facilitates a more efficient transfer of electrons [16–21].

Thus, this work focuses on the development of a novel electrochemical sensor for the determination of ethanethiol in wine, using a GCE modified with an electrosynthesized molecularly imprinted polypyrrole and AuNPs. According to the authors' knowledge, this type of electropolymerized MIP sensors have not been used in the analytical determination of ethanethiol in this type of complex samples.

2. Experimental

2.1. Reagents

Ultrapure water obtained from a Milli-Q water purifier (Millipore, Bedford, MA, USA) was used for the preparation of all solutions. 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 (Ercros, Barcelona, Spain) solutions were used to adjust the pH value of the buffer solutions.

Stock standard solutions of ethanethiol (Alfa Aesar, Haverhill, Massachusetts, USA) were prepared by dissolving the adequate amount in Milli-Q water. Pyrrole and LiClO$_4$, used to modify the working electrode surface, were purchased from Sigma-Aldrich (Steinheim, Germany) and Panreac (Barcelona, Spain), respectively. Ethanol (EtOH), used to remove the template molecules, was purchased from Scharlau (Barcelona, Spain).

0.25 mM of HAuCl$_4$ solutions were prepared by dissolving the appropriate amount of hydrogen tetrachloroaurate-(III) trihydrate (Acros Organics, Belgium) in 0.5 M sulfuric acid (Merck, Darmstadt, Germany).
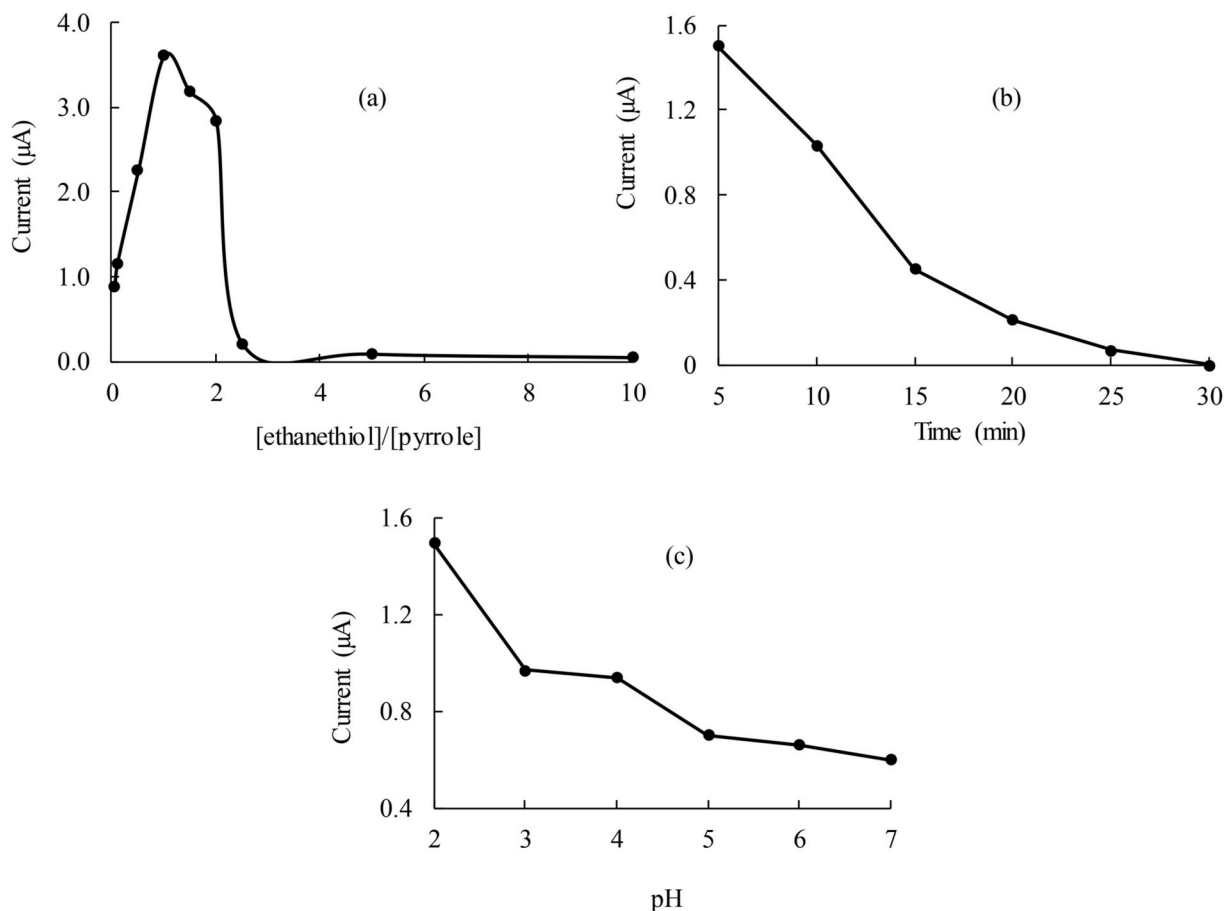
Fig. 2. (a) Oxidation current intensity values obtained by DPV for a solution containing 50 mg L^{-1} of ethanethiol using a MIP/GCE constructed using different [ethanethiol]/[pyrrole] ratios; (b) Oxidation current intensity values obtained by DPV in a Britton-Robinson pH 2 solution using a MIP/GCE after different washing times; (c) Oxidation current intensity values obtained by DPV for a solution containing 25 mg L^{-1} of ethanethiol using a MIP/GCE at different pH values. Scan rate, 100 mV s^{-1}; potential step, 100 mV; potential pulse, 20 mV; time pulse, 200 ms.

2.2. Instrumentation

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed using an EmStat3 potentiostat (Palmsens BV, Houten, The Netherlands) equipped with a three-electrode system consisting of a working electrode (GCE, MIP/GCE or AuNPs/MIP/GCE), an auxiliary platinum electrode and an Ag/AgCl reference electrode.

2.3. Procedures

2.3.1. Preparation of MIP/GCE

Prior to modification, the GCE was polished using alumina powder. After each polishing, the electrode was rinsed with Milli-Q water in order to remove any adsorbed substance on the surface. The GCE was then immersed into the electrochemical cell containing 10 mL of a 0.1 M LiClO$_4$, 5 mM pyrrole and 5 mM ethanethiol solution (except for the optimization process). The potential was cycled between −0.6 and + 1.8 V at a scan rate of 50 mVs^{-1} for 8 cycles. The electrode was finally immersed in a NaOH (0.2 M):EtOH (8:2, v/v) stirred solution during 30 min to remove the template [10,13]. The obtained electrode was washed with deionized water and denoted as MIP/GCE.

A non-imprinted polymer modified GCE, denoted as NIP/GCE, was also prepared by using the above-described electropolymerization procedure, without addition of ethanethiol template molecules.

2.3.2. Preparation of AuNPs/MIP/GCE

The AuNPs were electrochemically deposited on the MIP/GCE under

CV scanning from 0.2 to −1.0 V in 0.25 mM HAuCl$_4$ solution at a scan rate of 50 mVs^{-1} for 5 cycles, except for the optimization process [22]. The modified electrode was rinsed with deionized water and denoted as AuNPs/MIP/GCE.

2.3.3. Electrochemical measurements

DPV experiments were conducted at room temperature (approx. 20 °C) in an electrochemical cell containing 10 mL of Britton-Robinson buffer solution (pH 2, except for the optimization process). The potential was scanned from +0.8 V to +1.4 V when using a MIP/GCE and from +0.2 V to +0.8 V when using a AuNPs/MIP/GCE. The scan rate was 100 mV s^{-1} under a potential step of 0.01 V, a potential pulse of 0.2 V and a time pulse of 20 ms.

3. Results

3.1. DPV determination of ethanethiol using a MIP/GCE

The reduction response of ethanethiol in acid medium using a GCE was studied by means of DPV. It was observed that no reduction peak was obtained for the analyte (Fig. 1a), but nevertheless, ethanethiol oxidation measurements gave rise to an oxidation peak at a potential of +1.0 V aprox. related to the presence of the analyte (Fig. 1b). The intensity of this oxidation peak was higher as the concentration of ethanethiol present in the electrochemical cell increased and, therefore, it could be used for the quantification of this analyte. In order to improve the selectivity of this electrochemical response, a modification of the
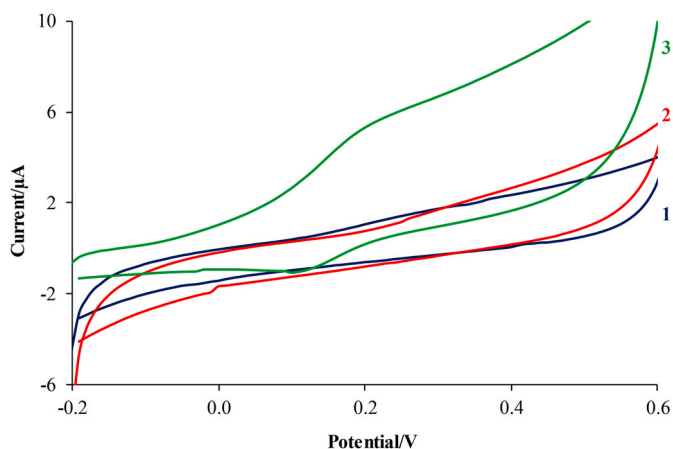
Fig. 3. Cyclic voltammograms obtained for a 5 mM ferricyanide solution prepared in KCl 0.1 M at 50 mV s^{-1}; using (**1**) a NIP/GCE; (**2**) a MIP/GCE; (**3**) a MIP/GCE after a washing time of 30 min.

electrode surface was carried out with a MIP following a procedure similar to that used in previous works [10,13]. This method consisted of the formation of the MIP by electropolymerization using a solution containing the target analyte and functional pyrrole monomers, as described in section 2.3. As it can be seen in Fig. 1c, the MIP cavities allow the oxidation of the analyte on the electrode surface, obtaining a quantifiable signal. However, there is no analytical response for the NIP/GCE.

3.1.1. Optimization of the electro-synthesis of MIP/GCE and measurement procedure

The response obtained for ethanethiol using a MIP/GCE was optimized in order to obtain the highest sensitivity in the analysis of this compound. The variables or factors that can influence this sensitivity were: [ethanethiol]/[pyrrole] ratio, washing time once the MIP is formed and pH value of the medium in which the voltammetric measurements were performed. pH value used in voltammetric measurements has a great influence both on the stability of the ethanethiol solutions and on the response of oxidation obtained, but it does not affect the formation of MIP on the electrode surface. Therefore, on the one hand, those variables that affect the formation of MIP ([ethanethiol]/[pyrrole] ratio and washing time) and, on the other, pH value can be perfectly optimized separately.

Different MIPs, using different [ethanethiol]/[pyrrole] ratios, were fabricated following the procedure described in section 2.3. The analytical response obtained for a solution of ethanethiol (50 mg L^{-1}) using these sensors is presented in Fig. 2a. This figure shows that the analytical response of ethanethiol increased from ratios ranging from 0.05 to 1.0 and then decreased for ratios higher than 1.0. Thus, this value was selected as the optimum for this parameter.

Once the optimum [ethanethiol]/[pyrrole] ratio was obtained, the washing time needed to completely remove the template molecule was analysed. Fig. 2b shows the oxidation current intensities recorded in the blank solution for different washing times. It can be seen that a washing time of 30 min is enough to completely eliminate the template molecule during the modification process. The generation of the MIP/GCE has been studied by cyclic voltammetry using the potassium ferri/ferrocyanide system as redox probe. As it can be seen in Fig. 3, no analytical signal is observed when using a NIP/GCE. In the same way, the measurements made with a MIP/GCE did not produce any analytical response, but after a washing period of 30 min, the peaks corresponding to the ferri/ferrocyanide redox system could be observed.

Finally, the response obtained for ethanethiol with the selected modification method was analysed at different pH values. The best analytical responses were obtained in pH 2 Britton-Robinson solutions

Table 1
Figures of merit obtained in the determination of ethanethiol by DPV using different electrodes.

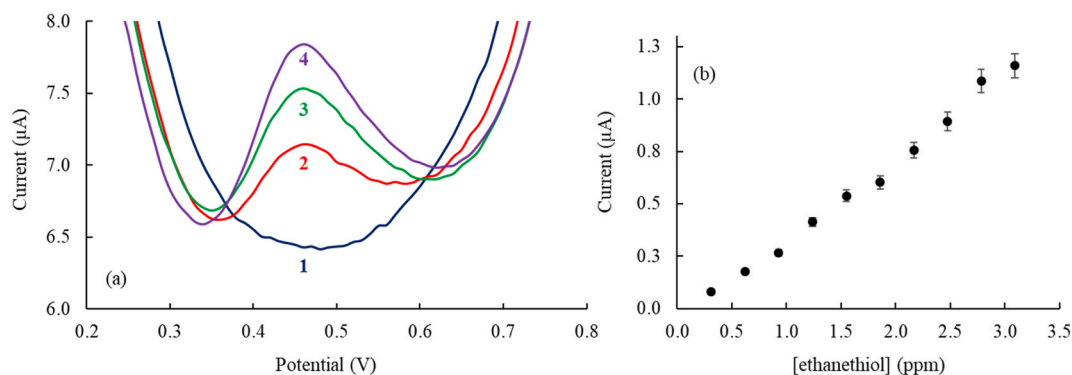|	MIP/GCE	AuNPs/MIP/GCE
Slope/µA mg^{-1} L	0.12	0.40
Intercept/µA	−0.03	0.11
Residual standard deviation (S$_{yx}$)	0.18	0.04
Coefficient of determination (R^2)	0.99	0.99
Decision limit (CC$_\alpha$/mg L^{-1})	3.7	0.2
Capability of detection (CC$_\beta$/mg L^{-1})	7.2	0.4
Reproducibility (% RSD)	10.4	4.1
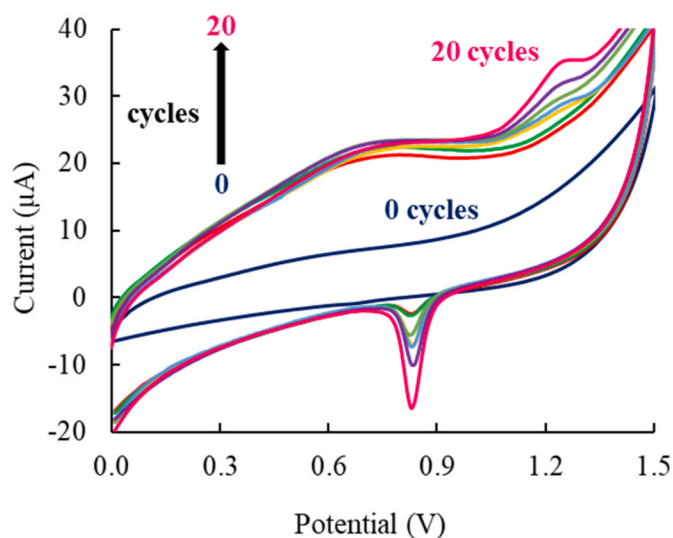
Fig. 4. Cyclic voltammograms in 0.05 M H$_2$SO$_4$ for AuNPs modified MIP/GCE prepared from 0.25 mM HAuCl$_4$ solution using different number of cycles at a scan rate of 100 mVs^{-1}.

(Fig. 2c), which is consistent with the greater stability that ethanethiol solutions present in acid medium, where the oxidation of the compound by air does not take place [7].

3.1.2. Precision and capability of detection of the MIP/GCE

The optimized MIP/GCE developed was tested for ethanethiol detection using DPV. The intensity of the peak corresponding to ethanethiol oxidation increased proportionally with its concentration, being the correlation between these parameters linear from 6.1 to 32.4 mg L^{-1}. Different calibration curves were built using ordinary linear regressions. In order to provide a correct evaluation of the calibration parameters, outlier points with a Studentized residual above 2.5 in absolute value were removed [23]. These properly evaluated linear regressions were used to estimate the precision and the capability of detection of the developed procedure. Thus, the precision of the method was determined in terms of the reproducibility of the slopes obtained for five different calibration sets, obtaining a relative standard deviation (RSD) value of 10.4%.

The capability of detection (CC$_\beta$) of the developed electrochemical procedure was assessed as the smallest concentration level of analyte that may be detected with a statistical certainty of 1-β (β, false negative). The lowest concentration level at which the method can discriminate if the target analyte is present in the analysed sample, with a statistical probability of 1-α (α, false positive) was also estimated and denoted as the decision limit (CC$_\alpha$) [24,25]. The values obtained for these parameters were 3.7 and 7.2 mg L^{-1} for CC$_\alpha$ and CC$_\beta$, respectively (α = β = 0.05) (Table 1).

Fig. 5. (a) Differential pulse voltammograms obtained in Britton-Robinson pH 2 using a AuNPs/MIP/GCE (ethanethiol concentration: (1) 0; (2) 1.2; (3) 2.2; (4) 3.1 mg L^{-1}); (b) Calibration data in Britton-Robinson pH 2 for ethanethiol concentration ranging from 0.3 to 3.1 mg L^{-1}. Scan rate, 100 mV s^{-1}; potential step, 100 mV; potential pulse, 20 mV; time pulse, 200 ms.
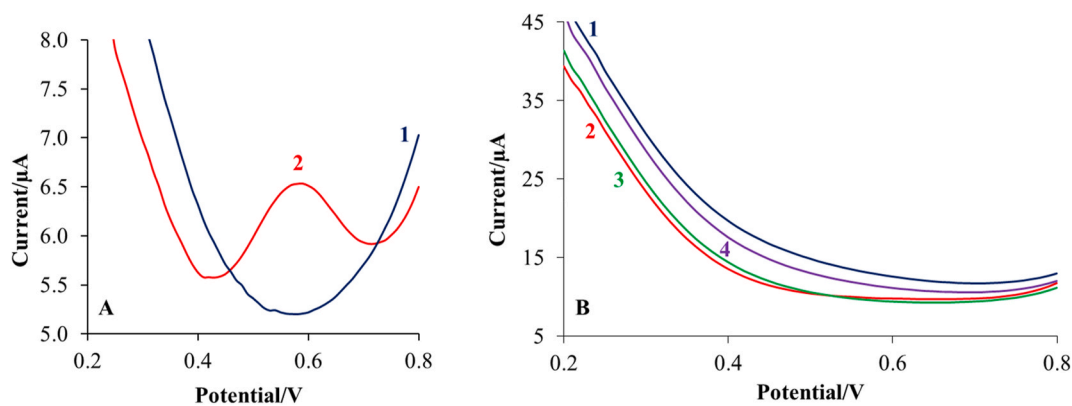
Fig. 6. Differential pulse voltammograms obtained in Britton-Robinson pH 2 using (A) a AuNPs/GCE: (**1**) Blank (**2**) [ethanethiol], 1.5 mg L^{-1}; (B) a AuNPs/NIP/GCE: (**1**) Blank; (**2**) [ethanethiol], 1.5 mg L^{-1}; (**3**) [ethanethiol], 3.0 mg L^{-1}; (**4**) [ethanethiol], 4.5 mg L^{-1}.

3.2. DPV determination of ethanethiol using a AuNPs/MIP/GCE

With the aim of improving the sensitivity of the described method in the determination of ethanethiol, the developed MIP/GCE was modified with AuNPs. The protocol used consisted of the electrochemical deposition of AuNPs on the optimized MIP/GCE by means of CV scanning from 0.2 to −1.0 V in a 0.25 mM HAuCl$_4$ solution at a scan rate of 100 mVs^{-1} [22]. In order to optimize the number of CV cycles for the AuNPs formation, different CVs were recorded in 0.05 M H$_2$SO$_4$ from 0 to +1.5 V, at a scan rate of 100 mVs^{-1} (Fig. 4). No peak was observed when a no modified MIP/GCE was used. However, when AuNPs was deposited on the electrode surface, a single reduction peak at +0.83 V was observed, which can be related to the reduction of gold surface oxide. The intensity of this reduction peak increased with the increase of number of cycles. When the number of cycles used in the generation of AuNPs was greater than 5, an oxidation peak was also observed at a potential of +1.25 V. The presence of this oxidation peak suggests the formation of a gold film over the electrode surface [26,27]. For this reason, a number of 5 cycles was chosen as the most adequate to guarantee the AuNPs formation on the MIP/GCE.

The AuNPs/MIP/GCE developed was also tested for ethanethiol detection using DPV. A well-defined oxidation peak at +0.45 V was observed in Britton-Robinson pH 2 in the presence of ethanethiol whose intensity increased proportionally with its concentration, being the correlation between these parameters linear from 0.3 to 3.1 mg L^{-1} (Fig. 5). The analytical signal obtained for ethanethiol using AuNPs/NIP/GCE and AuNPs/GCE have been also studied. As it can be seen in Fig. 6, a sensitive analytical signal is observed when using a AuNPs/GCE, but no oxidation peak was obtained for AuNPs/NIP/GCE. Thus, the

electrodeposition of gold nanoparticles inside the cavities generated explains the catalytic effect obtained, which gives rise to an increase in intensity and a decrease in the oxidation potential of ethanethiol.

The precision of the method was also calculated in terms of the reproducibility obtained for the slopes of 5 properly evaluated calibration sets performed using different electrode surfaces. The RSD value obtained (4.1%) also shows a higher reproducibility for this electrodic system. CC$_\beta$ and CC$_\alpha$ ($\alpha = \beta = 0.05$) were also calculated for the AuNPs/MIP/GCE. The values obtained for these parameters are reported in Table 1 and show a higher sensitivity for the sensor formed by using AuNPs. A CC$_\beta$ of 0.4 mg L^{-1} ($\alpha = \beta = 0.05$) may be considered enough for practical applications, since when wine contains more than 0.7 mg L^{-1} of mercaptans, an unpleasant odor is already manifested [28] and that it is possible to find wine samples with levels of ethanethiol higher than 2 mg L^{-1} [2]. Thus, the AuNPs/MIP/GCE sensor was selected for the following analytical steps.

3.2.1. Interference analysis

The selectivity of the AuNPs/MIP/GCE developed in the analysis of ethanethiol was studied by the analysis of the influence of different concentrations of other mercaptan species, 4-mercaptobenzoic acid. This molecule showed no influence on the oxidation signal of the target analyte even at high concentration levels (10 mg L^{-1}). In addition, the possible interference caused by other species frequently present in wine was also analysed. In this way, the influence of different phenolic compounds, including 4-ethylphenol and 4-ethylguayacol was tested. Different concentration levels ranging from 1.7 to 51.6 mg L^{-1} were studied, not finding interference by 4-ethylphenol. In the case of 4-ethylguayacol, some degree of interference in the determination of

Table 2
Determination of ethanethiol in a wine sample by DPV using a AuNPs/MIP/GCE.

Sample	Added (mg L^{-1})	Found (mg L^{-1})	Recovery
White wine 1	–	No detected	–
	1.0	0.99 ± 0.10	99%
White wine 2	–	No detected	–
	1.0	1.03 ± 0.19	103%
White wine 3	–	No detected	–
	1.0	1.02 ± 0.17	102%
Red wine	–	No detected	–
	1.0	1.07 ± 0.40	107%

ethanethiol was found at concentrations higher than 10 mg L^{-1}. Considering that the amount of 4-etylguayacol present in wine has been reported to be lower (from 1 μg L^{-1} to 2.6 mg L^{-1}) [29], its interfering effect was considered no significant.

3.2.2. Wine sample analysis

The analytical performance of the developed electrochemical sensor was checked by means of the determination of the analyte in spiked wine samples, using standard addition procedures that led the good results reported in Table 2. Four different commercial samples of white and red table wines from different origins and different grape variety were studied. The recovery values obtained oscillate from 99% to 107%, which indicates a good applicability and reliability of the developed analytical method.

4. Conclusions

In this work, a novel molecularly imprinted polypyrrole polymer sensor was developed for the selective and sensitive determination of ethanethiol in wine. The MIP was synthesized on a GCE surface using a simple electrochemical polymerization technique. The sensitivity of the sensor was significantly enhanced by the deposition of AuNPs, due to increasing electronic conductivity and effective surface area. Under optimized conditions, a correlation between the intensity of oxidation and the concentration of ethanethiol was achieved in the range of 0.3–3.1 mg L^{-1} with a low capability of detention (0.4 mg L^{-1}). Finally, the AuNPs/MIP/GCE sensor was successfully applied to the determination of ethanethiol in a wine sample with recoveries ranged from 99% to 107%.

Author statement

M. Asunción Alonso Lomillo: Conceptualization, Validation, Investigation, Writing – review & editing, Funding acquisition, **Olga Domínguez**: Conceptualization, Validation, Investigation, Writing – original draft, Funding acquisition

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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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