



A SO₂-selective electrode based on a Zn-porphyrin for wine analysis



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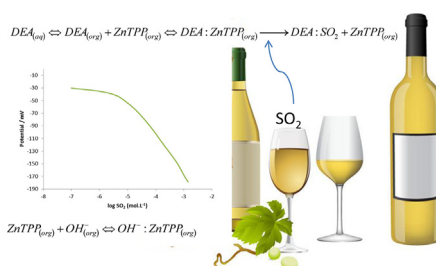
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HIGHLIGHTS

- An innovative SO₂-selective electrode based on coordinated complexes between amines and metalloporphyrins.
- Lower detection limits allow the evaluation of SO₂ in different wine preparation steps.
- Can be applied to the analysis of the free and total SO₂ in wine samples.
- Higher accuracy and precision when compared with a reference method.

GRAPHICAL ABSTRACT



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ABSTRACT

This work describes the assessment of a SO₂-selective electrode based on the use of the neutral carrier 5,10,15,20-tetraphenyl(porphyrinate)zinc(II) in a PVC membrane plasticized with 2-nitrophenyl phenyl ether. After being conditioned in 2 mol L⁻¹ diethylamine solution for 24 h, the electrode exhibited selective anionic response toward the analyte in a concentration interval of more than four decades, with a slope of $-59.5 \text{ mV dec}^{-1}$, a practical detection limit of $3.7 \times 10^{-6} \text{ mol L}^{-1}$ and a low limit of linear range of $7.2 \times 10^{-6} \text{ mol L}^{-1}$. The response mechanism is based on the displacement of the diethylamine:metalloporphyrin complex equilibrium within membrane bulk, inducing a variation in the cationic-sites to ionophore ratio. In turn, free hydroxyl ions are complexed by the displaced ionophore in a ratio 1:1 and translated as single negative charge nernstian response. Finally, the selectivity of the electrode is evaluated in view of its application to wine analysis. Results had high accuracy and precision when compared with a reference method.

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1. Introduction

Sulfur dioxide (SO₂) and other sulfites additives (E-220–228) are commonly used as preservatives in food and beverages industries (Directive 95/2/EC, Directive 2006/52/EC). Particularly in wine industry, SO₂ is an ally of the producer since it prevents the development of undesirable natural processes in the winemaking process which compromise the typical fruity flavor, color and freshness of wines. Indeed, SO₂ is added to must and juices both for a germicidal

action and for slowing down natural occurring oxidation processes [1–3].

At the pH of wine (3–3.8), part of the SO₂ added remains free as bisulfite anion (HSO₃⁻) and about 33–50% becomes chemically combined with other native compounds. Sulfites act as antioxidants by means of direct inhibition of polyphenoloxidases [4], hydrogen peroxide removal and through reduction of quinones meantime formed in the (bio)chemical oxidation processes [5]. The combined fraction is presented either in reversible or as irreversible adducts of aldehydes and ketones, due to its nucleophilic character. In part, most of the bound SO₂ can be released by proper heating or treating with a strong base. Nevertheless, the final amount present in wines has to be strictly controlled since high levels of it produce

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undesirable aromas and tastes and are also hazardous to human health.

Each country has regulations that establish the limit of total SO_2 permitted in wines which once more underlines the importance of its control [6]. It would be convenient to have an expeditious technique that could be used to analyze the content of total and free SO_2 in wines since the official method established by the European commission (EC) takes about 90 min per sample. For a simpler control, Portugal suggested the Ripper procedure; nevertheless this still takes about 30 min per sample [7]. Although the results obtained by the reference method are more accurate than those obtained by the Ripper method besides taking longer, it has the drawback of requiring the operator to be extremely attentive because the temperature, gas flow and time steps need to be carefully controlled [8].

Several methods have been published in the literature for the determination of sulfite in wines. Worth of mention are the large number of flow systems that have been proposed for this purpose, the main ones appearing in a review published in 2009 [4]. Generally, flow systems provide high sample throughput when compared to conventional batch techniques, and when coupled to electrochemical detection simple or none sample pre-treatment is needed [9]. However, the acquisition costs are higher and due to modular nature of the systems, require more skilled technicians. In recent years, voltammetric and amperometric (bio)sensors [10–13], chemiluminescence [14] and ion chromatography [15,16] methods have also been published for the SO_2 determination, although they usually only analyze the total SO_2 and they are indirect and time-consuming methods. The proposal of potentiometric methods is scarce and relies on the iodine oxidation by sulfite [17,18]. Previous distillation or the use of gas permeation devices was indispensable to improve selectivity relatively to other reducing compounds such as ascorbic acid in these methods.

Amines form coordinated complexes with metalloporphyrins in reactions whose equilibrium could be shifted through addition of strong nucleophiles [19]. Based on this a novel SO_2 -selective electrode for the analysis of the free and total SO_2 content of different kinds of wine is presented. The principle of response was based on the displacement of the complex formed between the diethylamine and the lipophilic zinc(II)metalloporphyrin in the bulk of a perm-selective membrane. The developed electrode provides a simple, economical and time-saving method which could be used by any winemaker or controlling body.

2. Experimental

2.1. Reagents and solutions

All chemicals were of analytical reagent grade and Milli-Q water was used throughout. Polyvinyl chloride (PVC) of high molecular weight (81392 Fluka), dioctyl sebacate (DOS) (CDS000559 Aldrich), 2-nitrophenyl phenyl ether (NPPE) (73307 Fluka), 2-fluoro-2-nitrodiphenyl ether (FNDPE) (47390 Fluka), tetradodecylammonium bromide (TDAbr) (87249 Aldrich), potassium tetrakis [3,5-bis-(trifluoromethyl)phenyl]borate (KTPB) (60588 Fluka), Araldite M (10951 Fluka), Ren HY 5162 (068620205 Ren-Shape Solutions), graphite powder (<45 μm) (496596 Aldrich) and tetrahydrofuran (THF) (186562 Sigma–Aldrich).

The ionophore 5,10,15,20-tetraphenyl(porphyrinate)zinc(II) (ZnTPP) was synthesized from 5,10,15,20-tetraphenyl-21H,23H-porphyrine (H_2TPP) (247367 Sigma–Aldrich) and ZnCl_2 (8816 Merck).

Sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$), diethylamine (DEA), hydrochloric acid (32%, w/w), sulfuric acid, chloroform, dimethylformamide (DMF), n-octanol, 0.5 mol L⁻¹ I_2 solution,

starch soluble, acetaldehyde, sodium hydroxide (NaOH), 2-(N-morpholino)ethanesulfonic sodium salt (MES), sodium chloride, potassium chloride, magnesium chloride hexahydrate, copper(II) chloride (CuCl_2), calcium chloride dehydrate, ferrous chloride tetrahydrated, sodium sulfite, sodium bicarbonate, sodium sulfate, di-sodium tartrate dihydrate, sodium dihydrogen phosphate anhydrous, sodium L-lactate, D,L-malic acid, histamine, tyramine, cadaverine, putrescine, phenylethylamine, spermine, L-proline, L-arginine, L-alanine and L-glutamine were also purchased from Sigma–Aldrich.

A 0.1 mol L⁻¹ $\text{Na}_2\text{S}_2\text{O}_5$ standard solution was prepared by dissolving 0.19011 g of the commercial product in 100.0 mL of water. Working solutions 0.01 and 0.001 mol L⁻¹ were prepared by dilution of the standard solution. A MES buffer solution of 0.1 mol L⁻¹ (pH = 5) and HCl/KCl solutions (pH = 1.6) at different KCl concentrations were also prepared. To obtain a 0.1 mol L⁻¹ standard solution of the corresponding sodium salt of malic acid, a 0.2 mol L⁻¹ solution of the acid was potentiometrically titrated with 0.2 mol L⁻¹ sodium hydroxide to end point. A 0.01 mol L⁻¹ iodine standard solution was obtained by dilution of the commercial solution.

2.2. Apparatus

Potentiometric measurements were made using a Crison MicropH 2002 potentiometer (Crison Instruments, S.A., Barcelona, Spain) and an Orion 90-00-02 Ag/AgCl double-junction electrode (Orion Research, MA) with a 10% KNO_3 solution in the outer compartment acting as reference electrode.

A spectrophotometer Jasco STR-707 V-660 and a pH-meter Crison GLP22 equipped with a Phillips GAH 110 combined pH glass electrode were namely used to characterize the synthesized ionophore 5,10,15,20-tetraphenyl(porphyrinate)zinc(II) and for the measurement of solution pH.

2.3. Procedures

2.3.1. Synthesis of the ionophore

The ionophore Zn-TPP was synthesized *via* metallation of the free porphyrin (H_2TPP) using ZnCl_2 [20]. Both the H_2TPP (0.1 g) and ZnCl_2 (0.3 g) were dissolved in 10 mL of DMF and then refluxed at 153 °C for 5 h. After the solution was cooled, DMF was completely evaporated under vacuum (175 mbar) at 97 °C in a rotary evaporator. The solid residue was dissolved in CHCl_3 and purified with a series of extractions in water. Afterwards, CHCl_3 was evaporated for several hours in cabinet and the remaining solid was allowed to dry overnight. The resulting Zn-TPP was characterized by thin layer chromatography and UV–vis spectrophotometry. The UV–vis spectra revealed the maximum absorbance for H_2TPP and ZnTPP at 417.8 and 421.8 nm, respectively. The obtained values were in accordance with those reported in the literature [19,21]. Thin layer chromatography was carried out in an n-octanol/ CHCl_3 (1:9) phase to corroborate the purity of the synthesized compound.

2.3.2. Electrode construction

The electrodes used in the present work consisted of solid contact electrodes with the PVC membrane added drop wise on the surface of a conducting solid support. To obtain this support a mixture of Araldite M and HR hardener 1/0.4 (w/w) was homogeneously prepared. Briefly, 0.24 g of graphite powder was added to 0.2 g of the prepared mixture and the obtained paste was kneaded to an appropriate homogeneity and consistency for incorporation in the electrode body. The paste thus obtained was sufficient to prepare about six electrodes. A portion of the paste was quickly introduced in one side of a common Perspex tube of 6 mm of internal diameter, to a height of 0.5 cm, taking care not to leave pores that might later have fluid leaks. On the opposite side a copper wire

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