



Short communication

## Free sulphite determination in wine using screen-printed carbon electrodes with prior gas-diffusion microextraction

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## ARTICLE INFO

## Article history:

Received 30 November 2015

Received in revised form 11 December 2015

Accepted 15 December 2015

Available online 23 December 2015

## Keywords:

Electroanalysis

Food quality

Sample preparation

Sulphurous

Volatile extraction

## ABSTRACT

Gas-diffusion microextraction was employed in the extraction of sulphites in wines aiming their electrochemical determination, which was achieved by square-wave voltammetry using screen-printed carbon electrodes. Sulphites are additives commonly used in many produced goods, particularly food products. The developed methodology showed good limits of detection ( $0.4 \text{ mg L}^{-1}$ ) and quantification ( $1.3 \text{ mg L}^{-1}$ ). The proposed method was also compared with the reference methodology used by the wine industry (the Ripper method, an iodometry) showing no significant differences in the obtained results. Therefore, a simple, cheap and portable alternative for the determination of sulphites in wine is presented.

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### 1. Introduction

Sulphite is a widely used food additive, though it is also used in many other industries like pharmaceutical development. It prevents microbial grow, browning reactions and can even be a flavour stabiliser. However, its use is limited to some health drawbacks, particularly to some people more susceptible like asthmatics [1]. This obliges beverage producers, in the European Union, to include the warning "contains sulphites" whenever a concentration of  $10 \text{ mg L}^{-1}$  is exceeded (EU regulation 1169/2011). Therefore, its analytical monitoring is quite common in a large and varied number of consumables.

Electroanalytical methodologies have been for long an alternative for someone who wishes to analyse sulphites [2], however, they are prone to suffer of matrix interference. Therefore, a previous analyte extraction may prove to be extremely useful. Such is intended by applying gas-diffusion microextraction (GDME)—a technique developed in the last decade that has the typical advantages of membrane-supported gas diffusion for analytical purposes within a microextraction concept [3,4]. Sample preparation plays a crucial role in analytical chemistry, often being the bottleneck in many analytical procedures.

Herein, the proof of concept of a combination between GDME and electrochemical detection technique is presented. In this case, the electrochemical determination was performed with a screen-printed carbon electrode (SPCE) by square-wave voltammetry (SWV). SPCEs

have several advantages including low manufacturing cost, portability, low reagent and sample consumption, amongst others [5]. Screen-printed electrodes are suitable for an *in situ* analysis due to, amongst others, low power requirement, quick response and ability to operate at room temperature [6].

### 2. Material and methods

#### 2.1. Chemicals and samples

All reagents were of analytical grade and used without further purification. All aqueous solutions were prepared using ultrapure water with resistivity not less than  $18.2 \text{ M}\Omega \text{ cm}$  at 298 K.

Sodium sulphite (Merck) was used as a source of sulphites, hydrochloric acid (HCl) solutions were prepared from the concentrated acid (Panreac), acetate buffer (pH 4.8,  $0.01 \text{ mol L}^{-1}$ ) was prepared with sodium acetate (Sigma-Aldrich) and acetic acid (Prolabo). Regarding the Ripper method: sulphuric acid solution (25%) was prepared from the concentrated acid (Sigma-Aldrich), EDTA, starch, potassium iodate and potassium iodide were acquired from Merck.

Wine samples were acquired in a local supermarket.

#### 2.2. Extraction

The GDME working principle has been described elsewhere [3,4,7,8]. However, the extractor design was modified, making it simpler to be replicated by other research groups. A simple adaptation to a

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commercial laboratory flask was performed. The flask material guaranteed stability under various temperatures and the flask lid perfectly sealed the headspace. The hydrophobic membrane was a Mitex PTFE (Millipore) with a porosity of 5.0  $\mu\text{m}$ .

The extraction system is depicted in Fig. 1. The extraction procedure, unless stated otherwise, was the following: (a) 10 mL of the sample were placed inside the thermostated sampling chamber; (b) 3 mL of 1 mol L<sup>-1</sup> HCl were added to the sample immediately before the extraction; (c) extraction occurred at 30 °C for 15 min; (d) the acceptor solution consisted of 1000  $\mu\text{L}$  of acetate buffer, pH 4.8; (e) 1 mL of 1 mol L<sup>-1</sup> HCl was added to the collected extract prior to the electrochemical analysis (after the acid addition, pH changed to a value below 1.0).

### 2.3. Electrochemical measurements

All voltammetric measurements were performed using a  $\mu\text{Autolab II}$  system operated by the software GPES v 4.9. Screen-printed carbon electrodes (SPCEs) were acquired from DropSens (ref. DRP-110); the working electrode had a 4 mm diameter, the counter electrode was also made of carbon, the pseudo-reference electrode was made of silver; all three electrodes were printed on a 3.3  $\times$  1.0  $\times$  0.05 cm ceramic substrate.

Measurements were performed at room temperature without any bubbling with nitrogen (ordinarily used to remove interfering oxygen). Since a “clean” extract was obtained and experiments were carried out without significant chemical species being adsorbed onto the electrode surface, the same SPCE could be used for more than one measurement with simple cleaning with water and acetate buffer.

## 3. Results and discussion

### 3.1. Sulphite extraction by gas-diffusion microextraction

To avoid the matrix effect, a common tactic found in literature is the use of enzymes, i.e., creating a biosensor. This can be achieved either by using just sulphite oxidase [9] or by a combination with cytochrome c [10] or tetrathiafulvalene [11], amongst others. Direct electrochemical analysis of sulphites in wine without any enzyme mediator is very challenging, though in literature some works can be found by means of, for example, nanoparticles [12,13].

Herein, the solution proposed instead was grounded in a clever choice in terms of sample preparation. This not only could enhance sensitivity and selectivity, but was also advantageous in terms of practicality. A simple technique that combines gas-diffusion extraction with a large ratio sample/extract, named gas-diffusion microextraction (GDME) [4], was employed. A commercial 100 mL laboratory flask was adapted, by a simple change in the lid (an opening with an internal snag where an O-ring could be fitted) that could accommodate a

sampling probe with a small hydrophobic membrane in the tip. A small volume of the acceptor solution was placed inside.

As explained in Section 2, the sample was acidified prior to the extraction, changing the pH to a value lower than 1.0, such that all hydrogen sulphite becomes sulphite (schematised in Fig. 1). Then, gaseous sulphur dioxide fills the headspace. A small quantity of this sulphur dioxide, which diffuses through the hydrophobic membrane, is entrapped in the acceptor solution by a pH change that modifies sulphur dioxide back into hydrogen sulphite.

### 3.2. Optimisation of voltammetric determination and electrode reaction

Square-wave voltammetry (SWV) is a well-known voltammetric technique, still of large relevance in electroanalysis, that although being of a fast sweep type holds high sensitivity [14]. The SWV parameters for sulphite analysis were swiftly optimised in terms of frequency (Fig. 2), potential step and wave amplitude. The chosen conditions were the following: SW frequency of 50 Hz, potential step of 5 mV and wave amplitude of 25 mV (resulting in scan rate of 250 mV s<sup>-1</sup>).

Sulphite reduction has been widely studied at various electrode materials, like mercury [15,16] or copper [17]. The pH here plays a major role, since the nature of the species changes, i.e., relative concentrations of sulphur dioxide (SO<sub>2</sub>), hydrogen sulphite (HSO<sub>3</sub><sup>-</sup>) and sulphite (SO<sub>3</sub><sup>2-</sup>) in a solution are highly dependent on the pH (pK<sub>1</sub> (Eq. (1)) and pK<sub>2</sub> (Eq. (2)), at 298 K, being generally accepted to be 1.9 and 7.2, respectively [17]).



Therefore, under highly acidic conditions (pH < 2), the dominant species is sulphur dioxide which, according to literature, undergoes a two-electron, two-proton reduction forming sulphoxylic acid (Eq. (3)) [15,17].



### 3.3. Method performance and method comparison

The method performance parameters were obtained from a calibration curve, which was constructed on the basis of the determination of sulphites after the extraction of six different sulphite standards ( $n = 6$ ), and they are the following:  $r^2$  of 0.9996, limit of detection (LOD) of 0.4 mg L<sup>-1</sup> and limit of quantification (LOQ) of 1.3 mg L<sup>-1</sup>.

LOD and LOQ are fully adequate for wine analysis, nevertheless, both can be decreased by increasing the extraction time. These limits make this methodology also suitable to determine sulphites in matrices with

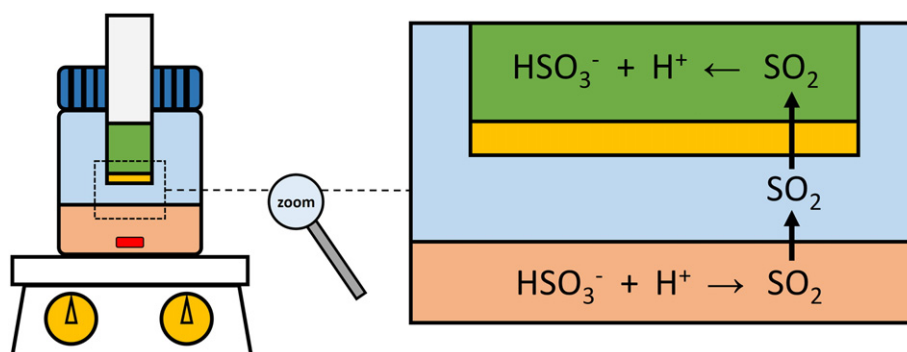


Fig. 1. The general schematics of the gas-diffusion microextraction (on the left) and a detail with some of chemical reactions involved (on the right).

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