

Full Research Paper

Amperometric Determination of Sulfite by Gas Diffusion-Sequential Injection with Boron-Doped Diamond Electrode

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Abstract: A gas diffusion sequential injection system with amperometric detection using a boron-doped diamond electrode was developed for the determination of sulfite. A gas diffusion unit (GDU) was used to prevent interference from sample matrices for the electrochemical measurement. The sample was mixed with an acid solution to generate gaseous sulfur dioxide prior to its passage through the donor channel of the GDU. The sulfur dioxide diffused through the PTFE hydrophobic membrane into a carrier solution of 0.1 M phosphate buffer (pH 8)/0.1% sodium dodecyl sulfate in the acceptor channel of the GDU and turned to sulfite. Then the sulfite was carried to the electrochemical flow cell and detected directly by amperometry using the boron-doped diamond electrode at 0.95 V (versus Ag/AgCl). Sodium dodecyl sulfate was added to the carrier solution to prevent electrode fouling. This method was applicable in the concentration range of 0.2-20 mg SO₃²⁻/L and a detection limit (S/N = 3) of 0.05 mg SO₃²⁻/L was achieved. This method was successfully applied to the determination of sulfite in wines and the analytical results agreed well with those obtained by iodimetric titration. The relative standard deviations for the analysis of sulfite in wines were in the range of 1.0-4.1 %. The sampling frequency was 65 h⁻¹.

Keywords: Sequential injection, sulfite, gas diffusion unit, boron-doped diamond electrode.

1. Introduction

Sulfites, or sulfiting agents, are widely used as additives in food and brewing industries to inhibit bacterial growth, prevent oxidation, and improve the final appearance of products. Despite these useful properties, the sulfite content in foods and beverages has been strictly limited due to its allergenic effect on hypersensitive people. Products containing more sulfite than the established threshold level must be adequately labeled. For example, in the United States, the Food and Drug Administration (FDA) has required labeling of products containing more than 10 mg/L of sulfite in foods and beverages. Therefore, the method for sulfite analysis is of great importance for food assurance and quality control.

Conventional methods for the analysis of sulfite, such as titration with iodine [1] and acid/base titration after oxidation [2], usually need extensive sample pretreatment and reagent preparation. Other developed methods for sulfite determination include spectrophotometry [3], spectrofluorimetry [4], chemiluminescence [5], electrochemistry [6,7], chromatography [8], and capillary electrophoresis [9]. Flow injection analysis (FIA) [10-12] and sequential injection analysis (SIA) [13,14] which can be automated and used for a broad range of samples with high sampling frequency have also been applied to determine sulfite and sulfur dioxide. To improve selectivity, a gas diffusion unit (GDU) has been incorporated in flow systems to separate the liberated sulfur dioxide from sample matrices [15-19]. Spectrometric and electrochemical detection are often coupled to flow systems for sulfite/sulfur dioxide determination. Spectrophotometric [20,21], fluorimetric [22], and chemiluminescence [23,24] detection can be performed after mixing with some reagents, which results in cost and complication of the analysis as well as the toxicity of certain reagents. Electrochemical detection is an attractive option due to the direct electrochemical oxidation of sulfite. The use of chemically modified electrodes in FIA experiments for sulfite determination has been reported [25,26]. A boron-doped diamond (BDD) electrode is an electrode material which offers a number of attractive electrochemical properties, including a wide potential window, low background current, and high electrochemical stability. The BDD electrode has been widely applied for the electrochemical detection of many types of analyte, such as biological compounds [27], organic pollutants [28], and metal ions [29].

Sequential injection analysis (SIA) has been proposed as an alternative to flow injection analysis (FIA) due to various advantages, such as lower reagent consumption and simple manifold, compared to FIA. In this paper, the gas diffusion sequential injection system with amperometric detection using the boron-doped diamond electrode was developed for the determination of sulfite content. The method was applied to the determination of sulfite in wines (usually reported as free and total sulfur dioxide). This method provided high sensitivity and reproducible responses because of the attractive features of the boron doped-diamond electrode. Moreover, the use of the sequential injection system was simple and provided high sample throughput and low reagent consumption.

2. Experimental Section

2.1. Reagents

All chemicals used were of analytical reagent grade and deionized water was used throughout. Sodium dodecyl sulfate (SDS) and ethylenediaminetetraacetic acid (EDTA) were purchased from Sigma (St. Louis, USA). Other chemicals were supplied by Merck (Darmstadt, Germany).

The phosphate buffer solutions (pH 5-9) were prepared from 0.1 M potassium dihydrogen orthophosphate and 0.1 M disodium hydrogen orthophosphate. A phosphate buffer (pH 4) was prepared from 0.1 M potassium dihydrogen orthophosphate and the pH was adjusted with 85% orthophosphoric acid. A phosphate buffer (pH 10) was prepared from 0.1 M disodium hydrogen orthophosphate with pH adjustment using 0.1 M sodium hydroxide.

A stock solution of sulfite was prepared daily by dissolving sodium sulfite in a 1 g/L EDTA solution as a stabilizing agent [14]. The stock solution was standardized by iodimetric titration. The working standard solutions were obtained by diluting the stock solution in a 1 g/L EDTA solution.

2.2. Apparatus

The cyclic voltammetry measurements were performed in a single-compartment, three-electrode glass cell. A BDD electrode (Toyo Kohan Co., Ltd., Japan), an Ag/AgCl with a salt bridge and a platinum wire were used as the working electrode, the reference electrode and the counter electrode, respectively. The BDD electrode was pressed against an O-ring (area 0.07 cm²) at the bottom of the cell. Ohmic contact was made by placing a brass plate on the backside of the Si substrate of the BDD electrode. The cell was housed in a faradaic cage to reduce the electronic noise. The electrochemical measurements were recorded using a PalmSens (Palm Instrument BV, Houten, The Netherlands).

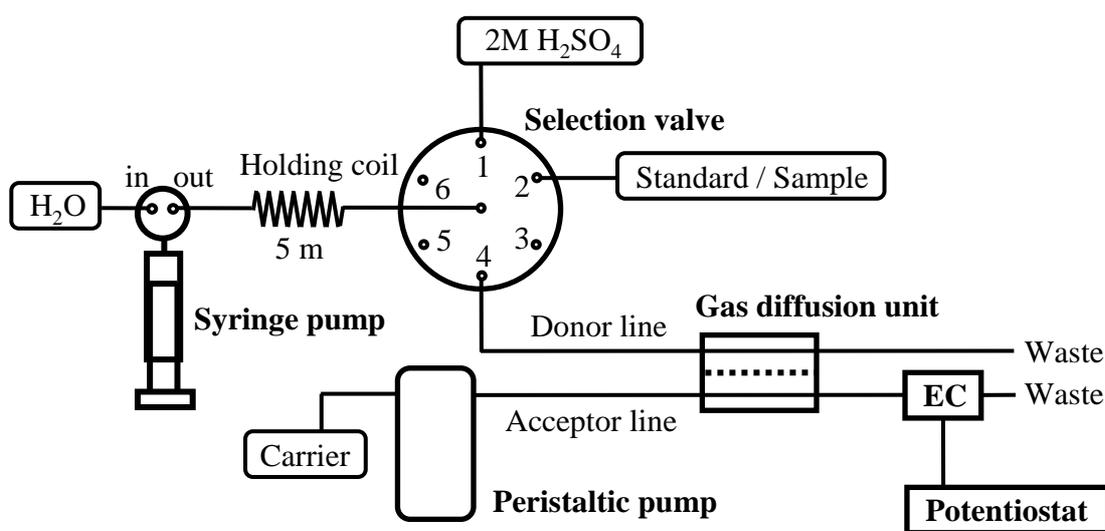


Figure 1. SIA manifold for the determination of sulfite: EC, electrochemical flow cell.

For sequential injection analysis with amperometric detection, the SIA system consisted of a syringe pump (Cavro XL 3000, Cavro Scientific Instruments Inc., USA) equipped with a 2.5 mL syringe, a six port selection valve (Cavro Smart Valve, Cavro Scientific Instruments Inc., USA), a gas diffusion unit, a peristaltic pump (SMP-23, EYELA, Japan), an electrochemical flow cell (Bioanalytical Systems Inc., USA), and a PalmSens. The system components were arranged as shown schematically in Figure 1. All tubing connecting the different components of the flow system was PTFE with 0.8 mm i.d. (Cole-Parmer Instrument Company, USA). The GDU consisted of two symmetric acrylic blocks, two silicone gaskets with a channel (31 mm long, 1.5 mm wide and 0.2 mm thick) as the spacer and a PTFE hydrophobic membrane (Sartorius, pore size 0.45 μm). The membrane was placed between two silicone gaskets which were sandwiched between two acrylic blocks. Two acrylic blocks were pressed against each other by four screws. The electrochemical flow cell consisted of a silicone gasket (0.5 mm thick) as a spacer (area 0.3 cm^2), the boron-doped diamond working electrode, the Ag/AgCl reference electrode, and the stainless steel tube counter electrode.

2.3. Sequential injection procedure

The carrier, 0.1 M phosphate buffer (pH 8)/0.1% SDS, was flowed through the electrochemical flow cell by a peristaltic pump. The operating sequence of the SIA system for the analysis of sulfite is listed in Table 1. The analytical cycle started with the aspiration of water into the syringe. Next, the sulfuric acid and the standard/sample solution were aspirated into the holding coil in which the gaseous sulfur dioxide was generated. The flow was then reversed and the mixture was propelled through the donor channel of the GDU. During this step, the generated sulfur dioxide diffused through the membrane into the carrier solution in the acceptor channel of the GDU. Then, the sulfite formed in the phosphate buffer (pH 8)/0.1% SDS carrier was carried to the electrochemical flow cell and detected directly at the BDD electrode. The amperometric measurements were carried out at the potential, giving a maximum signal-to-background (S/B) ratio in the hydrodynamic voltammograms. Each point of the analytical plot represents the average of four successive injections.

Table 1. SIA operating sequence for analysis of sulfite.

Step	Operation	Valve of pump	Port of selection valve	Volume (μL)	Flow rate ($\mu\text{L/s}$)
1	Aspirate water to syringe pump	in	–	600	100
2	Aspirate 2 M H_2SO_4 to holding coil	out	1	100	50
3	Aspirate standard/sample to holding	out	2	50	50
4	coil Dispense mixture to donor channel of GDU	out	4	750	25

3. Results and discussion

3.1. Optimization of pH

The optimum pH of the phosphate buffer for the electrochemical oxidation of sulfite was investigated from pH 4 to 10 using cyclic voltammetry. As shown in Figure 2, sulfite gave well-defined cyclic voltammograms in the neutral and alkaline buffers. In the acidic buffer, the decrease in pH of the phosphate buffer led to an increase in oxidation potential. This result indicates that the oxidation of sulfite in the acidic medium is more difficult than that in the neutral and alkaline media. It was also found that sulfite in phosphate buffer (pH 8) provided the highest peak current at the lowest oxidation potential. Therefore the phosphate buffer (pH 8) was chosen as the optimum pH.

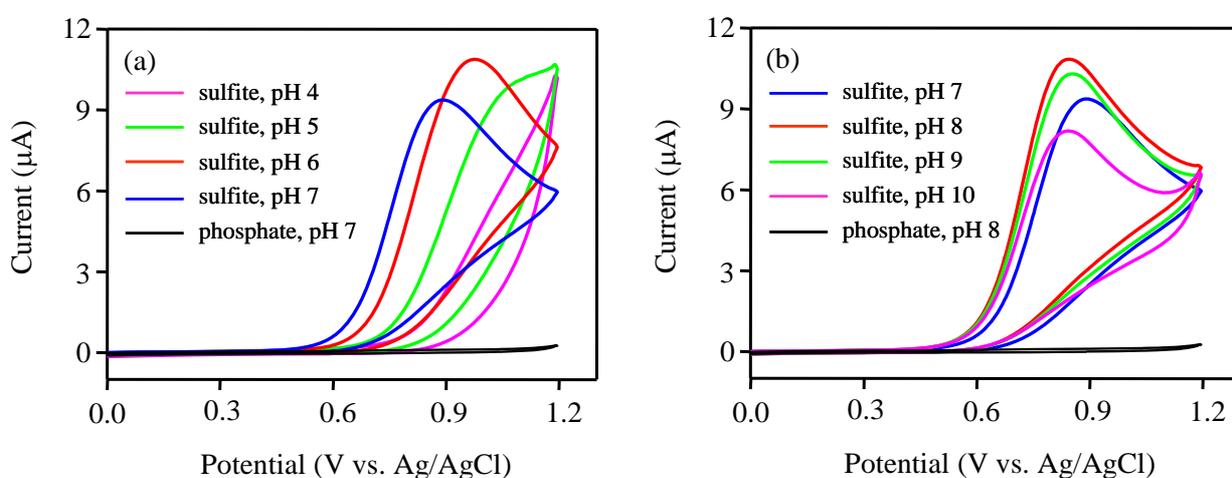


Figure 2. Cyclic voltammograms of 1mM Na_2SO_3 in 0.1 M phosphate buffer (a) pH 4-7 and (b) pH 7-10 at the BDD electrode. The sweep rate was 50 mV/s. The area of the electrode was 0.07 cm^2 .

3.2. Optimum potential for amperometric detection

In order to obtain the optimal potential for amperometric detection in sequential injection analysis, the hydrodynamic voltammetric behavior of sulfite was studied. Peak currents of sulfite and corresponding background currents at various potential from 0.70 V to 1.05 V are shown in Figure 3(a). It was observed that the hydrodynamic voltammogram for sulfite did not produce a sigmoid shape. Therefore the S/B ratios were calculated from Figure 3(a) and plotted as a function of potential as shown in Figure 3(b). The S/B ratio reached a maximum value at 0.95 V (versus Ag/AgCl). Thus this potential was selected for amperometric detection in the SIA experiment.

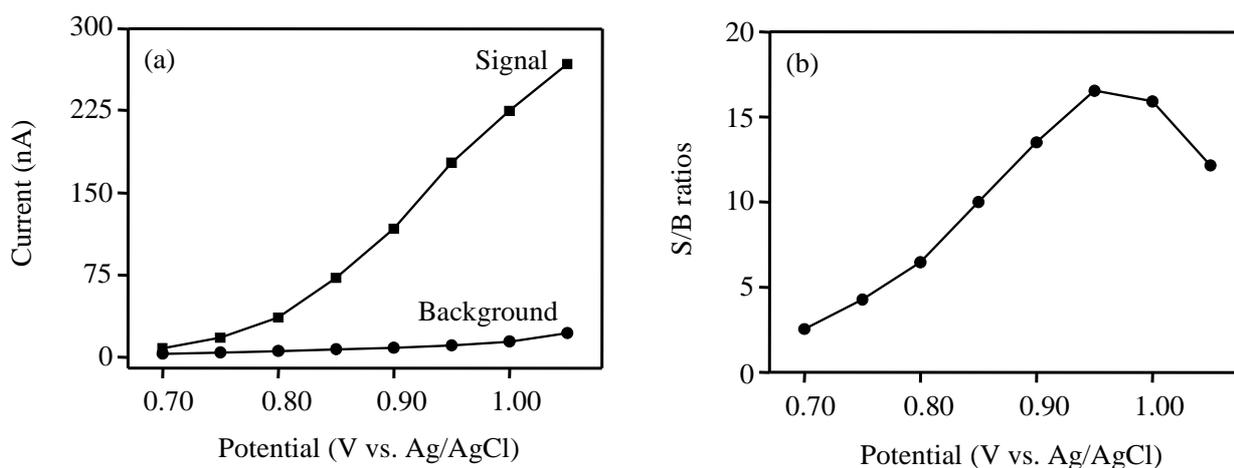


Figure 3. (a) Hydrodynamic voltammometric results for 10 mg $\text{SO}_3^{2-}/\text{L}$ (Signal) and 0.1 M phosphate buffer pH 8/0.1% SDS (Background) at 0.70-1.05 V (vs. Ag/AgCl). The SIA operating sequence is listed in Table 1. (b) Hydrodynamic voltammogram of signal-to-background ratios.

3.3. Effect of sodium dodecyl sulfate (SDS)

Preliminary SIA experiments revealed that electrode fouling occurred in the amperometric detection of sulfite with the BBD electrode. This problem can be solved by adding 0.1% sodium dodecyl sulfate (SDS) into the carrier of 0.1 M phosphate buffer (pH 8) as shown in Figure 4. The relative standard deviation of the peak current for 15 consecutive injections of 10 mg $\text{SO}_3^{2-}/\text{L}$ was 1.7 %.

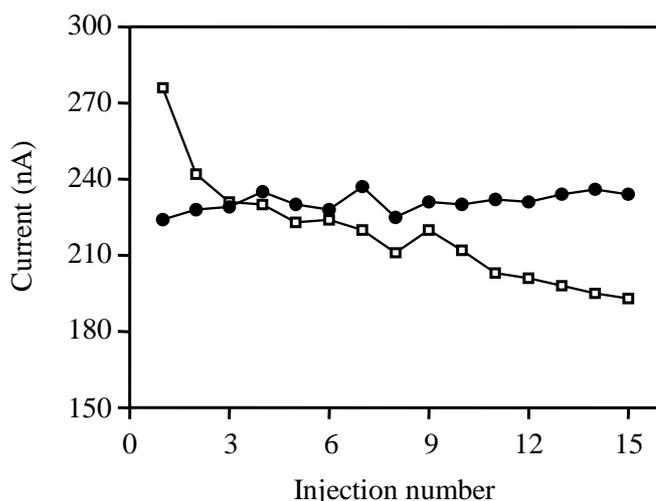


Figure 4. SIA with amperometric detection results for 15 consecutive injections of 10 mg $\text{SO}_3^{2-}/\text{L}$. Carrier was 0.1 M phosphate buffer pH 8 (-□-) and 0.1 M phosphate buffer pH 8/0.1% SDS (-●-). The SIA operating sequence is listed in Table 1.

3.4. Optimization of SIA parameters

The volume of sulfite solution was set at 50 μL . The concentration of 2 M for sulfuric acid was adopted from a study in a previous work [25]. The optimum volume of 2 M H_2SO_4 was studied over the range 20–140 μL at the sulfite concentration of 50 mg/L. A volume of 100 μL was chosen as the optimum volume because larger volumes did not improve the sensitivity. Similar results were obtained at the sulfite concentration of 10 mg/L. Aspiration of the second plug of H_2SO_4 after the aspiration of the first plug of H_2SO_4 (100 μL) and 10 mg/L sulfite (50 μL) was also studied over the range 0–60 μL at intervals of 20 μL . The relationship between the average peak current and the volume of H_2SO_4 was shown in Figure 5. It was observed that the peak current decreased as the volume of H_2SO_4 increased. The cause of this result is expected that there is the dispersion of generated sulfur dioxide in the second plug of 2 M H_2SO_4 . Therefore, the aspiration of the second plug of acid on the other side of the sample decreases the sensitivity.

In order to minimize sample dispersion, the length of the connection between the selection valve and the donor channel of the GDU was set at 15 cm and the length of the connection between the acceptor channel of the GDU and the electrochemical flow cell was set at 20 cm.

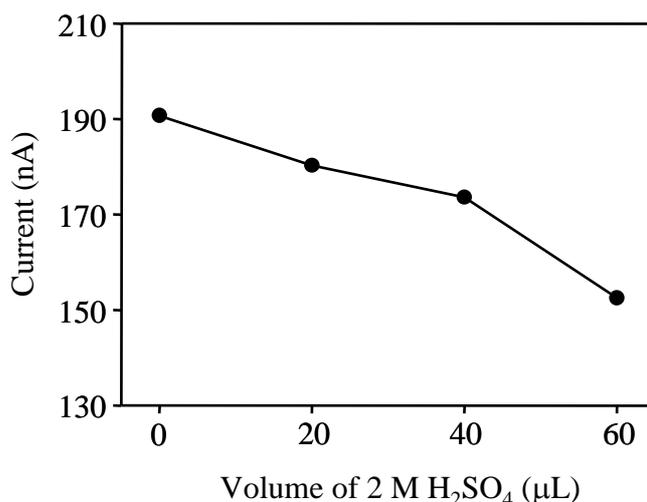


Figure 5. Relationship between the average peak current and the volume of the second plug of 2 M H_2SO_4 . The concentration of sulfite was 10 mg/L.

The effect of flow rate for propelling the acidified sample to the donor channel of the GDU was investigated in the range of 10–35 $\mu\text{L/s}$ at intervals of 5 $\mu\text{L/s}$. The highest current was obtained at the flow rate of 25 $\mu\text{L/s}$. Thus, the flow rate of 25 $\mu\text{L/s}$ was selected for subsequent experiments. The influence of flow rate of carrier for carrying sulfite to the electrochemical flow cell was also studied from 0.25 to 1.0 mL/min at intervals of 0.25 mL/min. As illustrated in Figure 6, the signal current increased as the flow rate of carrier decreased. However, the peak width at the flow rate of 0.25 mL/min is much broader than that at the flow rate of 0.5 mL/min. Therefore the flow rate of 0.5 mL/min was the chosen value as a compromise between sensitivity and sampling frequency.

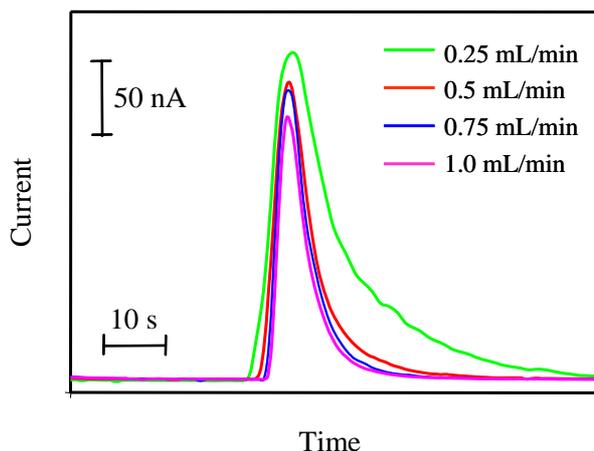


Figure 6. SIA with amperometric detection results at various flow rate of carrier for 10 mg $\text{SO}_3^{2-}/\text{L}$. Carrier was 0.1 M phosphate buffer pH 8/0.1% SDS. The SIA operating sequence is listed in Table 1.

3.5. Influence of sample volume

The influence of sample volume in the SIA operating sequence was studied over the range 10–50 μL at intervals of 10 μL . The relationship between the average peak current for 10 mg/L sulfite and the sample volume was shown in Figure 7. It was observed that signal currents increase with increasing sample volume. For example, signal currents increase about six times when sample volume was increased from 10 μL to 50 μL . This result indicated that the linear range of the SIA method can be changed easily by changing sample volume aspirated into holding. This is an interested choice of the SIA method for the gas diffusion separation in addition to the reduction of both reagent consumption and volume of effluent. The sample containing the high content of sulfite can be analyzed by reducing the sample volume in the SIA operating sequence without dilution. For wine, any change in composition of the wine, like dilution, will inevitably shift the equilibrium between bound and free sulfite.

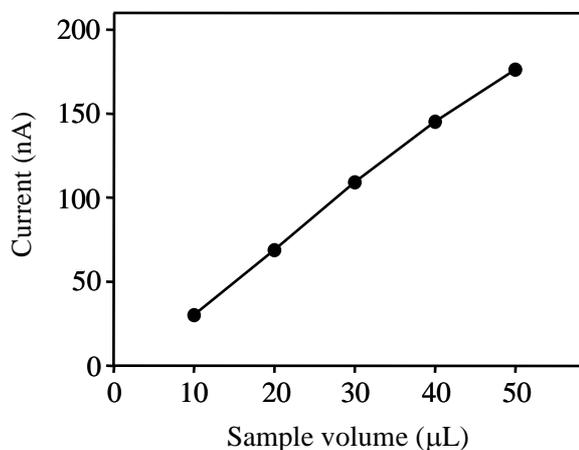


Figure 7. Relationship between the average peak current and the sample volume of 10 mg/L sulfite.

3.6. Standard curve and detection limit

The relationship between the signal current and the concentration of sulfite is shown in Figure 8. It was found that the signal current increased linearly with increasing concentration of sulfite from 0.2–20 mg/L ($R^2 = 0.9997$). The detection limit, based on a signal-to-noise ratio (S/N) of 3, was found to be 0.05 mg SO_3^{2-} /L.

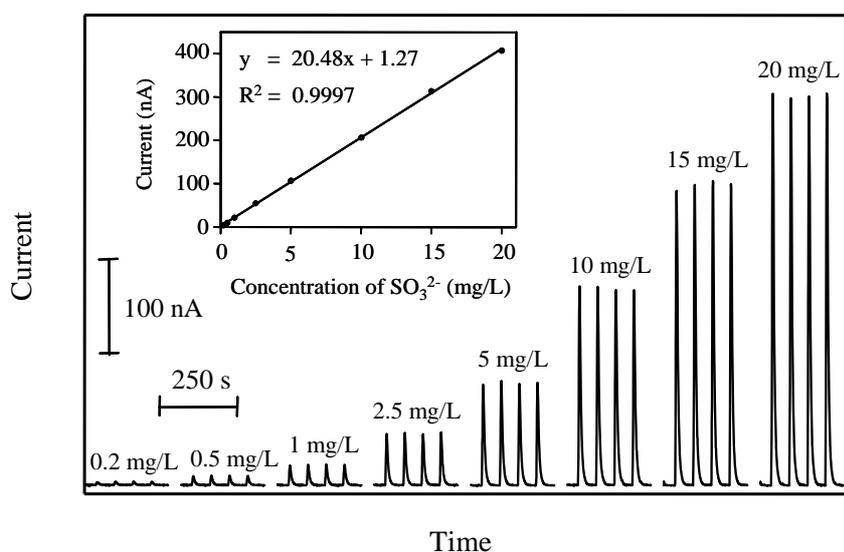


Figure 8. SIA with amperometric detection results for various concentrations of SO_3^{2-} . The SIA operating sequence is listed in Table 1. The calibration curve is shown in the inset.

3.7. Determination of sulfite in wine samples

In order to evaluate the accuracy of the proposed system, the method was applied to the determination of free and total sulfur dioxide in wines. The analytical results were compared with those obtained by iodimetric titration [1]. Since several matrix compounds in wine interfere with iodimetric analysis, correction of iodine consumption must be applied [25]. The same amount of wine was treated with formaldehyde, forming the methanesulfonate adduct, before titration with iodine. The amount of iodine consumed gives the amount of non-sulfite reducer in the sample. In the SIA analysis of free sulfur dioxide, the sample was directly aspirated into the holding coil. For the total sulfur dioxide determination, the sample was first treated with 1 M NaOH to release the bisulfite ions which were bound to some compounds, such as acetaldehyde and aldose sugars. The mixture was then acidified with 25% (v/v) H_2SO_4 and aspirated into the holding coil. In order to perform the SIA analysis in the linear concentration range of sulfur dioxide, the sample volume in the SIA operating sequence (Table 1) was reduced to 15 μL .

The results obtained by both methods are shown in Table 2. The experimental *t*-values obtained by the proposed SIA method were 0.532 for free sulfur dioxide and 0.914 for total sulfur dioxide. These *t*-values were smaller than the *t*-value (3.182) for three degrees of freedom at the 95% confidence level. This indicates that there is no significant difference between the results obtained by the proposed SIA

method and those of the iodimetric titrations. The relative standard deviations for the analysis of sulfite in wines were in the range of 1.0 – 4.1 %.

The sampling frequency was 65 determinations per hour. The consumption of 2 M H₂SO₄ per determination was 100 µL and the volume of 0.1 M phosphate buffer (pH 8)/0.1% SDS per determination was about 0.5 mL.

Table 2. Comparison of the results obtained by SIA and titration methods for free and total SO₂ in wines.

Sample	Free SO ₂ (mg/L) ^a		Total SO ₂ (mg/L) ^a	
	SIA method	Titration method	SIA method	Titration method
White wine 1	11.2 ± 0.3	11.9 ± 0.4	48.7 ± 0.9	47.5 ± 1.9
White wine 2	24.1 ± 0.3	22.2 ± 0.4	102.4 ± 1.1	105.8 ± 0.9
Red wine 1	11.9 ± 0.2	11.7 ± 0.4	55.2 ± 0.8	58.3 ± 0.9
Red wine 2	5.1 ± 0.1	5.3 ± 0.4	32.6 ± 1.3	31.8 ± 1.6

^a Mean ± standard deviation (n=3)

4. Conclusions

The use of a gas diffusion-sequential injection system with a boron-doped diamond electrode for sulfite determination proved to be an effective alternative. The addition of 0.1% SDS into the carrier of 0.1 M phosphate buffer (pH 8) can prevent electrode fouling. The SIA manifold for sulfite analysis is simple and the sensitivity of the method is good. The sensitivity of the method can be changed easily by changing the sample volume. Other advantages of the presented system are the use of few and non-toxic reagents and the reduction of both reagent consumption and volume of effluent. The developed SIA system allows the determination of free and total sulfur dioxide in different types of wines with high sample throughput.

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