

# Chronoamperometric Determination of Sulphite Using Gold- Printed Electrode

M. Khodari

Department of Chemistry, Faculty of Science, South Valley University, Qena, Egypt

**Abstract:** A chronoamperometric method for the determination of sulphite ions has been developed using disposable, screen-printed gold electrodes in presence of some mediators. The used mediators include: potassium hexacyanoferrate (III), hydroxymethylferrocene, 4-(methylamino) phenol sulphate. Calibration curves exhibit a linear relationship between the electrode response and the sulphite concentration over the range from 100  $\mu\text{M}$  to 3.00 mM. The correlation coefficient for calibration curve was equal to 0.992. The obtained limit of detection (LOD) was 30  $\mu\text{M}$ . The relative standard deviations were equal to or better than 6.96 % (n=5). The interferences of various ions were studied. The used sensors are successfully applied for the determination of sulphite in tap water and agriculture drain water. It was found that the used screen-printed electrodes have its initial response after storage in dry state at room temperature up to eight months.

**Keywords:** screen-printed electrodes, Chronoamperometry, Sulphite, Mediators, electroanalysis

## 1. Introduction

Due to the importance of sulphite ions, the present work aimed to establish a quick chronoamperometric method for the determination. Sulphite is well known due to its appearance in "acid rain" and its detrimental effect on nature. Sulphite appears as an environmental contaminant in rain, river and seawater. Sulphite is a widely used food preservative and whitening agent. According to Food and Drug Administration (FDA), sulphite has been recognized as safe for use in foods. In 1996 FDA revoked this status and required warning labels on any food containing more than 10 mg/kg of sulphite.

The presence of sulphite in natural water causes a reduction in oxygen concentration, which can have a detrimental effect on aquatic life; therefore a rapid, simple, inexpensive assay for this species is very desirable. Conventional methods have been developed for the determination of sulphite in a variety of samples such as preserved foods [1,2], fruit juices [3], mustard [4], brine [5], natural waters [6] and atmospheric waters [7].

The sulphite oxidize can utilize several electron acceptors: cytochrome c [8] and water-insoluble hexacyanoferrate(III) salts. Screen -printed electrodes were used to determine sulphite and some anions as reported elsewhere [9-11]

## 2. Experimental

### 2.1 Chemicals and reagents

All chemicals were of reagent grade and all solutions were prepared in second distilled water. The phosphate buffer solutions with different pH values were done by mixing the two appropriate solutions of disodium hydrogen phosphate, sodium dihydrogen phosphate and phosphoric acid until the desired pH, read on a pH meter, was obtained.

### 2.2 Preparation of the Screen-Printed Electrodes

The used sensors were fabricated as described elsewhere [10]. All measurements were done using printed platinum as a reference electrode and a platinum wire as a counter one.

### 2.3 Instrumentation

A computer-aided electrochemistry system was used in the voltammetric and amperometric studies. The system consists of a potentiostat Model 263A (EG&G PARC) Princeton Applied Research Corporation (made in USA) and Electroanalytical software Model 270/250 version 4.0 (PARC). The pH-metric measurements were carried out using a ThermoOrion Model 420A.

### 2.4 Procedures

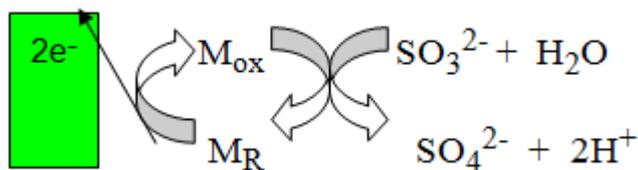
All experiments were carried out at room temperature. Voltammetric and chronoamperometric measurements were performed using 50 ml cell containing appropriate concentration of a mediator in 20 ml of 0.1 M sodium phosphate buffer without bubbling. Standard solution of 50 mM sulphite was prepared and the required concentration prepared by suitable dilution. Optimization of potential and buffer conditions was established using the chronoamperometric technique in an unstirred solution. The technique was applied to calibration, interferences and stability studies. Hydrodynamic voltammograms were obtained using unstirred solutions of 0.1 M sodium phosphate buffer containing appropriate concentrations of the selected mediator and sulphite anion. The potentials of the working electrodes were increased in steps; the resulting steady-state current responses were measured for each plateau and plotted against the applied potential. Screen-printed electrodes were rinsed by redistilled water, dried by plotting paper after each run and stored at room temperature without special humidity adjustment.

### 3. Results and Discussion

#### 3.1 Cyclic Voltammetric Measurements

Initial studies were performed using cyclic voltammetric technique to establish whether mediators show any redox behavior at the used screen-printed electrodes. Such behavior was a prerequisite for the development of an chronoamperometric  $\text{SO}_3^{2-}$  sensor. Cyclic voltammetric experiments were carried out using 0.1 M sodium phosphate buffer, pH 7.4, containing sulphite alone, mediator alone and mediator plus  $\text{SO}_3^{2-}$ . The results showed that the reversible redox behavior of  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , hydroxymethyl ferrocene, 4-(methylamino)phenol sulphate mediators was influenced by the addition of sulphite. Figure (1) illustrates cyclic voltammograms of 20 ml 0.1 M sodium phosphate buffer, pH 7.4, containing 10.00 mM of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  mediator before (a) and after (b) the addition of 10.00 mM sulphite at the used screen-printed electrodes. From this Figure it can be seen that, potassium hexacyanoferrate (III) shows a one-electron reversible behavior in the absence of sulphite. The addition of  $\text{SO}_3^{2-}$  leads to a significant variation of the voltammogram, where the cathodic peak current decreased and the anodic one increased. This fact indicates that the potassium hexacyanoferrate (III) mediator oxidizes sulphite to sulphate and simultaneously undergoes reduction to  $\text{K}_4[\text{Fe}(\text{CN})_6]$  which is re-oxidized at the used screen-printed electrodes leading to an increase in the anodic current. The enhancement in the anodic current was directly proportional to the amount of sulphite added. The same behavior was observed in presence of hydroxymethyl-ferrocene and 4-(methylamino)phenol sulphate mediators.

The suggested sequence of reactions which occurs during the operation of the proposed system (sulphite, mediator) is indicated in the following scheme



Initially, the mediator oxidizes sulphite to sulphate and simultaneously undergoes reduction. The reduced form of the mediator is re-oxidized at the screen-printed electrodes leading to an anodic current, which constitutes the analytical signal.

#### 3.2 chronoamperometric Measurements

Chronoamperometry was used to construct a hydrodynamic voltammogram for 3.00 mM sulphite in 0.1 M sodium phosphate buffer, pH 7.4, using Au/Au, Au/Pt and Pt/Pt screen-printed electrodes. The electrodes response reaches a plateau at + 0.40 V. It should be mentioned that other workers [12] reported that sulphite could be detected using

glassy carbon electrode at + 1.15 V vs. Ag/AgCl in a diffusion cell containing sulphuric acid solution. Therefore, the mentioned screen-printed electrodes might be expected to exhibit greater selectivity when compared to a device requiring such high potentials for operation. The optimum operating potential for amperometric determination of sulphite in presence of potassium hexacyanoferrate (III), hydroxy-methylferrocene and 4-(methylamino)phenol sulphate mediators was + 0.45 V. The chronoamperometric responses measured over a wide range of  $\text{SO}_3^{2-}$  concentrations without mediator and in the presence of different mediators. The collected results showed a linear range for the electrode response and the concentration of sulphite, the linear range of the electrode, characteristic parameters (correlation coefficient, linearity, sensitivity, relative standard deviations and detection limit) are cited in Table (1). The standard deviations shown in the Table have been calculated on five replicate determinations. From the Table, one can observe that potassium hexacyanoferrate (III) gave the best results. Thus, the effect of buffer kind, pH and concentration was investigated, to optimize the condition for the quantitative determination of  $\text{SO}_3^{2-}$ .

Different buffers were examined, these buffers include: sodium borate, sodium acetate, sodium phosphate, sodium citrate and Britton-Robinson buffer. Sulphite gave the highest response in sodium phosphate buffer.

The effect of the pH value of the sodium phosphate buffer on the response of sulphite was also investigated over the range 5 - 8.5. The response increased with increasing pH value and the highest response was observed at pH 7.4. This is in agreement with the range previously cited in the literature [13].

#### 3.3 Influence of Interferences

The influence of possible electrochemical interferents on the response of  $\text{SO}_3^{2-}$  at the different sensors has been tested. The interference resulting from direct oxidation of some anions ( $\text{S}_2\text{O}_3^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ) and electroactive substances (e.g. ascorbic acid) was examined in presence of 3.0 mM sulphite and 5.0 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$  mediator using chronoamperometric measurements at 0.45 V. The ratio of interferents concentrations to  $\text{SO}_3^{2-}$  concentration were 1:10, 1 : 2 and 1 : 1. The results indicate that, the investigated anions did not have a significant effect on the sulphite response obtained with different sensors. Ascorbic acid enhanced the sulphite response. The interference from ascorbic acid can be compensated by the use of the standard addition method, for the quantification of sulphite in real samples.

#### 3.4 Analytical Application

The chronoamperometric response of the used electrodes for the determination of sulphite were evaluated by monitoring samples of tap and agriculture drain waters

before and after the addition of known  $\text{SO}_3^{2-}$  concentration in presence of potassium hexacyanoferrate (III) as mediator. The pH of water samples was adjusted to 7.4 by addition of phosphate buffer. The standard deviations shown in the Table have been calculated on five replicate determinations. The percentage recoveries in the range of 97 to 104% and the RSD of 5 to 9% obtained for the various concentration of sulphite are reasonable. These results indicate that the used gold printed electrode should give reliable results for the determination of sulphite at the levels investigated. The advantage of the used sensors is, therefore, that it provides a rapid means of detecting elevated levels of  $\text{SO}_3^{2-}$  arising as a result of pollution. In addition, as chronoamperometric sensors, in general, have the potential to be portable; we envisage that the used electrodes may be applied in the field. This approach would eliminate any need to collect and stabilize water samples.

### 3.5 Operational and Storage Stability

The storage stability of any type of sensors is an important factor for market viability point of view. Sensors fabricated in batches of several hundreds by screen-printed technology have to be preserved for several weeks until they are used for real applications. Hence, we tested the influence of storage period and storage conditions on the signals of the sensors with the sulphite ion in presence of potassium hexacyanoferrate (III) mediator. The collected results agree with the reported one elsewhere [10]

## 4. Conclusion

Chronoamperometric method was developed for the determination of sulphite ions using disposable screen-printed electrodes containing gold as a working electrode. A detection limit of 30  $\mu\text{M}$  based on ( $S/N = 3$ ). The suggested sensor gave reasonable results when applied to determine the mentioned anion in different samples. Also a linear relationship over the range 100  $\mu\text{M}$  to 3.0 mM sulphite

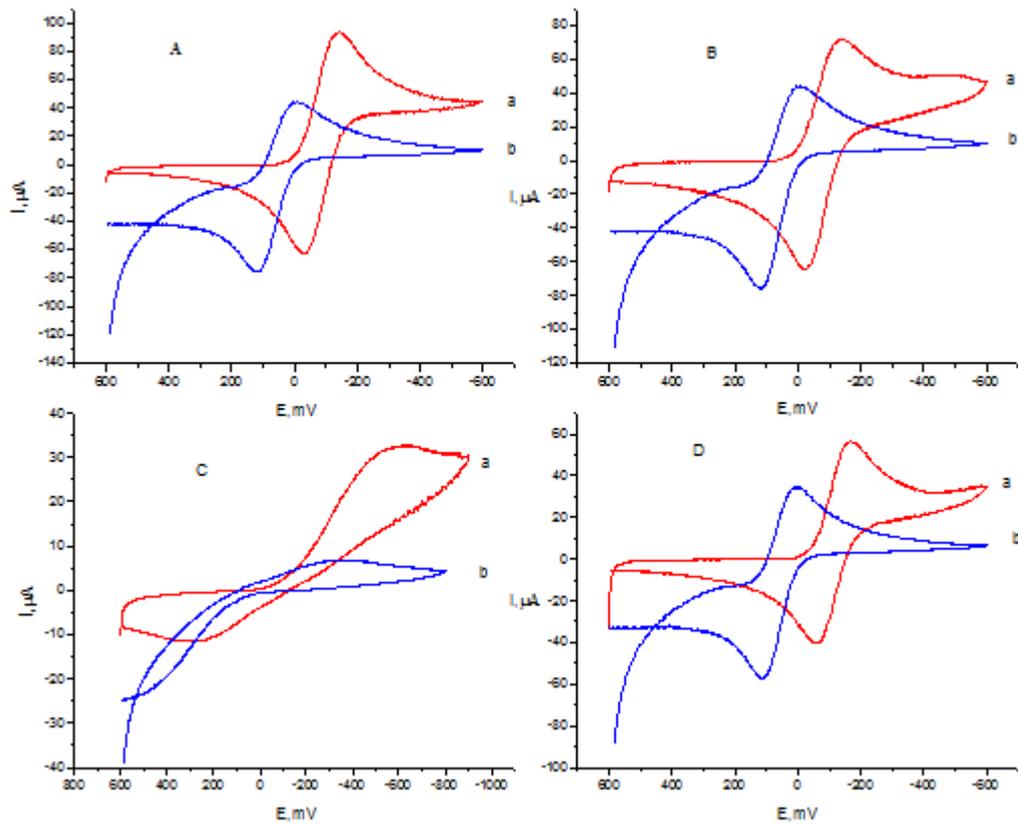
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**Table 1:** Characteristic parameters for the determination of  $\text{SO}_3^{2-}$  obtained by chronoamperometric measurements without mediator and in presence of the different used mediators

Mediator	Characteristic parameters	Au/Pt
Without mediator	Linear range ( $\mu\text{M}$ – mM)	100 – 3.00
	Linear correlation coefficient	0.996
	Sensitivity ( $\mu\text{A}/\text{mM}$ )	1.49
	Detection limit ( $\mu\text{M}$ )	300
	Relative standard deviation	4.28 %
hydroxymethyl ferrocene	Linear range ( $\mu\text{M}$ – mM)	100 – 3.00
	Linear correlation coefficient	0.993
	Sensitivity ( $\mu\text{A}/\text{mM}$ )	1.94
	Detection limit ( $\mu\text{M}$ )	100
	Relative standard deviation	5.51 %
$\text{K}_3[\text{Fe}(\text{CN})_6]$	Linear range ( $\mu\text{M}$ – mM)	100 – 3.00
	Linear correlation coefficient	0.987
	Sensitivity ( $\mu\text{A}/\text{mM}$ )	859.2
	Detection limit ( $\mu\text{M}$ )	30
	Relative standard deviation	5.51 %
4-(methylamino) phenol sulphate	Linear range ( $\mu\text{M}$ – mM)	100 – 1.00
	Linear correlation coefficient	0.993
	Sensitivity ( $\mu\text{A}/\text{mM}$ )	3.79
	Detection limit ( $\mu\text{M}$ )	100
	Relative standard deviation	1.90 %



**Figure 1:** Cyclic voltammograms of 20 ml 0.1 M sodium phosphate buffer, pH 7.4, containing 10.00 mM of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  mediator in absence (a) and presence (b) of 10.00 mM  $\text{SO}_3^{2-}$  at the screen-printed electrodes Au/Au (A), Au/Pt (B), C/Pt (C) and Pt/Pt (D) using scan rate of 50 mV/s