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THE INVESTIGATION OF THE VIABILITY OF THE Pt ELECTRODE IN SULPHITE CYCLIC VOLTAMMETRIC ASSAY

Aurelia Magdalena PISOSCHI

University of Agronomic Sciences and Veterinary Medicine of Bucharest,
Faculty of Veterinary Medicine, 105 Splaiul Independentei, District 5, 050097, Bucharest, Romania

Corresponding author email: aureliamagdalenapisoschi@yahoo.ro

Abstract

This paper aims at the study of Pt electrode ability to act as working electrode in cyclic voltammetric sulphite assay. The analytical signal is represented by the intensity measured for the voltammetric peak, that corresponds to analyte anodic oxidation. The measured peak intensity depends linearly on sulphite concentration within the range 0.031 g/L – 4 g/L. The assay is characterized by a limit of detection of 12.4 mg /L, a relative standard deviation of 2.74%, and the process proved controlled by the analyte diffusion to the electrode.

Key words *cyclic voltammetry, platinum electrode, sulphite, anodic oxidation, linear potential sweep.*

INTRODUCTION

Sulphite is a widely used preservative agent in foods and drinks, being incorporated in wines, beer, processed meat, fruit juices, jams and jellies (Pisoschi, 2014; Banu et al., 2000; Stan, 2007; Pisoschi, 2012).

It is recognized for its reductive and antibrowning activity. Its reductive properties constitute the basis of most assessment methods. Sulphite can be easily oxidized during its reaction with iodine, as follows:

$$SO_3^{2-} + I_2 + H_2O \longrightarrow SO_4^{2-} + 2\ HI$$

Excess iodine can be detemined by thiosulphate titration (Musagala et al., 2013):

$$I_2 + 2\ Na_2S_2O_3 \longrightarrow 2\ NaI + Na_2S_4O_6$$

Sulphite can be determined photocolorimetrically, with 5,5'-dithiobis 2-nitrobenzoic acid at 575 nm, allowing a linear range of analytical response between 0.10 şi 4.3 mg L^{-1} (Li and Zhao, 2006). Fuchsin reagent can also be used in sulphite spectrophotometric assay (Leinweber and Monty, 1987).

Voltammetry and amperometry involve the current intensity measurement, at fixed or constantly varying potential. Amperometric assays employ sulphite oxidase-based biosensors, with enzyme immobilization on Prussian blue/polypyrrole nanoparticles composite, electrodeposited on an indium oxide working electrode (Rawal and Pundir, 2012). Voltammetry at graphite (Lu et al., 1999), platinum (Skavas and Hemmingsen, 2007), modified glassy carbon electrodes (Wang et al., 2013). The linear analytical range for sulphite corresponded to 5 µM-0.41 mM, at 1 µM detection limit and a relative standard deviation value of 1.1%, at a glassy carbon electrode modified with graphene-chitosan and gold nanoparticles (Wang et al., 2013). Cyclic voltamograms at $Ni–Pt_{3layers}$ electrode proved the electrocatalytical potential of this material in sulphite oxidation (Enache et al. 2016).

The voltammetric sulphite electro-oxidation to sulphate was confirmed as an irreversible process (Lu et al., 1999).

MATERIALS AND METHODS

A KSP potentiostat-galvanostat, laboratory made by Professor Slawomir Kalinowski, University Warmia and Mazury (Olsztyn), as well as the respective software Cyclic Voltammetry, were used for recording the cyclic voltammograms.

A Pt strip electrode Radelkis OP-0612P was used as working electrode. As reference, a saturated calomel electrode (SCE), Radelkis was used. The counter electrode was a Pt strip Radelkis OP-0612P electrode.

The stock solution of sodium sulphite (5 g/L) was prepared daily by dissolving Na_2SO_3 (Merck, ACS ISO,) in a 0.10 M KCl electrolyte solution (Chimopar, Bucharest, Romania).

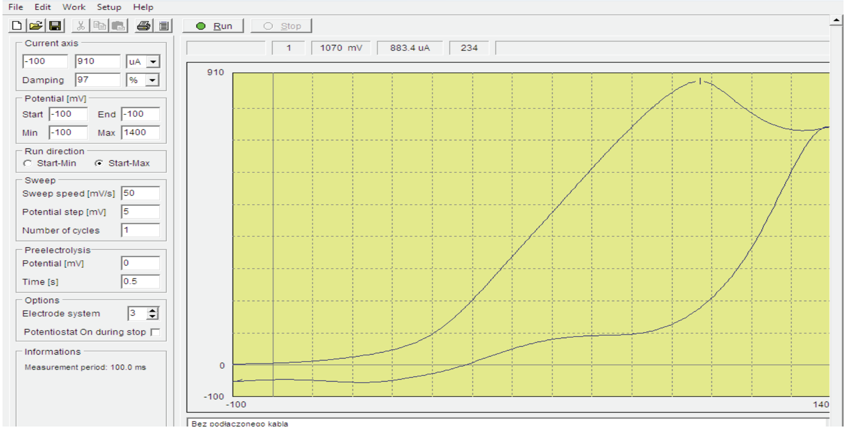
Standard solutions of sulphite (as Na_2SO_3) subject to analysis, with concentrations comprised between 5 mg/L and 5 g/L were obtained by dilution of the stock solution with 0.10 M KCl solution. The volume of the analysed sample was 50 mL and all measurements were performed at 23^0 C, using a 0.10 M KCl solution as supporting electrolyte.

Before each determination, the Pt working electrode was cleaned mechanically and electrochemically by applying a -1.5 V potential pulse for 3 seconds. For the cyclic voltammetric measurements, the potential was scanned within the range -100 to 1500 mV, with a 50 mV/s scan rate.

For the investigation of the influence of the scan rate, the potential sweep rate varied between 25 and 200 mV/s.

RESULTS AND DISCUSSIONS

Cyclic voltammograms were recorded, at sulphite increasing concentrations comprised between 5 mg/L and 5 g /L, using the Pt strip electrode. A representative cyclic voltammogram is presented in Figure 1.



Current axis
-100 910 uA
Damping 97 %
Potential [mV]
Start -100 End -100
Min -100 Max 1400
Run direction
○ Start-Min ● Start-Max
Sweep
Sweep speed [mV/s] 50
Potential step [mV] 5
Number of cycles 1
Preelectrolysis
Potential [mV] 0
Time [s] 0.5
Options
Electrode system 3
Potentiostat On during stop ☐
Informations
Measurement period: 100.0 ms

1 | 1070 mV | 883.4 uA | 234

Bez podłaczonego kabla

Figure 1: An illustrative cyclic voltammogram obtained for 1g/L sulphite solution, in the presence of KCl 0.1 M as electrolyte

The developed calibration curve (Figure 2) showed a linear range of analytical response corresponding to 0.031 g/L – 4 g/L.

The equation of the calibration graph corresponded to y = 423.57 x + 331.6, R2 = 0.9883.

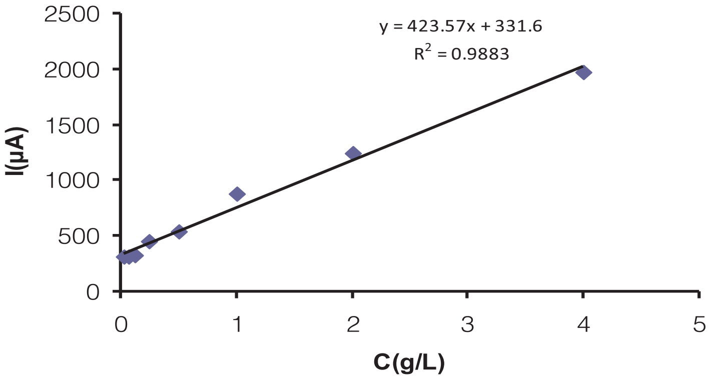


Figure 2: Calibration graph (obtained by plotting the peak current intensity in microamperes, versus concentration) obtained at sulphite voltammetric determination at a Pt strip electrode, in the presence of KCl 0.1 M as electrolyte .

The value of the relative standard deviation RSD was 2.74 %, calculated as 100 x standard deviation / the mean of determinations, c = 125 mg/L; n = 10).

The obtained detection limit was 12.4 mg/L, calculated as LOD = 3 s/m, where s represents the square mean error calculated for the KCl electrolyte solution as blank, and m represents the slope of the calibration graph.

The electroactive process proved diffusion-controlled observing Randles-Sevcik law, as shown by the linear dependence of the current intensity on the square-root of the potential-sweep rate (Figure 3).

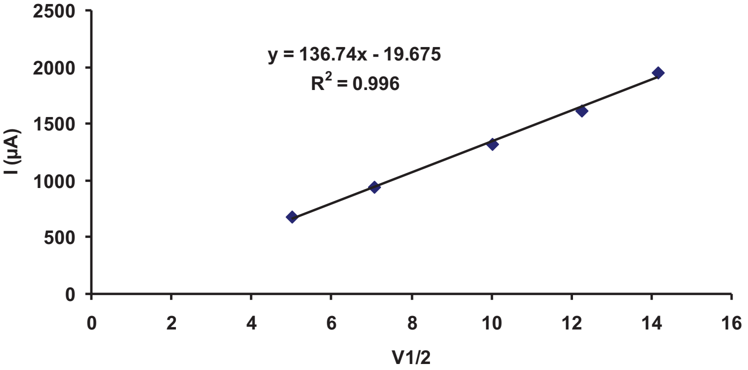


Figure 3: The dependence of the peak current intensity on the square root of the potential sweep rate, as obtained for 1 g/L sulphite, in the presence of KCl solution 0.1 M as supporting electrolyte

Hence, the magnitude of the analytical signal, considered as the measured current intensity at the voltammetric peak, is controlled by analyte diffusion from the solution to the electrode/solution interface.

CONCLUSIONS

The anodic voltammetric peak corresponding to sulphite oxidation increases with analyte concentration. The linear range of analytical response corresponds to 0.031 g/L – 4 g/L sulphite concentration, with good correlation coefficient R^2= 0.9883.

This, along with a sensitivity value of 423.57µA/g/L (as given by the slope of the calibration graph), a detection limit as low as 12.4 mg /L and a relative standard deviation of 2.74%, proved the method's viability, and offers prospects for future studies regarding optimization and application.

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