

VOLTAMMETRIC BEHAVIOR OF THE CUBIC SILSESQUIOXANE MODIFIED WITH PURPALD® FOR DETERMINATION OF SULFITE

D. R. Silvestrini¹; L. A. Soares¹; Y. Wang²; T. F. S. Silveira¹, U. O. Bicalho¹ and D. R. Do Carmo¹

¹Faculdade de Engenharia de Ilha Solteira UNESP–Univ. Estadual Paulista, Departamento de Física e Química.

²Shanghai University, Department of Chemistry College of Science.

¹Av. Brasil Centro, 56 CEP 15385-000, Ilha Solteira, SP, Brazil. Fax: +55 (18) 3742-4868.

²Shangda Road, 99 Zip Code 200444, BaoShan District, Shanghai, China. Fax: (+86) 18801912699.

Silsesquioxanes or spherosiloxanes are nanostructured materials which have the empirical formula $(R\text{SiO}_{1.5})_n$, where R can be a hydrogen or any organic group and n is an integer number that can vary, in $n \geq 4$ [1]. 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole, also known as Purpald®, is a chromogenic agent that is widely used in the determination of aldehyde. Purpald® possesses S–C–N linkages and displays potential ligands for metal complexes that may also be biologically active just like some other amine- and thione-substituted triazoles [2].

A novel composite formed by interaction of a octa(3-chloropropyl)octasilsesquioxane [3] modified with Purpald®, and its subsequent reaction with silver and hexacyanoferrate (III) (AgHSP), was synthesized and initially characterized by Fourier transform infrared spectra (FTIR) and cyclic voltammetry. The cyclic voltammogram of the modified graphite paste electrode with AgHSP (20% w/w), showed a redox pair with formal potential $E^0 = 0.64\text{V}$ (vs Ag/AgCl, KNO_3 , 1.0 mol L^{-1} ; $\nu = 20\text{ mV s}^{-1}$), attributed to the $\text{Fe}^{2+}(\text{CN})_6/\text{Fe}^{3+}(\text{CN})_6$ process [4]. Studies on various supporting electrolytes (KNO_3 , NaNO_3 and NH_4NO_3) for studies of cations are illustrated in Fig. 1. It was observed that the nature of the cations affected the average potential (E^0) and the current intensities, but was not verified any interference of anions with exception of chloride (Cl^-).

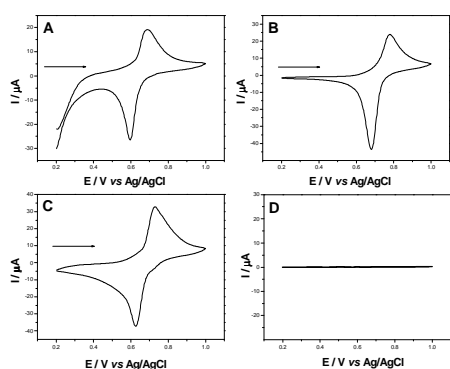


Figure 1. Cyclic voltammograms of graphite electrode modified with AgHSP: (A) NaNO_3 , (B) KNO_3 , (C) NH_4NO_3 and (D) KCl (1.0 mol L^{-1} ; $\nu = 20\text{ mV s}^{-1}$; 20% (w/w)).

Fig. 2 illustrates the voltammetric behavior of the graphite paste electrode modified with AgHSP for the electro-oxidation of sodium sulfite. The modified electrode showed a linear response from 7.0×10^{-5} to $1.0 \times 10^{-3}\text{ mol L}^{-1}$ with the corresponding equation $Y(\mu\text{A}) = 18.05 + 29.983 \times 10^3 [\text{sulfite}]$, and a correlation coefficient of $r=0.999$ (Fig. 3). The method showed a

detection limit of $0.115 \times 10^{-4}\text{ mol L}^{-1}$ with a relative standard deviation of $\pm 4\%$ ($n = 3$) and amperometric sensitivity of $29.983 \times 10^{-3}\text{ A mol L}^{-1}$.

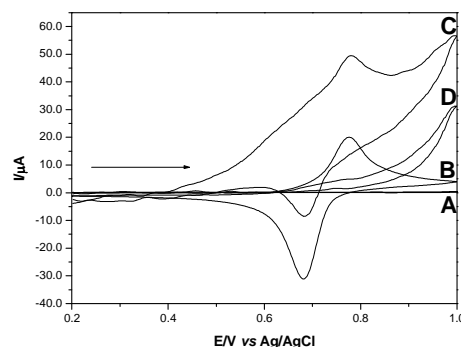


Figure 2. Cyclic voltammograms: (A) of the graphite paste electrode; (B) graphite paste electrode modified with AgHSP; (C) graphite paste electrode modified with AgHSP and $1.0 \times 10^{-3}\text{ mol L}^{-1}$ of sulfite; (D) graphite paste electrode and $1.0 \times 10^{-3}\text{ mol L}^{-1}$ of sulfite (KNO_3 1.0 mol L^{-1} ; 20 mV s^{-1} ; 20% (w/w)).

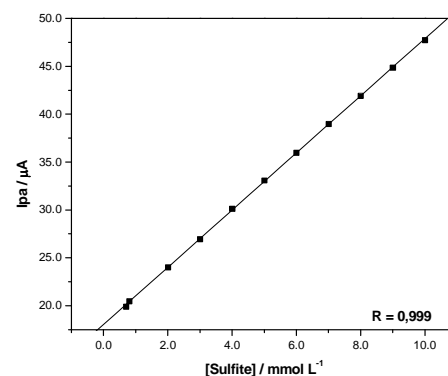


Figure 3. Analytical curve for the determination of sodium sulfite using the graphite paste electrode modified with AgHSP (KNO_3 1.0 mol L^{-1} ; 20 mV s^{-1} ; 20% (w/w)).

The electrocatalytic oxidation of sulfite occurs as follows: Fe^{3+} produced during anodic scan, chemically oxidize the molecule sulfite when it is reduced to Fe^{2+} , which will again be electrochemically oxidized to Fe^{3+} .

Conclusion

Quantitation in millimolar range of sulfite in pharmaceutical can be achieved using graphite paste electrode modified with AgHSP. The modified electrode showed an excellent stability and good reproducibility during experiments.

Acknowledgements

The authors are grateful for Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP - Procs. 2012/05438-1 and 2012/11306-0).

References

- [1] D. B. Cordes, P. D. Lickiss, F. Rataboul, *Chem. Rev.* 110 (2010) 2081-2173.
- [2] A. K. Sen, R. N. Singh, R. N. Handa, S. N. Dubey, P. J. Squattrito, *J. Mol. Struct.*, 470 (1998) 61.
- [3] J. Chojnowski, W. Fortuniak, P. Rościszewski, W. Werel, J. Łukasiak, W. Kamysz, R. Hałasa, *J. Inorg. Organomet. Polym. Mater.*, 16 (2006) 219.
- [4] D. Jayasri, S. Narayanan, *Sens. Actuators, B*, 119 (2006) 135.