DESENVOLVIMENTO DE UM ELETRODO DE PASTA DE CARBONO MODIFICADO COM AZUL DE METILENO EM SÍLICA/NIÓBIO PARA A ANALISE DE SULFITOS

DEVELOPMENT OF CHEMICALLY MODIFIED ELECTRODE WITH METHYLENE BLUE ANCHORED ONTO SILICA/NIOBIUM FOR SULFIDE ANALYSIS

MACEDO, I.Y.L[1]; LOBÓN, G.S.[2]*; MATIAS, A.L.B.[1]; LIÃO, L.M.[1]; SCALIZE, P. S.; GIL, E.S.[1].

[1] Universidade Federal de Goiás, Faculdade de Farmácia Rua 240, S/n - Setor Leste Universitário, Goiânia – CEO 74605-170 – Goiânia - GO, Brasil

[2,] Universidade Federal de Goiás, Instituto de Química, Avenida Esperança, s/n, Campus Samambaia CEP 74690-970 - Goiânia - GO., Brasil
(fone: +55 (62) 98435-4645; fax: +55 62 3521-1167)

** Autor correspondente*
e-mail: manger84@gmail.com

Received 07 December 2016; received in revised form 15 December 2016; accepted 19 December 2016

RESUMO

O sulfureto é um composto de alta toxicidade, mesmo em baixas concentrações. É liberado para o ambiente por muitas fontes, o que pode levar a impactos ambientais e à saúde. Assim, a detecção de esses compostos requer métodos de alta sensibilidade, praticidade e baixo custo. Algumas metodologias analíticas para a detecção são baseadas na reação com o azul de metileno (MB) que tem sido utilizado no desenvolvimento de eletrodos modificados (MEs). Os MB-MEs podem ser ferramentas promissoras para detectar este ânion eletroativo. Desta forma, foram desenvolvidos e caracterizados os MEs de sílica-niobio-azul de metileno (SNMB). Estes métodos foram avaliados por cronoamperometria e técnicas voltamétricas, em diferentes condições experimentais. Nas condições ótimas, as SNMB-ME apresentaram uma resposta linear contra sulfureto de 7,6 a 63,4 x µM, (r = 0,9979), enquanto o limite de detecção e quantificação foi de 2,03 mM e 6,77 mM, respectivamente. Tais resultados confirmam a potencial aplicabilidade do SNMB-ME para análise e monitoramento de sulfeto em amostras.

Palavras-chave: monitorização eletroquímica, compostos de enxofre, técnicas cronoamperometricas, técnicas voltametricas.

ABSTRACT

Sulfide released in the environment, due to high toxicity, even at low concentrations, may lead to serious environmental and health impacts. Therefore, is mandatory to develop highly sensitive, practical and inexpensive methods for detecting sulfide. Some of these analytical approaches are based on the methylene blue (MB) reaction, which has been successfully used in modified electrodes (MEs) development. MB-MEs hold promise as tools for detecting this electroactive anion. This study developed and characterized silica-niobium-methylene blue (SNMB) MEs, and evaluated their performance in sulfide determination through chronoamperometric and voltammetric techniques, under different experimental conditions. Within optimum conditions, the SNMB-MEs exhibited a linear response to sulfide anions from 7.6 to 63.4 µM, (r = 0.9979), whereas the detection and quantification limits were 2.03 mM and 6.77 mM, respectively. These results confirm the potential applicability of SNMB-ME for sulfide analysis and monitoring.

Keywords: electrochemical monitoring, sulfur compounds, chronoamperometric techniques and voltammetric techniques.

1. INTRODUCTION

Sulfide is a toxic corrosive compound that is released into the environment from natural and anthropogenic activities, such as volcanic eruptions, petrochemical transformation processes or motor vehicle combustion. Sulfur is highly soluble in water, and so is highly mobile. Its natural cycling allows atmospheric forms to settle and accumulate in soil and aquatic environments, where it causes unpleasant odors and can lead to the formation of hydrogen sulfide, a weak acid that has corrosive properties and is very harmful to most aquatic life (FEITOSA and MANOEL, 1997; ESTEVES, 1998).

The effects of sulfide on human health vary with concentration and exposure (acute or chronic) time. Cardiac and respiratory symptoms (e.g. tachycardia, palpitations and cardiac arrhythmias, bronchitis, pulmonary edema, respiratory depression and respiratory paralysis, usually accompanied by nausea, vomiting and diarrhea) are related to acute exposure, whereas chronic exposure can lead to neurological problems, which include dizziness, irritability, headache, seizures and even coma (LILIAMTIS and MANCUSO, 2003).

Therefore, due to the high toxicity of sulfide ions, even at low concentrations, their monitoring and control has great relevance. Several analytical methods have been described for sulfide analysis, including iodometric titration, flow injection analysis, spectrophotometry, chromatography and electrochemical methods (Patnaik, 199; AGA, 2015; PAWLAK and PAWLAK, 1999). Nevertheless, the official method, USEPA-Methylene Blue, first described by Fischer in 1883 is still widely used (Fischer 1883). Despite, having good selectivity and sensitivity, colorimetric methods are not very accurate and have slow reaction times and somewhat erratic when conditions are not optimal (Cline 1969).

In this sense, electroanalytical methods based on modified electrodes are promising alternatives that combine the required sensitivity and selectivity with low cost and speed. Different electrochemical technic and electrodes have been testes in the last years, amperometric approach (LAWRENCE *et al*, 2000), mercury-film electrode (KOVALEVA, CHEREMUKHINA and GLADYSHEV 2003), carbon nanotube immobilized onto the glassy carbon electrode (LAWRENCE *et al*, 2004) or nanocopper-oxide screen-printed (THAKUR *et al*, 2016). In fact, taking into account the affinity of sulfide, an electroactive anion, to MB, an electron mediator, a MBME had been proposed yet (SCOTTI *et al*. 2006). Moreover, more recently, amperometric and voltametric analyses with boron-doped diamond electrodes have been combined (BACIU, *et al*, 2015). In this work, the MB was previously immobilized on a silica/niobium surface, and different amounts of the resulting SNMB were used to develop modified carbon-paste electrodes. The SNMB-MEs were evaluated by voltammetry in different experimental conditions. Within optimal conditions, the developed SNMB-ME was used to determine sulphide ions in water samples.

2. EXPERIMENTAL

2.1. Chemicals

Potassium chloride, hydrochloric acid and sodium hydroxide were purchased from Sigma-Aldrich Co. (St Louis, USA); acetic acid, sodium chloride, potassium hydroxide, sodium phosphate, sodium sulfate and sodium sulfide were purchased from Merck (Darmstadt, DE). All reagents were standard and all electrolytic solutions were prepared in ultrapure water (Millipore-Q).

2.2. SiO_2/Nb_2O_5 synthesis

The sol–gel process was used to produce the SiO_2/Nb_2O_5 material. First, TEOS (tetraethylorthosilicate) was pre-hydrolyzed and subsequently dissolved in ethanol in the molar proportion of 1:3 (MILLER and LANKSHMI 1998). Then, 0.86 mL of concentrated HCl was added to 50 mL of this solution (solution A), and further, it was refluxed at 353 K for 2.5 h. Another solution, named solution B, was prepared with 0.08 mol of $NbCl_5$ and dissolved in 100 mL of ethanol under a N_2 atmosphere. A 50 mL portion of solution B was added to solution A, and the mixture was stirred at room temperature for 3 h, after which. Next, 140 mL of H_2O was slowly added, followed by stirring at room temperature for 2 h. Finally, the mixture was allowed to sit at 333 K until complete gelation. The solid was washed first with water numerous times in a Buchner funnel and then

with ethanol. The residual solvent was evaporated from xerogel by heating at 383 K for 24 h, and the remaining dried compound was heated to 1,473 K in order to form silica/niobium oxide (SN).

2.3. Immobilization of methylene blue on SN surface

The adsorption of MB was carried out by suspending 200 mg of SN in 5 mL aqueous solution containing 0.5 mg of MB. This suspension was magnetically stirred for 1 h at 298 K. The material was filtered and washed until the filtered solution became colorless. The resultant material was named SNMB.

2.4. Characterization of SNMB

The SNMB material was characterized by FTIR spectroscopy, in a JASCO 4 100 spectrophotometer with a resolution of 4 cm^{-1}, with the accumulation 250 scans.

The amount of Nb_2O_5 present in the SNMB material was determined by X-Ray Fluorescence spectrometry in a Shimadzu EDX 720 operated with $ZnK\alpha$ = 8.62 keV. The sample elements under investigation were utilized in combination with a 35 mm mask and a 5 mm fine collimator.

Surface area of the SNMB material was calculated by the Brunauer–Emmett–Teller (BET) method from the nitrogen adsorption–desorption data, which was measured on a Quantachrome Nova 2200 analyzer.

The amount of methylene blue adsorbed on the SNMB material was determined by elemental analysis with a PE-2400 elemental analyzer.

2.5. Preparation of SNMB modified electrodes

The modified carbon paste electrodes were prepared by mixing rigorously (i.e. 10 min) 60 mg of graphite powder with 0, 5, 10, 15 or 20 mg of the SNMB. The homogeneous powder was mixed rigorously with 20 mg of mineral oil (nujol®) by 10 minutes in order to get the final carbon paste.

2.6. Electrochemical methods

Electrochemical measurements were carried out using a three-electrode system: the working electrode, SNMB-M (area of 1 mm^2); the reference electrode, saturated calomel (Hg/Hg_2Cl_2, KCl_{sat}); and the counter electrode, platinum wire. The electrochemical cell was attached to μAutolab III potentiostat/galvanostat (The Netherlands) coupled to GPES 4.9 software. Cyclic voltammetry was performed from -0.3 V to 1.3 V at a scan rate of 100 mVs^{-1}, whereas differential pulse (DP) voltammograms were performed with a pulse amplitude of 50 mV, a pulse width of 4 s and a scan rate of 10 $mV \cdot s^{-1}$.

The chronoamperometric method was used for quantification of sulfide ions in a broad range of concentrations (0 to 1 mM). The best pH range (2 to 9) and interference by electrolyte solutions were also investigated. The chosen applied oxidation potential for sulfide was fixed at 250 mV.

3. RESULTS AND DISCUSSION:

3.1. SNMB Characterization

X-Ray Fluorescence showed that the SNMB possessed 260 μmol of Nb_2O_5 per gram of material, while the elemental analysis showed the presence of 41 μmol of methylene blue per gram of material.

The specific surface area of SN and SNMB (Figure 1) was determined from the adsorption/desorption isotherm of nitrogen by applying the BET equation, and were 375 and 310 m^2g^{-1}, respectively. The immobilization of methylene blue caused the decrease in surface area because methylene blue occupies part of the SN surface, which is reduced with the incorporation of organic groups. This easily explained by the fact that these groups partially block the adsorption of nitrogen molecules to the surface, resulting in a decrease of surface area.

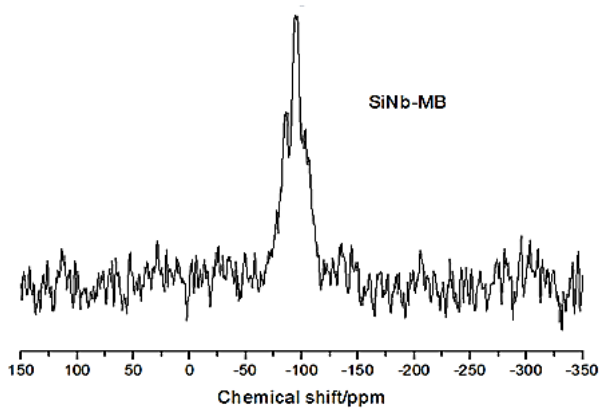

***Figure 1**. The Si-29 NMR spectrum of the SNMB material.*

The Si-29 NMR spectrum of the SNMB material presented three characteristic peaks. One peak at 89 ppm was related to the chemical environment Q^2 of silicon, assigned to bonds $Si(OSi)_2(OH)_2$, $Si(OSi)_2(ONb)_2$, or $Si(OSi)_2(ONb)(OH)$. The second peak was observed at 95 ppm, which is attributed to the Q^3 environment, and was related to bonds $Si(OSi)_3(OH)$ or $Si(OSi)_3(ONb)$. The third peak was observed at 108 ppm, which is related to the Q^4 silicon environment $Si(OSi)_4$ (GUO, *et al.*, 2002).

3.2. Effect of SNMB-ME composition on sulfide response

The carbon paste was modified in different SNMB proportions. Them sensibility to 10 μM sulfide solution was evaluated using DPV and linear voltammetry in a pH 8.0, 0.1 M KCl electrolyte solution.

The results are presented in Table 1, in which data for blank and unmodified carbon paste (CP) electrodes are also provided for further comparisons.

***Table 1.** Anodic peak current, I_{pa} obtained for different SNMB-ME proportions in response to 10 μM Sulfide solution (pH~ 8.0) at E_{pa} = 170 mV.*

	SNMB:CP	I_{pa} μA	***Relative response %***
CP	0:70	0.9	8
SNMB-ME	*5:70*	*11*	*100*
SNMB-ME1	10:70	10	91
SNMB-ME2	15:70	7	63
SNMB-ME3	20:70	6	55

The response of SNMB-ME was 7 to 13 fold greater than that observed for the conventional carbon paste electrode. This result may be related to the electron mediating properties of MB improving the electrochemical oxidation of sulfide ions. Moreover, the chemical affinity between the MB and the analytic may exert pre-concentration effect, leading to a higher amount of sulfide on the electrode surface (MILLER and LAKSHMI, 1998; SOUZA, FERTONAN and PASTRE, 2003)

3.3. Effect of experimental conditions

The influence of pH on SNMB-ME performance was investigated with both the stability of the electrode and the efficiency of electrochemical oxidation being taken into account (Figure 2).

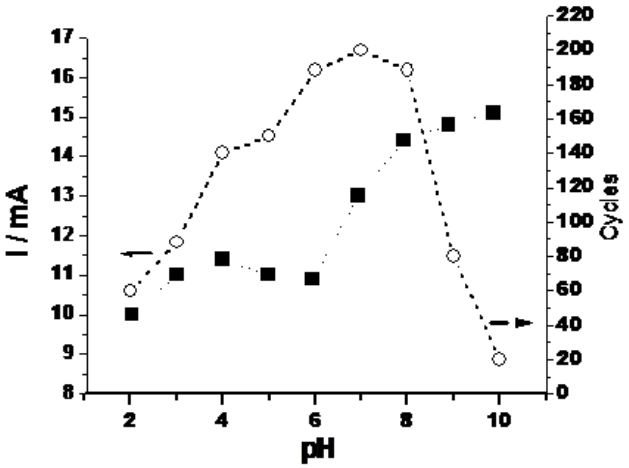

***Figure 2.** Effect of pH on the SNMB-ME response to 1 mM Sulfide solution. Left side: peak current (■). Right side: stability of signal after successive cycles (○).*

Though the anodic oxidation of sulfide to sulfate is favored in alkaline medium, the stability of the electrode system diminishes in extreme pH conditions. Moreover, the property of MB to act as a redox mediator involves the participation of protons, whereas the amino functional group can undergo protonation or deprotonation with the processes of oxidation and reduction (SCOTTI, *et al*., 2006.). The highest maintenance of peak current levels was achieved in the pH range of 6.0 to 8.0, in which at least 90% of the signal was obtained even after 200 cycles. These results also indicate that in this pH range the

hydrosoluble MB is not leached from the SN surface. Therefore, the pH chosen for subsequent evaluations was 8.0.

It was also found that inorganic salts (e.g. acetate, phosphate, chroride and sulfate salts of sodium and potassium) that are commonly used as supporting electrolytes did not have a great influence on the electrocatalytic response of sulfide. Nevertheless, capacitive current level was slightly lower for chloride and higher for sulphate anions.

3.4. Calibration curve

The response of SNMB-ME was evaluated against successive additions of sulfide by means of cyclic voltammetry (Figure 3).

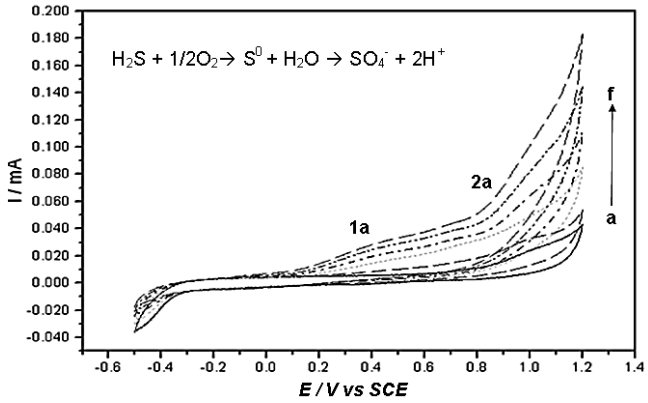

Figure 3*. Cyclic voltammograms obtained for different concentration of sulfide: a) 5.0, b) 10.0, c) 20.0, d) 30.0, e) 40.0 and f) 50.0 μM at SNMB-ME in KCl 0.1 mol L^{-1}, pH ~ 7.0. Scan range from -0.5 to 1.2 V, scan rate of 100 mVs^{-1}.*

The broad anodic peaks, 1a and 2a, at Epa ~ 0.3 V and 0.7 V are in agreement with data from the literature and are related to the electrochemical oxidation of sulfide to elemental sulfur, which then oxidizes to sulphate (LOVRIC, LOVRIC and SCHOLZ, 1997; LIMA and VELA, 2009; SANTOS e REZENDE, 2002; TEIXEIRA, RAMIREZ and GUASTALDI 2002.). Therefore, peak 1a is associated with the direct electroxidation of the sulfide anion to sulfur how was related by LAWRENCE *et al*, 2004; and the anodic peak 2a could be related with indirect oxidation.

Calibration studies were performed by chronoamperometry in a pH 8.0 buffer solution using a constant potential of 0.25 V vs. SCE. The electrochemical sensor was allowed to reach steady state in the buffer solution, and then aliquots of 0.1 M Na_2S standard solution were added successively at regular intervals (Figure 4).

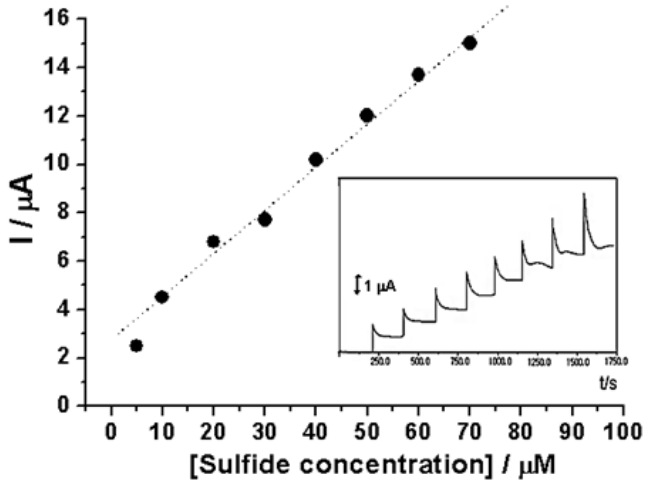

Figure 4. *Calibration curve, SNMB-ME against incremental concentration of sulfide, in pH 8.0, 0.1 M phosphate buffer. Inset: the related chronoamperograma. Applied potential: 250 mV.*

Figure 4 shows that peak current varies linearly with concentration from 7.59 to 63.4 μM, with a correlation coefficient (r) of 0.9979. The corresponding linear equation was Ipa = 2.03 + 0.18 [S^{2-}], in which the peak currents are expressed in □A and the sulfide concentration in □M.

The detection limit of 2.03 □M and quantification limit of 6.77 □M are below the security levels established by environmental legislation, above which sulfide can diminish water quality and cause damage to human health (LIMA and Vela 2009). Brazilian legislation, CONAMA Resolution 357, establishes limits for total sulfide and H_2S not dissociated, in compounds of different classes, present in surface waters. For river class 1, which includes most of the surface waters used for domestic and industrial use, the threshold for these compounds is 250 mg L^{-1} and 0.1 mg L^{-1} respectively (BRASIL, 2005). For drinking water, the Ordinance 2914 provides the limits and regulations of the above compounds, for which different threshold values apply, 250 mg L^{-1} to total sulfide and 0.002 mg L^{-1} to H_2S not dissociated (BRASIL, 2011).

CONCLUSION

The anodic reaction of sulfide anions on the surface of SNMB-ME was much higher than those observed for conventional carbon-paste electrodes. The SNMB-ME electrode exhibited higher sensitivity in an alkaline medium, whereas higher stability was observed in the pH range of 6.0 to 8.0. The good stability, broad linear range and low limit of detection makes SNMB-ME a promising tool for sulfide analysis.

REFERENCES:

1. AGA S/A. **Ficha de Informações de Segurança de Produto Químico**. Available: <http://www.lindegas.com.br/International/Web/Lg/br/likelgbr.nsf/repositorybyalias/pdf_msds_h/$file/Hydrogen%20Sulfide.pdf> Accessed: 20/03/2015.
2. Baciu, A.; Ardelean, M.; Pop, A.; Pode, R.; Manea, F. Electrode. Sensors. **2015.** 15, pp. 14526-14538.
3. BRASIL. Ministério do Meio Ambiente. Conselho Nacional de Meio Ambiente - CONAMA. Resolução n. 357. Dispõe sobre a classificação dos corpos de água e diretrizes ambientais para o seu enquadramento, bem como estabelece as condições e padrões de lançamento de efluentes, e dá outras providências. Brasília. 17 mar. **2005**. Available: <http://www.mma.gov.br/port/conama/res/res05/res35705.pdf> Accessed: 03/20/2015
4. BRASIL. Ministério de Estado da Saúde. Portaria n° 2914, de 12 de dezembro de 2011. Dispõe sobre os procedimentos de controle e de vigilância da qualidade da água para consumo humano e seu padrão de potabilidade. Diário Oficial [da] União, Brasília, 14 dez. **2011**. Available: <http://www.saude.mg.gov.br/images/documentos/PORTARIA%20No-%202.914,%20DE%2012%20DE%20DEZEMBRO%20DE%202011.pdf> Accessed: 03/20/2015.
5. Cline, J. D. Limnol. Oceanogr. **1969**. 14, pp. 454-458.
6. Esteves, F. A. *Fundamentos da Limnologia*. Editora Interciência, Rio de janeiro, 1998.
7. Feitosa, C. F. A.; Manoel Filho, J. *Hidrogeologia: conceitos e Aplicações*, LABHID-UFPE, Fortaleza. CE, Editra CPRM, 1997.
8. Guo, F., Esser, L., Singh, S.K., Maurizi, M.R., Xia, D. (2002) J Biol Chem**. 2002**. 277 (48), pp. 46753-46762. Doi: 10.1074/jbc.M208104200
9. Kovaleva, S.V., Cheremukhina, N.M., Gladyshev, V.P. J. Anal. Chem. **2003**. 59 (8), pp. 749 - 752.
10. Lawrence, N.S., Davis, J., Jiang, L., Jones, T.G.J., Davies, S.N. Electroanalysis. **2000**. 12 (18), pp. 1453-1460. Doi: 10.1002/1521-4109(200012)12:18<1453::AID-ELAN1453>3.0.CO;2-Z
11. Lawrence, N.S., Deo, R.P., Wang, J. Anal. Chim. Acta. **2004**., 517 (1–2), pp. 131-137. Doi: 10.1016/j.aca.2004.03.101
12. Liliamtis, T. B.; Mancuso, P. C. S. Saude Soc. **2003.** São Paulo, 12 (2).
13. Lima, R. B.; Vela J. A. A. Estudo eletroquímicos voltados para a eletroxidação de sulfetos. Available: <http://www.cetem.gov.br/publicacao/serie_anais_X_jic_2002/Renata.pdf>. Accessed: 20/03/2015. CETEM (2009) 195.
14. Lovric, S. K. ; Lovric, M.; Scholz, A. F. Mikrochim. Acta. **1997**. 127, pp. 95-99.
15. Miller, J. M.; Lakshmi, L. J. The J. Phys. Chem. B. **1998**. 102 (34) pp. 6465-6470.
16. Patnaik, P.A. *Comprehensive Guide to the Hazardous Properties of Chemical, Substances*. 2th edition. Wiley, New York. 1999.
17. Pawlak, Z. and Pawlak, A.S. Talanta. **1999**. 48 (2), pp. 347-353. Doi: 10.1016/S0039-9140(98)00253-7
18. Santos, F. F.; Rezende, M.O.O. Quím. Nova. **2002** 25 (1) pp. 53-58.
19. Scotti, R., Lima, E. C., Benvenutti, E. V., Piatnicki, C., Dias, S. L., Gushikem, Y., & Kubota, L. T. Química nova. **2006**. 29 (2) pp. 208-212.
20. Souza, G. R.; Fertonan, I. F. L.; Pastre, I. A. Ecl. Quím. **2003**. 28 (1) pp. 77-83.
21. Thakur, B., Bernalte, E., Smith, J. P., Foster, C. W., Linton, P. E., Sawant, S. N., & Banks, C. E. Analyst. **2016**. 141 (4) pp. 1233-1238.

22. Teixeira, C. M.; Ramirez, I.; Júnior, O. G.; Guastaldi, A.C. Quim. Nova. **2002**. 25 (1) pp. 20-26.