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Article

Determination of Cu, Ni and Pb in Aqueous Medium by FAAS After Pre-Concentration on 2-Aminothiazole Modified Silica Gel

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Este trabalho descreve a síntese e caracterização da sílica gel modificada com grupos 2-aminotiazol (SiAT), e os resultados de um estudo de adsorção e pré-concentração (em batelada e em fluxo, utilizando-se um sistema por injeção em fluxo acoplado com um espectrômetro de absorção atômica) de Cu(II), Ni(II) e Pb(II) em meio aquoso. A capacidade máxima de adsorção da SiAT determinada para os íons metálicos estudados em mmol g^{-1} foram: Cu(II)= 1,18, Ni(II)= 1,15 and Pb(II)= 1,10. Os resultados obtidos nos experimentos em fluxo, mostraram uma recuperação de praticamente 100% dos íons metálicos adsorvidos em uma mini-coluna empacotada com 100 mg de SiAT, utilizando-se 100 μL de HCl 2 mol L^{-1} como eluente. A sorção-desorção quantitativa dos íons Cu(II), Ni(II) e Pb(II), permitiu a aplicação do sistema em fluxo na pré-concentração e posterior quantificação desses íons metálicos em amostras de águas naturais digeridas e não digeridas por oxidação com radiação UV.

This work describes the synthesis and characterization of 2-aminothiazole modified silica gel (SiAT), and the results of a study of the adsorption and pre-concentration (in batch and using a flow-injection system coupled to an absorption atomic spectrometer) of Cu(II), Ni(II) and Pb(II) in aqueous medium. The adsorption capacities for each metal ions in mmol g^{-1} were: Cu(II)= 1.18, Ni(II)= 1.15 and Pb(II)= 1.10. The results obtained in the flow experiments showed a recovery of practically 100% of the metal ions adsorbed in a mini-column packed with 100 mg of SiAT, using 100 μL of 2.0 mol L^{-1} HCl solution as eluent. The sorption-desorption of the metal ions made possible the application of a flow-injection system for the pre-concentration and quantification by FAAS of metal ions at trace level in natural water samples digested and not digest by an oxidizing UV photolysis.

Keywords: pre-concentration, 2-aminothiazole modified silica gel, water samples, FAAS

Introduction

The toxic effects of heavy metals (e.g., Cd, Cr, Hg, Pb) have been demonstrated in certain "at-risk" humans.[1,2] Since the main sources of these metals for humans are water and food. It is of paramount importance to control the metal content in natural water. For the direct determination of heavy metals in aquatic environments a number of sensitive instrumental methods (e.g., atomic spectroscopy) are available, which, however, can suffer from systematic interferences by water constituents. For this reason, a pre-concentration step is often necessary before quantifying these analytes.[3]

In recent years, the use of chemically modified silica gel with various chelating organofunctional groups aiming the adsorption and pre-concentration of metal ion from solutions, have been described.[3-6] Particularly, a column packed with the material in line with flow analysis systems has been suggested as an effective and reliable process for pre-concentration of the metal ions before analysing by atomic absorption spectrometry method.[7-13] In such

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combined method the enrichment of analyte and removal of interfering matrix constituents, can considerably improve the method of analysis extending the limit of detection to lower concentration.

This paper describes the preparation of silica gel chemically modified with 2-aminothiazole aiming to find an efficient material for separation and chemical analysis of the metal ions present in natural water samples. Primarily the material was tested with a synthetic aqueous solution containing some metal ions and further it was used to analyse real samples.

Experimental

Reagents, analytical solutions and samples

All solutions were prepared with high purity chemical and distilled-deionized water (Milli-Q system, Millipore). Hydrochloric and nitric acids used were Suprapur (Merck).

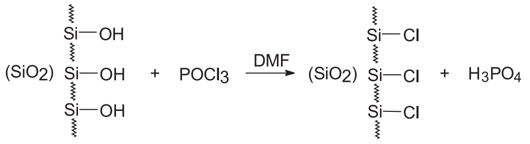
Copper, nickel and lead standards solutions (40 - 200 μg L^{-1}) were prepared by stepwise dilution from 1000 mg L^{-1} stock solution (Merck – Titrisol) with Milli-Q water.

Samples collected from natural water (Tietê River, Paranapanema River; Paraná River, SP/Brazil.) were immediately filtered through a 0.45 μm membrane. After acidification (pH < 2.0) with 6.0 mol L^{-1} HNO_3 solution, they were stored in highly purified polyethylene containers. The river water samples were digested by oxidizing UV-photolysis in the presence of H_2O_2 10 mol L^{-1} using a low-pressure Hg-lamp which was installed into a closed quartz vessel.[14]

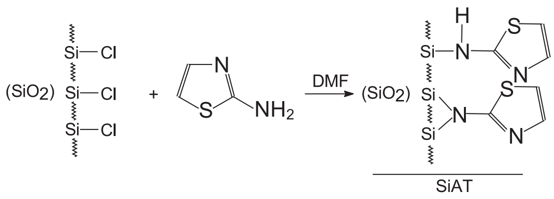
Preparation of modified silica gel [15]

Silica gel (Merck) with specific surface area of 500 m^2 g^{-1} and average pore diameter of 0.6 nm, was activated at 420 K under vacuum (0.133 Pa). About 50 g of this silica was immersed in 200 mL of purified dimethylformamide and 12 mL of phosphorus oxychloride was added. The mixture was refluxed under nitrogen atmosphere for 36 h, filtered, washed with dimethylformamide, ethanol and heated under vacuum in order to eliminate all the solvent. The resulting solid was immersed in 135 mL of purified dimethylformamide and 18 g of 2-aminothiazole was added. The mixture was stirred for 36 h at 380 K under nitrogen atmosphere. The resulting modified silica was filtered off, washed with dimethylformamide, ethanol and heated for 8 h at 348 K under vacuum (0.133 Pa).

The equations 1 and 2 describe the preparation of the material:



(1)



(2)

The quantity of 2-aminothiazole attached to the silica surface was determined by the nitrogen analysis using the Kjeldhal method.[13] The specific surface area was determined by the BET method, starting from the nitrogen adsorption isotherms at 77 K in automated Micromeritics ASAP 2010 equipment.

Infrared spectra

Diffuse reflectance infrared Fourier Transform (DRIFT) spectra were obtained with a Nicolet spectrometer model Nexus 670 with Smart Collector, in Kubelka-Munk units, with 1mg of material mixed with 500 mg of KBr.

Adsorption of the metal ions by SiAT

Adsorption of $MX_{n(aq)}$ by SiAT from a solution can be described by the equilibrium:

$$\mathrm{mSiAT}_{(s)} + \mathrm{MX}_{n(aq)} \rightleftharpoons (\mathrm{SiAT})_m\mathrm{MX}_{n(s)} \qquad (3)$$

were mSiAT represents the mass of the modified silica gel and MXn the concentration of metal ions in the aqueous solution.

The time required to this reaction achieves the equilibrium condition was previously determined immersing 100 mg of SiAT in 50 ml of 5x10^{-3} mol L^{-1} of the metal solution and shaking. At different time intervals, an aliquot of the supernatant solution was separated and the concentration of metal ions was determined by complexometric titration using Na_2EDTA.

The quantity of the adsorbed metal, N_f, was calculated applying the equation 4:

$$N_f = \frac{N_i - N_s}{m} \qquad (4)$$

where N_i represents the initial mole number of the metal ion in the solution phase, N_s the mole number of the metal ion in equilibrium with the solid phase and m is the mass of the adsorbent.

Effect of pH

The effect of pH on the adsorption of metal ion on SiAT was evaluated by varying the pH over range of 1.0-5.0 with addition of 0.10 mol L^{-1} HNO_3.

Isotherms of adsorption

The adsorption capacity of SiAT was determined at 298 K using the batch technique. In 50 mL of aqueous solutions of the metal ions (concentrations between $2x10^{-5}$ and $5x10^{-3}$ mol L^{-1}), about 100 mg of SiAT were added and the resulting mixture was shaken for 10 min. The solid phase was separated by centrifugation and the metal ion was determined in the supernatant solution by complexometric titration.

Apparatus

A SHIMADZU Model AA-6800 atomic absorption spectrometer equipped with a copper, nickel and lead hollow cathode lamps and deuterium lamp for background correction was used for the determination of metals. The operating conditions adjusted in the spectrometer were carried out according to the standard guidelines of the manufacturers. The atomic absorption signal was measured as a peak height mode against an analytical curve.

Ismatec Model IPC-8 peristaltic pump furnished with tygon pumping tubes (i.d. 0.5 mm) and homemade injector-commutator of perspex were used in the flow injection system.

Flow injection system

The flow diagram of the system with the SiAT packed mini-column is shown in Figure 1, consisted of a peristaltic pump, an injection valve (homemade injector-commutator) and a mini-column (glass tubing, 5.5 cm length and 3 mm i.d.) packed with 100 mg of SiAT. Standard solutions or water samples in the 40 – 200 μg L^{-1} Cu(II), Ni(II) and Pb(II) concentration range were passed through the column at 1.0 mL min^{-1} for 5 min for the sorption of metal ions in the column. The metal ions were eluted with 100 μL of 2.0 mol L^{-1} HCl solution, added through the injection valve at 1.0 mL min^{-1}. The metal ions eluted were transported to the burner of spectrometer and the signal was recorded as a peak height.

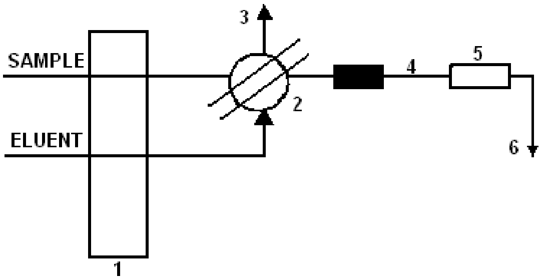


Figure 1 . Flow Injection system for copper, nickel and lead pre-concentration by FAAS. (1) peristaltic pump; (2) injection valve; (3) waste; (4) mini-column; (5) FAAS; (6) waste.

Results and Discussion

Characteristics of material

The infrared spectra confirms the presence of 2-aminothiazole groups bounded to the silica surface. The absorption band observed at 2784 cm^{-1} is due to the C-H stretching of aromatic olefins. The other two bands of interest observed at 1471 and 1395 cm^{-1}, can be assigned to the $\delta_{C=N}$ and δ_{N-H}, both dislocated from low frequencies due to strong absorption at 1630 cm^{-1} of δ_{Si-O} of the remaining groups of silica gel.[15]

The chemical analysis of SiAT yield a 1.24±0.07 mmol g^{-1} of the functional groups attached to silica surface and 354±0.6 $m^2 g^{-1}$ of the specific surface area. The attached functional groups were very stable under the various cycles of adsorption-elution of the metal ions by the adsorbent in a column. Losses of the adsorption capacity for individual metal ions were not detectable during the experiments.

Adsorption isotherms

An important aspect of this material is the time necessary for the adsorption process to achieve an equilibrium condition.[9,13] Figure 2 shows the plot of N_f against time for Cu (II) as an example. The system achieves

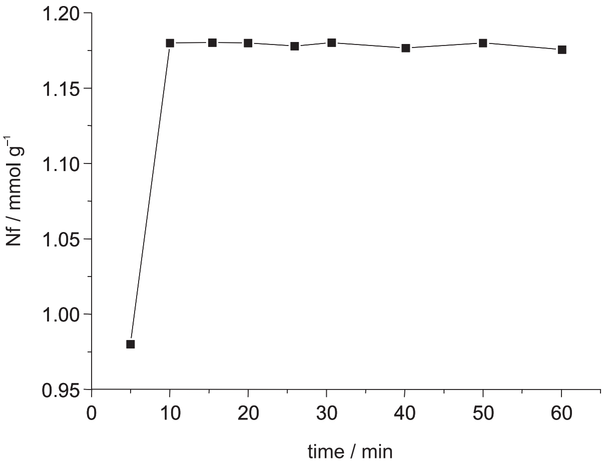


Figure 2. Plots of Nf versus time from Cu(II) aqueous solution at 298 K.

equilibrium condition very fast, about 10 min, because in the present case, the functionalization occurs on the matrix surface having sufficiently large pores (0.6 nm).

The influence of the pH value on pre-concentration by SiAT is plotted in Figure 3, showing that the exchange of metal ions strongly decreases with the acidity of the solution. Obviously, a pH value 5.0 is optimal for the adsorption of metal ions. Exchange experiments at pH values higher than 5.0 were not carried out considering the risk of hydrolysis.[16]

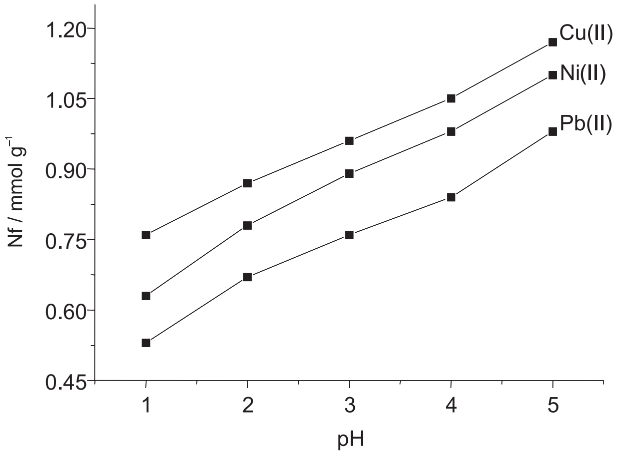


Figure 3. Influence of pH on the adsorption of metal ions from aqueous solutions at 298 K.

The adsorption capacity for each metal ion, determined from saturation condition of the isotherms shown in Figure 4, in mmol g^{-1} was, Cu = 1.18, Ni = 1.15 and Pb = 1.10. The fraction of surface-attached ligand bonded to metal ion is given by equation 5:

$$\phi^{max.} = N_f^{max.}/N_o \qquad (5)$$

where N_o is the amount of organofunctional groups (mmol) per mass of SiAT (g). The values of $\phi^{max.}$ for each metal were, Cu = 0.95, Ni = 0.93 and Pb = 0.90. As $\phi^{max.}$ approximately the same for all metal ions, it is possible to infer that the complexes formed is presumably of the metal:ligand = 1:1 type. This assumption is reasonable taking into account that the coordination of metal could be done in the following ways: (a) at the nitrogen atoms; (b) at the thiazole sulphur atom.

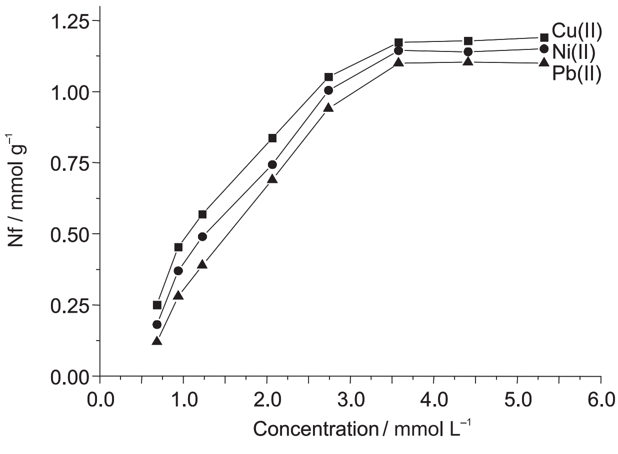


Figure 4. Adsorption of metal ions from aqueous solution at 298 K.

Effect of pre-concentration and elution flow rates of metal ions

The pre-concentration and elution flow rates were varied from 0.5 to 5 mL min^{-1}, while keeping the amount of injected Cu (II) ions at 100 μg L^{-1}. As shown in Figure 5 (graph a) an optimum peak absorbance was obtained at flow rate about 1.5 mL min^{-1}. In the same Figure (graph b), it was observed that the values of absorbance increased with increasing elution flow rate, remaining constant from 2.0 mL min^{-1}. Considering the best values of absorbance, the pre-concentration and elution flow rates selected were 1.0 and 2.0 mL min^{-1}, respectively. As a compromise between loading capacities and eluent volumes, different column lengths and inner diameters were tested and the dimensions selected were 5.5 cm and 3 mm, respectively.

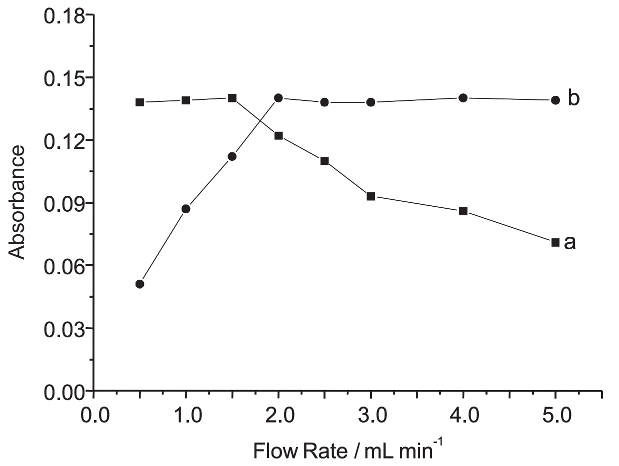


Figure 5. Effect of flow rate on peak absorbance. Experimental conditions: [Cu(II)] = 100 μg L^{-1}; pH 5.0; 2 mol L^{-1} HCl as eluent solution; flow rate: a - pre-concentration flow rate; b - elution flow rate.

Analytical performance

A linear calibration curve was obtained for the 40 - 200 μg L^{-1} range of Cu(II) using sampling times of 3, 4, and 5 min (volumes injected in triplicate). Accordingly, the calibration slopes increased, but not proportionally, with the increase of sampling time, which means that the retention efficiency in not constant.

The experimental pre-concentration factor was calculated as the ratio of slope of the calibration graphs obtained using the pre-concentration system proposed ($A = -0.0046 + 0.0022[Cu(II)]$; $A = 0.0003 + 0.0011[Ni(II)]$; $A = -0.0051 + 0.0009[Pb(II)]$) and without pre-concentration ($A = -0.0012 + 4.2x10^{-5}[Cu(II)]$; $A = -4x10^{-5} + 2.2x10^{-5}[Ni(II)]$; $A = -1.1x10^{-4} + 1,9x10^{-5}[Pb(II)]$), using sampling time of 5 min. The pre-concentration factors calculated in this conditions were 52, 50 and 47, for Cu(II), Ni(II) and Pb(II), respectively. Differences between the pre-concentration factor and the added and eluted volumes can occur due to loss of efficiency with increasing sample volume. As can be seen in Table 1, the pre-concentration efficiency declines from 99%-95% with the increase of sample volumes from 3 to 5 mL through the column. The pre-concentration factor under these conditions increase from 29 to 48. The precision expressed as RSD for twelve independent determinations, was 4% for 100 μg L^{-1} of metal ions solutions. The detection limits calculated for Cu(II), Ni(II) and Pb(II) in respect of blanks of elements[17], were 0.30, 0.80 and 2.80 μg L^{-1}, respectively. The sampling frequency was fifteen samples per hour.

The reproducibility of the pre-concentration column expressed as SD, tested by sampling 100 μg L^{-1} Cu(II), Ni(II) and Pb(II) solutions for 5 min through twelve independently prepared mini-column, was about 98 ± 4 μg L^{-1}.

Determination of metal ions in river water samples

The proposed method was successfully applied recovery tests of Cu, Ni and Pb using river water samples spiked with 150 μg L^{-1} of Cu(II), Ni(II) and Pb(II). The results obtained with the proposed method are shown in Table 2. Accordingly, recoveries within 95%-99% for digested sample and 70%-75% for samples without previous digestion were found. This difference has been attributed to formation of inert complexes of metal ions with aquatic humic substances (HS), being less accessible for the functional groups of the collector.[18] After digestion (by oxidizing UV-photolysis in the presence of H_2O_2), the metal ions bound to HS as inert complexes can quantitatively react with functional groups of SiAT.

Conclusions

The proposed method offers a good alternative for copper, nickel and lead determination at trace levels in aqueous medium. The high stability of the mini-column packed with SiAT is evidenced by its utilization during five hours per day for one month. The proposed method allows on-line copper, nickel and lead determination by FAAS of natural water samples, however, requires a previous sample digestion, for instance by UV photolysis, necessary for elimination of the interference of aquatic organic matter, particularly aquatic humic substances, that can form inert complexes with metal ions.

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Table 1. Enrichment factor and efficiency of Cu(II), Ni(II) and Pb(II) pre-concentration (Metal ions concentration = 100 μg L^{-1}; eluent - 100 μL of 2 mol L^{-1} HCl solution; flow rate = 1.0 mL min^{-1}, n = 3)

Sampling time (min)	Experimental pre-concentration factor			Theoretical pre-concentration factor[a]			Efficiency (%)		
	Cu	Ni	Pb	Cu	Ni	Pb	Cu	Ni	Pb
3	29±1	29±2	28±1	30	30	30	98	97	95
4	39±2	38±3	38±2	40	40	40	97	96	95
5	49± 3	49±4	48±2	50	50	50	99	98	96

[a] Volume added/volume eluted.

Table 2. Determination of Cu, Ni and Pb in different water samples (spiked with 150 μg L^{-1} Cu(II)), Ni(II) and Pb(II) by FAAS with pre-concentration on-line on a mini-column packed SiAT, with and without UV-Photolysis digestion. Experimental conditions: eluent – 100 μL of 2 mol L^{-1} HCl solution; sampling time = 5 min with flow rate = 1.0 mL min^{-1}, n = 3)

Samples	SiAT-FAAS/UV-P			SiAT-FAAS		
	Cu	Ni (μg L^{-1})	Pb	Cu	Ni (μg L^{-1})	Pb
Tietê River	145± 4	142± 3	142± 3	110± 5	106± 4	105± 5
Parapanema River	149± 3	146± 2	144± 2	112± 3	110± 3	109± 3
Paraná River	148± 5	145± 3	143± 3	111± 4	108± 3	107± 4

References

1. Balls, P. W.; *Mar. Pollut. Bull.* **1989**, *20***,** 8.
2. Wilken, R. D.; *Fresenius J. Anal. Chem.* **1992**, *342***,** 795.
3. Padilha, P. M.; Gomes, L. A. M.; Padilha, C. C. F.; Moreira, J. C.; Filho, N. L. D.; *Anal. Lett*. **1999,** *32* , 1807.
4. Gomes, A. M.; Padilha, P. M.; Moreira, J. C.; Filho, N. L. D.; Gushikem, Y.; *J. Braz. Chem. Soc.* **1998,** *9*, 494.
5. Filho, N. L.. D.; Gushikem, Y., Rodrigues, E., Moreira, J. C.; Polito, W. L.; *J. Chem. Soc. Dalton Trans.* **1994**, *9***,** 1493.
6. Filho, N. L.D.; Gushikem, Y.; Polito, W. L.; *Anal. Chim. Acta* **1995**, *306*, 167.
7. Filho, N. L. D.; Gushikem, Y.; *J. Mol. Struc. (Theochem)* **1995**, *335*, 175.
8. Lessi, P.; Filho, N. L.D.; Moreira, J. C.; Campos, J. T. S.; *Anal. Chim . Acta* **1996**, *327*, 183.
9. Moreira, J. C.; Gushikem, Y.; *Anal. Chim. Acta* **1985**, *176*, 263.
10. Filho, N. L. D.; Gushikem, Y.; Moreira, J. C.; Polito, W. L.; Rodrigues, E.; *J. Braz. Chem. Soc.* **1994**, *5*, 53.
11. Filho, N. L. D.; Gushikem, Y.; Polito, W. L.; Moreira, J. C.; Ehrim, E. O.; *Talanta* **1995**, *42*, 1625.
12. Gushikem, Y.; Moreira, J. C.; *J. Colloid Interface Sci.* **1985**, *107*, 70.
13. Kubota, L. T.; Ionashiro, M.; Moreira, J. C.; *Ecl. Quim.* **1988**, *13*, 19.
14. Burba, P.; Wilmer, P. G.; *Fresenius J. Anal. Chem.* **1992**, *324*, 167.
15. Roldan, P. S.; Ancântara, I. L.; Castro, G. R.; Rocha, J. C.; Padilha, C. C. F.; Padilha, P. M.; *Anal. Bioanal. Chem.* **2003**, *375*, 574.
16. Padilha, P. M.; J. C., Rocha; Moreira, J. C; Campos, J. T. S.; Federici, C. C.; *Talanta* **1997**, *45*, 317.
17. Zih-Perényi, K.; Lásztity, A.; Horváth, Zs.; Lévai, Á.; *Talanta* **1998**, *47*, 673.
18. Toscano, I. A. S.; Rocha, J. C.; Burba, P.; *Talanta* **1997**, *44*, 69.

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