Article

Preconcentration and Determination of Copper and Zinc in Natural Water Samples by ICP-AES After Complexation and Sorption on Amberlite XAD-2

Sérgio Luis Costa Ferreira[a], Hilda Costa dos Santos[a], Janeide Reis Ferreira[a], Neyla Margarida Lopo de Araújo[a], Antônio Celso Spinola Costa[a], and Djane Santiago de Jesus[b]

[a]*Universidade Federal da Bahia, Instituto de Química,*

40170-290 Salvador - Bahia, Brazil; e-mail: slcf@ufba.br

[b]*Centro Federal da Educação Tecnológica da Bahia, Salvador - Bahia, Brazil*

O presente trabalho descreve um procedimento para separação, preconcentração e determinação sequencial de quantidades traço de cobre e zinco em amostras de água natural, por espectrometria de emissão atômica com plasma indutivamente acoplado (ICP-AES). Este método é baseado na complexação dos íons cobre(II) e zinco(II) pelo 1-(2-thiazolylazo)-2-naphthol (TAN) e sorção sobre a resina Amberlite XAD-2. Parametros tais como: quantidade de TAN, efeito de pH sobre a complexação e sorção dos complexos, tempo de agitação para completa sorção, concentração dos íons metálicos, massa de resina Amberlite XAD-2 necessária, dessorção dos íons metálicos da resina XAD-2 e volume da amostra foram estudados. Os resultados demonstraram que os íons cobre(II) e zinco(II), na faixa de 0,10 a 100,00 μg, contidos em volume de solução amostra de 400 mL, na faixa de pH de 5,7 a 8,3, sob a forma de complexos do TAN, é quantitativamente retido sobre a resina XAD-2. O tempo de agitação requerido para sorção é de 1 hora usando uma massa de resina de 1,4 g. A solução para determinação de cobre e zinco por ICP-AES é obtida, após a dessorção dos íons da resina, usando 5 mL de ácido clorídrico 2 mol L^{-1}, agitando o sistema por 5 min. O procedimento foi aplicado na determinação de cobre e zinco em várias amostras de água natural. A técnica da adição padrão foi aplicada e as recuperações obtidas revelaram que o procedimento proposto tem uma boa exatidão e precisão. Um alto fator de enriquecimento (80) e a simplicidade são as principais vantagens neste procedimento.

The present paper describes a procedure for separation, preconcentration and sequential determination of trace amounts of copper and zinc in natural water samples, by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The proposed method is based on the complexation of copper(II) and zinc(II) ions by 1-(2-thiazolylazo)-2-naphthol (TAN) and sorption on to Amberlite XAD-2 resin. Parameters such as: TAN amount, pH effect on the complexation and sorption of TAN complexes, agitation time for complete sorption, concentration of metal ion, mass of Amberlite XAD-2, desorption of metal ions from XAD-2 resin and sample volume were studied. The results demonstrated that the copper(II) and zinc(II) ions, in the range of 0.10 to 100.00 μg, contained in a solution sample volume of 400 mL, in the pH range of 5.7 to 8.3, on the form of TAN complexes had been quantitatively retained on to XAD-2 resin. The shaking time required for sorption is 1 h using a resin mass of 1.4 g. The solution for determination of copper and zinc by ICP-AES is obtained, after desorption of the ions from the XAD-2 resin, using 5 mL of 2 mol L^{-1} hydrochloric acid and shaking the system for 5 min. The procedure was applied to the determination of copper and zinc in several natural water samples. The standard addition technique was applied

and the obtained recoveries revealed that the proposed procedure has a good accuracy. A high enrichment factor (80) and simplicity are the main advantages in this analytical protocol.

Keywords: *copper preconcentration, zinc preconcentration, solid-phase extraction, Amberlite XAD-2, natural water*

Introduction

The determination of heavy metals in natural waters is a task for analytical chemists frequently asked by environmentalists, for the evaluation and phenomenon interpretation of aquatic systems. However, in many cases the available analytical instrumentation does not show enough sensibility for the realization of the analysis in these natural samples. As such, a previous step of preconcentration is necessary, and for this reason many enrichment procedures have been proposed. The process involving extraction on a solid phase has received more acceptance due to a number of possible advantages including: availability of the solid phase, obtainment of large preconcentration factors, and facility for enrichment using systems with continuos flow. Besides, they usually do not need the use of organic solvents, which may be toxic[1].

Beinrohr *et al.*[2] proposed a procedure for preconcentration and determination of seven metal cations including zinc and copper by flame AAS. In it, the cations in the form of dithizonate complexes, were collected on a thin layer of activated carbon.

A chelating sorbent loaded with dithizone was obtained by chemical reaction with styrene-DVB (5%) copolymer as matrix. This was prepared by Chwastowska and Kosiarska[3] and used for the preconcentration of copper, lead, nickel, cobalt and zinc.

Singh and Kumar[4] have determined zinc and cadmium in mineral waters, using atomic absorption spectrometry after preconcentration with Amberlite XAD-2 loaded with pyrocatechol Violet(PV) and desorption by 4 M hydrochloric acid or nitric acid.

A column containing silica loaded with 8-hydroxyquinoline was used by Azeredo *et al.*[5] for preconcentration and determination of zinc and copper, among others, by graphite furnace atomic absorption spectrometry.

Santelli *et al.*[6] used a column containing ammonium pyrrolidinedithiocarbamate adsorbed on activated carbon for copper determination in waters by atomic absorption spectrometry.

Nagahiro *et al.*[7] proposed a procedure for simultaneous preconcentration of copper and aluminium. They used a column of naphthalene loaded with alizarin red-S.

Soylak and Doºan[8] proposed a procedure for copper determination in water samples. In it, copper has been preconcentrated on a chromatographic column packed with activated carbon after complexation with 1-nitroso-2-naphthol or hexamethylene dithiocarbamate and elution with 2 M hydrochloric acid in acetone.

A flow injection system combining on line preconcentration with immobilized chloroxine and spectrophotometric detection was developed by Elmahadi and Greenway[9] for the determination of copper, zinc and other elements.

Bortoli *et al.*[10] proposed a procedure for preconcentration and determination of cadmium, cobalt, copper, manganese, nickel, lead and zinc for spectrometric techniques (ICP-MS or GFAAS). The metal cations were complexed with diethyldithiocarbamate, adsorbed on a C_{18} column and eluted with methanol.

Perez-Cid *et al.*[11] determined copper in mineral waters by flame atomic absorption spectrometry by using a solid phase extraction with diethyldithiocarbamate loaded on silica gel.

Saxena *et al.*[12-14] have proposed the use of Amberlite XAD-2 functionalized with chelating reagents for the preconcentration and determination of metal cations by spectrometric techniques. In this way, Amberlite XAD-2 modified with alizarin red-S[12], salicylic acid[13] and pyrocatechol violet[14] were recommended for the preconcentration and determination of zinc and other ions.

Recently, Lee *et al.*[15] proposed the use of a styrene-DVB resin chemically modified with 4-(2-thiazolylazo)resorcinol for sorption and determination of copper and uranium.

This paper proposes an analytical procedure for preconcentration and determination of zinc and copper in natural waters, using atomic emission spectrometry with inductively coupled plasma, after chelation with 1-(2-thiazolylazo)-2-naphthol (TAN) and sorption on Amberlite XAD-2.

TAN is a chromogenic reagent proposed for the spectrophotometric determinations of metal cations[16]. In our laboratory, it has been used for the spectrophotometric determination of iron[17] and zinc[18].

Experimental

Apparatus

An applied Research Laboratories model 3410 mini-torch sequential inductively coupled plasma spectrometer with an IBM PC-AT computer was used. The emission intensity measurements were made under the conditions

shown in Table 1. The calibration graph (0-2.0 µg mL^{-1}) of copper and zinc were obtained with solutions prepared from 1 mg mL^{-1} stock solution. The detection limits are shown in Table 2. The correlation coefficients were 0.9997 and 0.9998 for zinc and copper, respectively.

A 300 ANALYSER pH meter was used to measure the pH values.

A VKS-100 Mechanical Shaker 100 cpm was used for shaking of the solutions.

Reagents

All reagents were of analytical grade unless otherwise stated. Double distilled water was used for the preparation of solutions. The nitric acid and hydrochloric acid were of Suprapur quality (Merck). The laboratory glassware was kept overnight in a 10% nitric acid solution. Before the use, the glassware was washed with deionized water and dried in a dust free environment.

Copper solution (10.00 µg mL^{-1}) was prepared by diluting a 1000 µg mL^{-1} copper solution (Merck) using a 5% hydrochloric acid solution.

Zinc solution (10.00 µg mL^{-1}) was prepared by diluting a 1000 µg mL^{-1} zinc solution (Merck) using a 5% hydrochloric acid solution.

Triton-X100 (10%) solution was prepared by dissolving 25 g (Aldrich) in 250 mL of water.

TAN solution (1200 µg mL^{-1}) was prepared by dissolving 0.30 g (Merck) in 25 mL of ethanol and diluting to 250 mL with 10% Triton-X100 solution.

Table 1. Operating parameters for the inductively coupled plasma spectrometer

Incident output power	650 W
Reflected power	5 W
Nebulizer	Glass, Meinhard
Plasma gas flow rate	7.5 L min^{-1}
Auxiliary gas flow rate	0.81 L min^{-1}
Aerosol carrier gas flow	0.81 mL min^{-1}
Solution uptake rate	2.5 L min^{-1}
Signal integration time	5 s
Integration for determination	3

Table 2. Experimental Conditions of Cu and Zn analyzed by ICP-AES.

Element	λ (nm)	Limit of Detection (µg L^{-1})
Zinc	213.826	5
Copper	324.758	2

Hexamine buffer solution (pH 6.5) was prepared with 0.40 M hexamine solution adjusted to pH 6.5 with nitric acid and/or sodium hydroxide.

Conservation and preparation of the water samples

By using Teflon flasks natural water samples were collected on the surface of the aqueous systems, from different locations in the city of Salvador, Bahia, Brazil on June, 1997. They were acidified with 1.0 mL of concentrated nitric acid per liter of sample. The samples were filtered through a cellulose membrane (Millipore) of 45 µm pore size.

Enrichment procedure

Into a flask were added: 400 mL of sample solution containing copper(II) and zinc(II) ions (in the range 0.10-100 µg), 20 mL of buffer solution and 5 mL of 0.12% TAN solution. After shaking, a mass of 1.40 g of XAD-2 resin was added. The system was then shaken mechanically for 1 h, and the Amberlite XAD-2 resin loaded with TAN and their complexes were collected on a glass crucible by vacuum filtration. The resin was transferred to a polypropylene flask where copper(II) and zinc(II) ions were back extracted with 5.00 mL of 2 mol L^{-1} hydrochloric acid solution with agitation for 5 min. The suspension was filtered on a sintered glass filter and the solution was collected in a 10 mL calibrated flask. The contents were diluted with deionized water to the mark and the zinc and copper in the solutions were determined by inductively coupled plasma atomic emission spectrometry.

Results and Discussion

Effect of pH on the extraction of copper and zinc

The pH effect on the sorption of copper and zinc was studied. The results demonstrated that the extraction of the TAN complexes were maximum and constant in the pH range from 5.7 to 8.3. These results can be seen in Fig. 1. The pH control was done using acetate buffer with pH 4.5 to 5.7, hexamine buffer with pH 6.0 to 7.0, borate buffer with pH 8.3 and an ammonium buffer with pH 9.0. The proposed procedure recommends the extraction with the pH of the solution at 6.5 ± 0.1, because the increase of pH can allow the reaction of TAN with other metallic cations.

Amount of Amberlite XAD-2 required for extraction

The amount of XAD-2 resin required for complete sorption of 100.00 µg of zinc and copper in the form of TAN complexes was studied. The results demonstrated that for a sample volume of 400 mL, using 6000 µg of TAN and 1.2 g of XAD-2 resin an agitation time of 50 min was sufficient. In the proposed procedure a mass of 1.40 ± 0.10 g is recommended to garantee the efficiency of sorption.
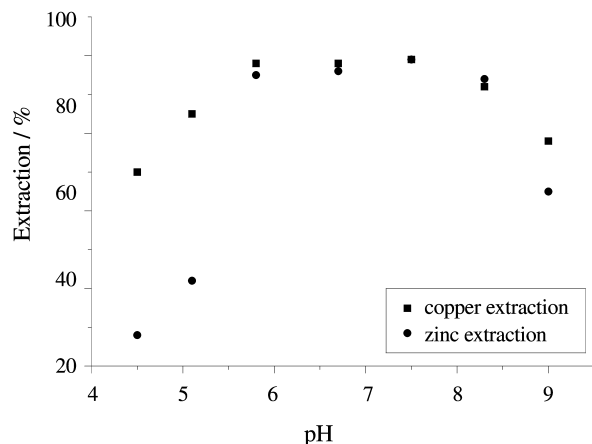
Figure 1. pH effect on the extraction of copper and zinc.
copper(II): 100.00 µg;
zinc(II): 100.00 µg
XAD-2 resin mass: 1.50 g
TAN mass: 6000 µg
Agitation time: 60 min.

Determination of the amount TAN required for quantitative sorption

In order to determine the mass of TAN reagent required for a quantitative extraction, the proposed procedure was applied to 400 mL of solutions containing simultaneously copper and zinc (both 100.00 µg), changing only the TAN mass from 1000 to 10000 µg. It was found that the extraction efficiency increased with the chelating mass for both ions, reaching a maximum and constant value over 5000 µg. The results are described in Fig. 2. In this way, the TAN mass recommended is 6000 µg. This mass is enough for preconcentration of copper and zinc from natural waters, because the concentrations of these elements in these samples are usually very low.

Effect of the agitation time on the extraction

The agitation time required for quantitative extraction of the TAN complexes was also studied. The results demonstrated that for a solution volume of 400 mL and a resin mass of 1.40 g, 40 min for copper and 50 min for zinc are required, as can be observed in Fig. 3. The proposed procedure recommends an agitation time of 1 h for the simultaneous extraction.

Back extraction of the copper and zinc from XAD-2 resin

Solutions of nitric acid and hydrochloric acid were tested for back extraction of copper and zinc from XAD-2 resin. The results demonstrated that 5.0 mL of solution of 2 mol L^{-1} hydrochloric acid can be used for quantitative elution of both ions. Recovery data are shown in Table 3. During the back extraction process, TAN is not eluted by the acid solutions, and its elution is possible using acetone.
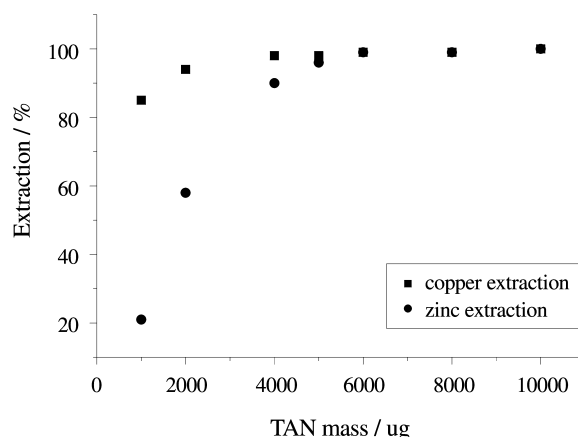

Figure 2. Effect of the TAN mass on the extraction of copper and zinc.
copper(II): 100.00 µg;
zinc(II): 100.00 µg
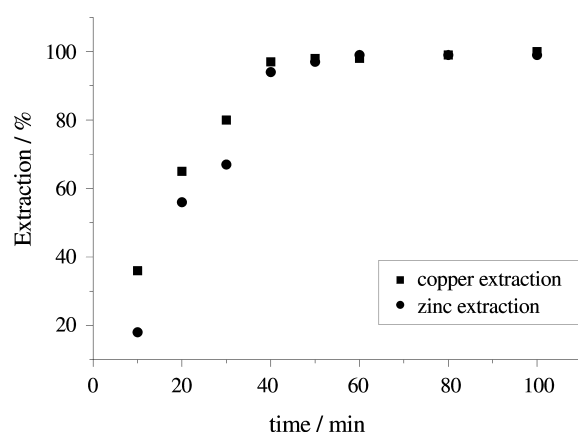XAD-2 resin mass: 1.50 g
Agitation time: 60 min.
pH: 6.50

Figure 3. Time effect on the extraction of copper and zinc.
copper(II): 100.00 µg;
zinc(II): 100.00 µg
XAD-2 resin mass: 1.40 g
TAN mass: 6000 µg
pH: 6.50

Applications

The proposed procedure can be applied to the preconcentration of copper and zinc in the range from 0.1 to 100.00 µg, contained in a volume of 400 mL of natural water samples. Higher volumes can be used however, the agitation time must be optimized. A higher resin mass could decrease the agitation time, however, it would need a larger acid solution volume during the back extraction process, thus decreasing the preconcentration factor.

The Amberlite XAD-2 resin can be reused by treatment with acetone for dissolution of the reagent and complexes

Table 3. Back extraction of copper and zinc from XAD-2 resin.

Solutions	copper recovery (%)	zinc recovery (%)
1 mol L^{-1} hydrochloric acid	90.2	94.1
2 mol L^{-1} hydrochloric acid	98.2	99.1
1 mol L^{-1} nitric acid	85.2	99.6

Table 4. Determination of copper and zinc in natural water samples.

Sample	Mass of added copper (µg)	Copper found * (µg L^{-1})	Recovery of copper (%)	Mass of added zinc (µg)	Zinc found* (µg l^{-1})	Recovery of zinc (%)
Abaete lake water	0	4.8 0.2	...	0	12.2 ± 0.5	...
	12.5	17.0 0.7	98	12.5	24.9 ± 0.9	102
Pituaçu river water	0	2.0 0.2	...	0	6.2 ± 0.4	...
	12.5	14.2 0.6	98	12.5	18.9 ± 0.9	102
Tororo lake water	0	3.6 0.2	...	0	12.3 ± 0.6	...
	12.5	16.8 0.7	106	12.5	24.5 ± 0.8	98
Rio vermelho sea water	0	0.13 0.01	...	0	1.4 ± 0.1	...
	12.5	12.6 0.1	99	12.5	13.3 ± 0.6	95
Ondina Sea water	0	1.2 0.1	...	0	4.9 ± 0.3	...
	12.5	13.3 0.8	97	12.5	17.0 ± 0.9	97

* at 95% confidence level.

and subsequent treatment with 4 mol L^{-1} hydrochloric acid solution to guarantee the discontamination.

The present method was applied to the determination of copper and zinc in river and sea water samples from the city of Salvador, Bahia-Brazil. A volume of 400 mL of water sample was used for analysis. The standard addition technique (using 12.5 µg of copper(II) and zinc(II) ions) was applied and the obtained recoveries revealed that the proposed procedure has a good accuracy. Results are shown in Table 4.

Conclusions

The results showed that the proposed preconcentration procedure provides a fast, simple and economical method for the enrichment of copper and zinc from natural water samples.

The sodium chloride present in the sea water does not interfere in the application of the separation procedure.

The obtained recovery, measured through the standard addition technique, revealed that the procedure has good accuracy.

The values found for zinc and copper in the samples are compatible with data reported in the literature[19].

Acknowledgments

References

1. Christian, G.D. *Analytical Chemistry*, John Wiley & Sons, INC., New York, 1994.
2. Beinrohr, E.; Rojcek, J.; Garaj, J. *Analyst* **1988**, *113*, 1831.
3. Chwastowska, J.; Kosiarska, E. *Talanta* **1988**, *35*(6), 439.
4. Singh, A.K.; Kumar, T.G.S. *Microchemical Journal* **1989**, *40*, 197.
5. Azeredo, L.C.; Sturgeon, R.E.; Curtius, A.J. *Spectrochimica Acta* **1993**, *48*B, 91.
6. Santelli, R.E.; Gallego, M.; Valcarcel, M. *Talanta* **1994**, *41*(5), 817.
7. Nagahiro, T.; Wang, G.F.; Satake, M. *Microchemical Journal* **1995**, *52*, 247.
8. Soylak, M.; Doˇan, M. *Anal. Lett.* **1996**, *29*(4), 635.
9. Elmahadi, H.A.M.; Greenway, G.M. *Microchemical Journal* **1996**, *53*, 188.
10. Bortolli, A.; Gerotto, M.; Marchiori, M.; Mariconti, F.; Palonta, M.; Troncon, A. *Microchemical Journal* **1996**, *54*, 402.
11. Perez-Cid, B.; Rio-Segade, S.; Bendicho, C. *Microchemical Journal* **1997**, 55, 319.
12. Saxena, R.; Singh, A.K.; Sambi, S.S. *Anal. Chimica Acta* **1994**, *295*, 199.
13. Saxena, R.; Singh, A.K.; Rathore, D.P.S. *Analyst* **1995**, *120*, 403.

14. Saxena, R.; Singh, A.K. *Anal. Chimica Acta* **1997**, *340*, 285.

15. Lee, C.H.; Kim, J.S.; Suh, M.Y.; Lee, W. *Anal. Chim. Acta* **1997**, *339*, 303.

16. Cheng, K.L.; Ueno K.; Imamura T. *Handook of Organic Reagent,* CRC Press, 1992,

17. Ferreira, S.L.C.; Nano, R.M.W. *Talanta* **1994**, *41*(11), 1937.

18. Ferreira, S.L.C.; Lopo, N.M.L.; Dantas, A.F.; Costa, A.C.S. *Microchimica Acta* **1995**, 118, 123.

19. Smith, F.G.W. In *Handbook of Marine Science* CRC Press, 1974.