

Solid-Phase Extraction of Cu(II) Using Polyurethane Foam and Eriochrome Black T as Ligand for its Determination in Waters by Flame Atomic Absorption Spectrometry

Silvio Soriano and Ricardo J. Cassella*

Departamento de Química Analítica, Universidade Federal Fluminense,
Outeiro de São João Batista s/n, Centro, 24020-141 Niterói-RJ, Brazil

Este trabalho descreve o desenvolvimento de uma metodologia para a pré-concentração seletiva de Cu(II) usando espuma de poliuretano (PUF) como suporte e o negro de eriocromo T (EBT) como ligante. A extração quantitativa do Cu(II) foi obtida em um meio contendo 60 mg L⁻¹ de EBT e pH 1,5 (ajustado com solução de HCl). O tempo mínimo para extração do Cu(II) foi de 30 min quando 200 mg de PUF foram agitados com 100 mL de amostra. A dessorção do Cu(II) retido na fase sólida pode ser obtida apenas quando a PUF carregada com o analito foi digerida em forno de microondas na presença de HNO₃ concentrado (15 min, 600 W). O método foi aplicado na determinação de Cu(II) em águas por espectrometria de absorção atômica com chama. Testes de recuperação foram realizados pela adição de 20 e 100 µg L⁻¹ de Cu(II) sendo observadas recuperações entre 99,4 e 107%.

This work reports the development of a methodology for the selective preconcentration of Cu(II) onto polyurethane foam (PUF) using the Eriochrome Black T (EBT) as ligand. The quantitative extraction of Cu(II) was achieved in a medium containing 60 mg L⁻¹ of EBT and pH 1.5 (adjusted with HCl solution). The minimum time required to obtain total extraction of Cu(II) from solution was 30 min, when 200 mg of PUF were stirred with 100 mL of the samples. The recovery of Cu(II) from the solid-phase only could be performed by digesting the loaded PUF with concentrated HNO₃ in a microwave oven (15 min, 600 W). The method was applied for the determination of trace concentrations of Cu(II) in waters by flame atomic absorption spectrometry. A recovery test was performed by spiking of the samples with 20 and 100 µg L⁻¹ of Cu(II) and recovery percentages of 99.4-107% were obtained.

Keywords: solid-phase extraction, polyurethane foam, copper, eriochrome black T, FAAS

Introduction

The use of polyurethane foams (PUF) is now widespread as solid-phase for the separation/preconcentration of a number of chemical substances prior to their determination by different analytical techniques. Polyurethane foams are characterized by the presence of polar and non-polar groups in their structures, which make them very suitable for the adsorption of substances with different chemical behaviors.¹ Besides, they can be easily purchased in the market and present very low cost and toxicity, being very attractive for using in routine procedures.

The first work about the use of PUF in chemical separations was published in 1970, by Bowen.² In this work, the adsorption of several chemical species was studied by

the author that proved the excellent adsorption capacity of the material. According to Bowen, PUF are able to retain, preferentially, highly polarizable free molecules such as I₂, aromatic compounds and metallic dithionates, and complex anions such as thiocyanate and chloride complexes of metals. In this sense, unloaded PUF has been utilized in different analytical procedures for the separation/preconcentration of metals³⁻⁸ and organic substances.⁹⁻¹⁵

The modification of PUF with organic reagents is a very common approach employed in the separation/preconcentration of metals.¹⁶⁻²⁰ The addition of specific reagents to the solid-phase increases the efficiency of retention as well as the adsorption kinetics.¹ On the other hand, only few papers deal with the complexation of the metals prior to the adsorption onto PUF. In this field, dithiocarbamate derivatives such as sodium diethyl dithiocarbamate (DDTC)²¹⁻²² and ammonium pyrrolidine

*e-mail: cassella@vm.uff.br

dithiocarbamate (APDC)²³ were successfully employed in the development of solid-phase extraction procedures for metals with PUF. These reagents form complexes with metallic cations with low-solubility in water that present high affinity for the hydrophobic PUF. Sant'Ana *et al.*²¹⁻²² demonstrated that both Cu(II) and Cd(II) can be efficiently retained on PUF in the form of DDTC complexes. In both cases, the retention of the metals was close to 100%, evidencing the strong affinity between the foam and the metal-DDTC complexes. Anthemidis *et al.*²³ employed PUF for the preconcentration of Cu(II), Pb(II) and Cr(VI) with APDC as complexing reagent. The metallic complexes were released from PUF with isobutylmethylketone (IBMK) and measured by flame atomic absorption spectrometry.

Belyukova *et al.*²⁴ studied the sorption of Y onto PUF after complexation of the analyte with 8-hydroxyquinoline and its halogenated derivatives (5,7-dichloro; 5,7-dibromo and 5-chloro-7-bromo). In the optimized conditions, the highest extraction efficiency (approximately 95%) was achieved with the 5,7-dichloro derivative. The developed method was employed in the determination of Y in rocks, exploring the luminescence of the complex adsorbed on the PUF.

The goal of this work was to develop a method for the separation/preconcentration of Cu(II) with PUF using, for the first time, Eriochrome Black T (EBT) as reagent. The methodology was simple, efficient and utilized a reagent easily found in most analytical laboratories. Also, the acid mineralization of PUF is proposed for the release of Cu(II) from the foam, since the complex was strongly attached to the solid-phase. This strategy was shown to be very attractive because of the low cost and low thermal stability of the PUF, which allowed its fast digestion in the microwave oven.

Experimental

Apparatus

Flame atomic absorption measurements were carried out with a Perkin-Elmer (Norwalk, CT, USA) Analyst 100 spectrometer equipped with a copper hollow cathode lamp. The instrument was operated at optimum conditions suggested by the manufacturer (wavelength = 324.8 nm, lamp current = 4 mA and slit width = 0.5 nm). The background correction was performed with a continuum source of deuterium.

The extraction of Cu was carried out by stirring the samples with PUF, in a 150 mL beaker, with a Fisatom 752A magnetic stirrer (São Paulo, Brazil) at 600 rpm stirring velocity, using a PTFE covered bar.

A Provecto Analitica DGT 100 Plus (Jundiaí City, Brazil) microwave oven, equipped with 100 mL PFA (perfluoroalkoxy) flasks, was used for the acid mineralization of the loaded PUF aiming Cu recovery.

Reagents and solutions

All solutions used in this work were prepared with deionized water obtained (resistivity higher than 18.2 M Ω cm) in a Milli-Q system (Millipore, Bedford, MA, USA) and reagents of analytical grade.

A 6 mol L⁻¹ HCl solution was prepared by transferring, slowly, 500 mL of concentrated HCl (Tedia, Fairfield, OH, USA) to a 1000 mL volumetric flask containing 300 mL of deionized water. Then, the volume was made up to the mark with deionized water. Concentrated HNO₃ (Tedia, Fairfield, OH, USA) was also used in this work for the acid dissolution of the polyurethane foam loaded with Cu(II).

A 500 mg L⁻¹ EBT solution was prepared by dissolving 0.25 g of the reagent, supplied by Vetec (Rio de Janeiro City, Brazil), in approximately 300 mL of purified water. The obtained solution was quantitatively transferred to a 500 mL volumetric flask and the volume was made up to the mark with purified water.

Copper (II) solutions were prepared daily by adequate dilution of a 1000 mg L⁻¹ Cu (II) stock standard solution, supplied by Tedia (Fairfield, OH, USA), with purified water. The standard solutions of the other metals evaluated in this study as possible interferents (Fe(III), Ca(II), Cd(II), Co(II), Mg(II), Mn(II), Ni(II), Pb(II) and Zn(II)) were also prepared by dilution of the respective 1000 mg L⁻¹ stock solutions, also supplied by Tedia.

A commercial polyurethane foam (Guararapes Ltda, Brazil), polyether-type with a density of 22.5 mg cm⁻³, was employed in the experiments. In order to use PUF as sorbent, the foam was comminuted in a blender with purified water and ethyl alcohol and washed several times with purified water. Afterwards, the powdered PUF was left to dry at ambient temperature and then sieved through a 2 mm plastic sieve. The treated PUF was stored in a plastic flask, which was placed in a light-free environment.

Cu(II) separation/preconcentration

During the optimization of the methodology, the solid-phase extraction of Cu(II) was performed by stirring 100 mL of the acidic solution (HCl) of Cu(II) and Fe(III) (1 mg L⁻¹ each) containing EBT with 200 mg of powdered PUF. The concentrations of HCl and EBT were in accordance with the experiments planned for optimization.

For the samples, the extraction of Cu(II) was performed by mixing 100 mL of the sample with 6 mg of EBT and concentrated HCl enough to adjust the pH of the solution to 1.5, and stirring the obtained solution with 200 mg of PUF. In both cases, after elapsed the time needed to extract Cu(II) quantitatively with PUF, the solution was filtered with a Gooch filter, under vacuum, and the PUF was transferred to the microwave oven flask for Cu recovery.

Cu(II) recovery from PUF

In order to remove Cu(II) from PUF, the solid-phase was digested with concentrated nitric acid. For this purpose, the 200 mg of PUF loaded with Cu(II) were transferred to the microwave oven flask and 5 mL of the concentrated HNO₃ were added. The flask was sealed and irradiated for 15 min at 600 W. Then, the flask was taken out of the oven and cooled to room temperature. The solution obtained was quantitatively transferred to a 10 mL volumetric flask and the volume was made up to the mark with purified water.

Results and discussion

Effect of the concentration of EBT

The first step of this work was to evaluate the influence of EBT concentration on the retention of Cu(II) on PUF. As the retention of Cu(II) depends on the formation of Cu(II)-EBT complex, the concentration of the reagent in the medium plays important role in the extraction procedure. In order to evaluate the influence of this parameter, the concentration of EBT was varied from 0 (no addition of reagent) to 80 mg L⁻¹. The retention of Cu(II) was tested in the presence of Fe(III), which was identified as the main interferent on the Cu(II) adsorption. The concentration of both Cu(II) and Fe(III) in the solution was 1 mg L⁻¹ and the pH of the medium was not adjusted (the final pH of the solution was 3.0). The stirring time was 90 min and 200 mg of PUF were used.

As expected (Figure 1), Cu(II) was not retained on PUF without the addition of the reagent, proving that the adsorption, in fact, depended on the Cu(II)-EBT complex formation. When the concentration of EBT was increased, a strong increase of the Cu(II) extraction was observed up to 40 mg L⁻¹. For concentrations higher than 40 mg L⁻¹, the extraction efficiency remained constant, indicating that the excess of EBT could not improve the process. The extraction efficiency was close to 100%, evidencing the high affinity of the Cu(II)-EBT complex for the PUF. The sorption of Fe(III) on PUF also increased with the increase of the EBT concentration, reinforcing the idea that the process is highly dependent on the metal-EBT

complex formation. The concentration of EBT selected was 60 mg L⁻¹ to ensure the robustness of the method and it was employed in all further experiments.

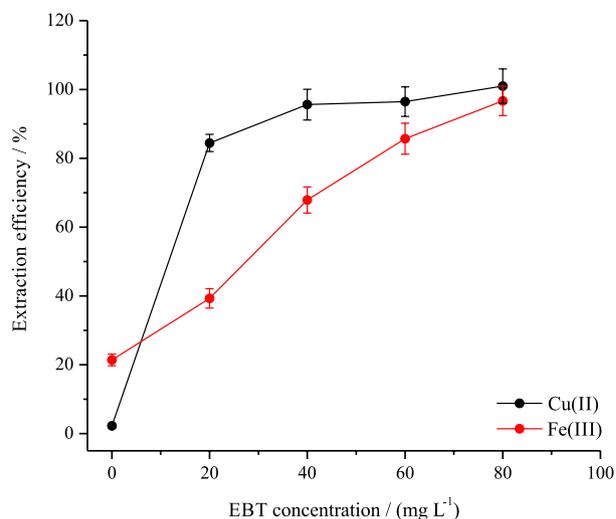


Figure 1. Influence of the EBT concentration on the extraction of Cu(II) and Fe(III) by PUF. The concentration of the metals in the solution (100 mL) was 1 mg L⁻¹, the stirring time was 90 min and the acidity was not adjusted.

Evaluation of the influence of the pH

The next step of the study was the evaluation of the influence of the pH of the medium on the extraction. This study was divided in two parts. In the first part, the extraction of ten metallic cations (Cu(II), Ca(II), Cd(II), Co(II), Fe(III), Mg(II), Mn(II), Ni(II), Pb(II) and Zn(II)) was tested using PUF as solid-phase and EBT as reagent. The experiment was performed in a range of pH of 2.0-12.0 and the results are shown in Figure 2. It is important to highlight that the concentration of EBT was 60 mg L⁻¹ (optimized previously),

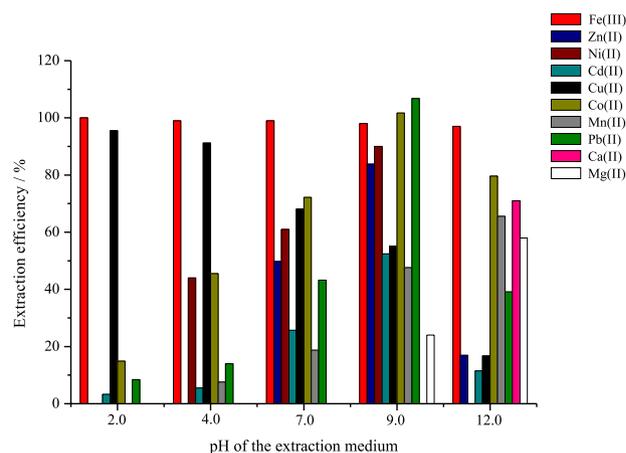


Figure 2. Influence of the pH on the retention of the selected metallic cations by PUF employing EBT as reagent. The concentration of each metal in the solutions (100 mL) was 1 mg L⁻¹, the concentration of EBT was 200 mg L⁻¹ and the stirring time was 90 min.

the mass of PUF was 200 mg and the pH of the solutions was adjusted with diluted solutions of HCl and NaOH. All solutions were stirred for 90 min with the foam to ensure the extraction of the metallic cations.

It was observed that non-selective extraction of the metallic cations by PUF can be attained in alkaline medium (pH 9 to 12), probably because the formation of metal-EBT complexes was increased due to the higher dissociation degree of EBT, which enhances its complexing capacity. On the other hand, in acidic medium (pH = 2), only Cu(II) and Fe(III) could be extracted with reasonable efficiency. According to Inczedy²⁵, the metal-EBT formation constants for Cu(II) ($\log K_f = 21.38$) and Fe(III) (K_f not available) are higher than those observed for Ca(II), Cd(II), Co(II), Mg(II), Mn(II), Pb(II) and Zn(II), which can explain the results observed in the experiment. In order to prove the formation of Cu(II)-EBT complex in pH = 2.0, the speciation graph of this ion in a medium containing 1 mg L⁻¹ Cu(II) (1.57×10^{-5} mol L⁻¹) and 60 mg L⁻¹ EBT (1.30×10^{-4} mol L⁻¹) was constructed (Figure 3). As it can be noted, when the pH is equal or higher than 1.0, all Cu(II) present is chelated by EBT, which could explain the excellent extraction efficiency (near to 100%) verified at pH = 2.0. It is important to remark that in this condition, the Cu(II)-EBT complex assumes its neutral form²⁶ that is preferentially retained on PUF, probably through a solvent-like mechanism. Several authors²⁷⁻³² already reported that neutral species are efficiently extracted by solid PUF and proposed that the foam act as a polymeric solvent able to retain neutral substances (or substances with very low charge density), as the case of Cu(II)-EBT complex. The same behavior could be expected for Fe(III) in the presence of EBT, since the stability of the Fe(III)-EBT is higher than the stability of Cu(II)-EBT²⁵

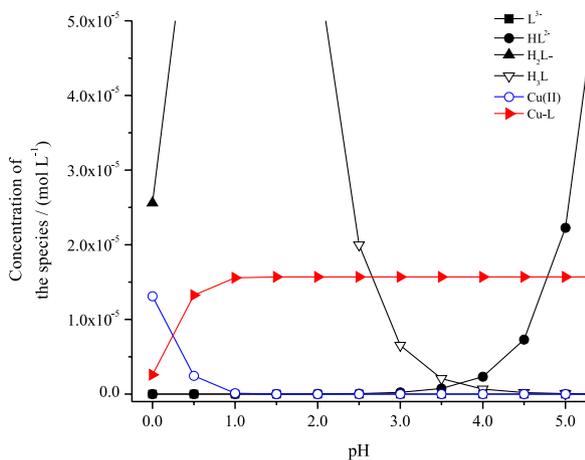


Figure 3. Speciation graph of Cu(II) ($1.0 \text{ mg L}^{-1} = 1.57 \times 10^{-5} \text{ mol L}^{-1}$) in the presence of 60 mg L^{-1} ($1.30 \times 10^{-4} \text{ mol L}^{-1}$) of EBT. EBT dissociation constants: $\text{p}K_1 = 1$, $\text{p}K_2 = 2.6$, $\text{p}K_3 = 6.3$ and $\text{p}K_4 = 11.5$; Cu(II)-EBT formation constant: $\log K_f = 21.38$. The constants were obtained from the reference 23.

and its charge density is very low, despite the fact that the complex is cationic.

The second part of the experiment was devoted to a detailed evaluation of the influence of pH on the extraction of only Cu(II) and Fe(III) (possible interferent) in a narrower range of pH (1 to 3). Again, the concentration of EBT was 60 mg L^{-1} , the concentrations of Cu(II) and Fe(III) were 1 mg L^{-1} and the stirring time was 90 min.

As it is shown in Figure 4, there was no variation of the extraction efficiency of Cu(II) in the whole range of pH evaluated. The extraction efficiency for Cu(II) was always higher than 95%, indicating that Cu(II)-EBT complex can be formed and retained by PUF even at a pH as low as 1.0. These results showed that the adsorption of neutral Cu(II)-EBT complex was not affected by the high acidity of the medium. In this situation, the nitrogen atoms of the polyurethane structure could be protonated and impair the retention of the complex. The results obtained also showed that the adsorption of Fe(III) decreased when the pH of the medium was lower than 2. This behavior occurred, probably because, in this condition, the nitrogen atoms of the PUF were protonated, causing charge repulsion to the cationic Fe(III)-EBT complex, which avoids its retention on foam surface.²⁶ So, in order to work in a more robust condition and minimize the influence of Fe(III) (and other cations, as well) on Cu(II) extraction, the pH of the medium was always adjusted to 1.5 using 6 mol L^{-1} HCl solution.

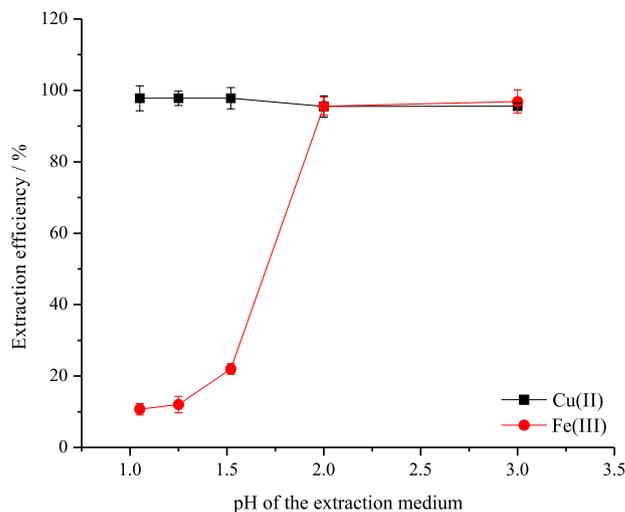


Figure 4. Influence of the pH on the extraction of Cu(II) and Fe(III) by PUF in the range of pH of 1-3. The concentration of the metals was 1 mg L^{-1} , the concentration of EBT was 60 mg L^{-1} and the stirring time was 90 min.

Effect of the extraction time

The adsorption process depends on the effective collisions between the solid-phase (PUF) and the molecule

of solute (metal-EBT complex), which is enhanced with the stirring of the solution. Even with the efficient stirring, certain time is required to achieve maximum transfer of Cu(II) from liquid to the solid-phase. In order to establish the minimum time needed to complete the solid-phase extraction of Cu(II) (as EBT complex), the effect of the extraction time was investigated. The experimental conditions were those previously optimized (concentration of EBT = 60 mg L⁻¹ and pH = 1.5) and the concentrations of Cu(II) and Fe(III) were 1 mg L⁻¹.

For an adsorbent mass of 200 mg and a volume of solution of 100 mL, the extraction efficiency increased with the increase of the stirring time (Figure 5). Quantitative extraction of Cu(II) was observed with a minimum stirring time of 30 min, which was selected for the method. The extraction of Fe(III) was always negligible (around 10%), probably because of the pH of the medium. This result indicated that Fe(III) should not be considered as an important interferent for the Cu(II) extraction and determination.

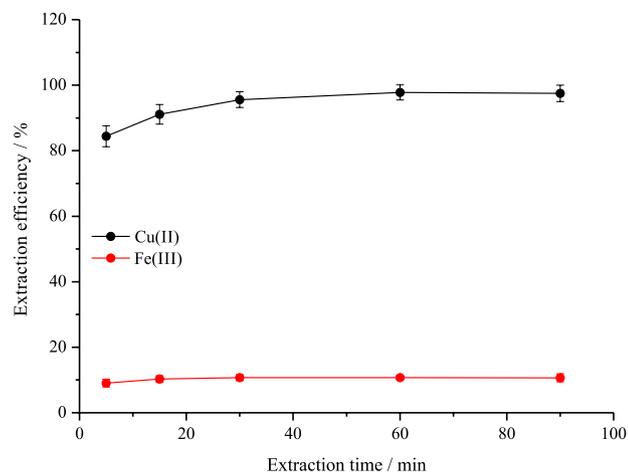


Figure 5. Effect of the stirring time on the extraction of Cu(II) and Fe(III) by PUF. The concentration of the metals in the solution (100 mL) was 1 mg L⁻¹, the concentration of HCl was 0.030 mol L⁻¹ and the concentration of EBT was 60 mg L⁻¹.

Effect of the volume of solution employed in the extraction

The volume of solution (sample) employed in the extraction affects the adsorption process, since the collisions between the adsorbent and the solute tend to be enhanced when the volume of solution decreases. This behavior occurs when the stirring conditions and the mass of adsorbent are constant. On the other hand, the use of bigger volume of solution would permit the improvement of the preconcentration factor because the amount of analyte retained by the adsorbent would increase. So, in order to verify the optimum volume of solution (sample)

that could be employed for the quantitative extraction of Cu(II), the volume of solution was varied from 50 to 300 mL. It is important to remark that the mass of PUF was kept constant (200 mg) as well as the stirring conditions. The concentration of Cu(II) was always 1 mg L⁻¹ and the concentrations of HCl and EBT were those optimized previously.

The extraction efficiency did not vary when either 50 or 100 mL of solution were used. In these cases, they were in the range of 97-100%. However, a strong and continuous decrease of the extraction efficiency was noted when the volume was increased to both 200 and 300 mL, being observed extraction efficiencies of 63 ± 2 and 22 ± 3%, respectively. So, in order to avoid non quantitative extraction of Cu(II), a volume of 100 mL of sample was established for the method.

Studies on the recovery of Cu from PUF

The first step of the method was the adsorption of Cu(II) onto PUF surface, which was successfully reached using the optimized conditions. The next step was the evaluation of different solutions to promote the desorption of Cu(II) from the adsorbent and allow its determination by FAAS. For this purpose, acid solutions of HNO₃ were initially tested. In this experiment, the desorption of Cu(II) was tried using 10 mL of HNO₃ solutions with concentrations of 2 and 6 mol L⁻¹. The solutions were shaken with the solid-phase loaded with Cu(II) using three strategies: (i) one step with a portion of 10 mL; (ii) two steps with two portions of 5 mL and (iii) five steps with five portions of 2 mL. The quantitative recovery of Cu(II) from solid-phase was not observed in all cases. (Table 1), evidencing the strong interaction between Cu(II)-EBT complex and PUF. For this reason, it was decided to mineralize completely the structure of the PUF to release Cu(II), since the foam can

Table 1. Results obtained in the evaluation of different strategies for the recovery of Cu(II) adsorbed on PUF. The concentration of Cu(II) in the solution used for the preconcentration was 100 µg L⁻¹

Solution / (mol L ⁻¹ HNO ₃)	Strategy / mL	Recovery / %
2	1 × 10	62.3 ± 4.0
2	2 × 5	75.0 ± 4.3
2	5 × 2	60.8 ± 7.5
6	1 × 10	37.0 ± 6.0
6	2 × 5	16.7 ± 3.5
6	5 × 2	27.6 ± 5.8
Concentrated HNO ₃	5 mL in the microwave oven (15 min, 600 W)	100 ± 3.2

be easily mineralized by heating with concentrated HNO_3 .¹ Additionally, the reuse of the adsorbent is not necessary because of its very low cost and high availability. The mineralization of PUF with 5 mL of concentrated HNO_3 in the microwave oven yielded a quantitative recovery of Cu(II) and the final volume of solution was 10 mL, which made possible the preconcentration of the analyte in relation to the initial volume of sample used (100 mL). Besides, the process of mineralization of the loaded PUF in the microwave oven was fast, spending no more than 15 min (at 600 W) to yield a clear and transparent solution. So, this strategy was employed for the recovery of Cu(II) from the PUF in the analysis of the samples.

Interference studies

The flame atomic absorption spectrometry, as well as other atomic spectrometric techniques, presents a remarkable characteristic that is its intrinsic selectivity. However, when working with a procedure based on the solid-phase extraction of metallic complexes, as proposed in the present work, the presence of metallic cations can affect the retention of the analyte by competition of their complexes (metal-EBT, in the case) for the PUF active sites. Hence, several possible interferent species were considered, especially those which form complexes with EBT. So, an experiment was run in order to test the selectivity of the proposed method in relation to Cu(II) determination. For this purpose, the retention of Cu(II) was evaluated in the presence of Ca(II), Cd(II), Co(II), Fe(III), Mg(II), Mn(II), Ni(II), Pb(II) and Zn(II). In all experiments, the concentration of Cu(II) was 1 mg L^{-1} and the interferents was varied from 0.5 to 10 mg L^{-1} . Additionally, the influence of some anions was investigated. Chloride, nitrate and sulfate were tested in the range of 5 to 100 mg L^{-1} . In the optimized conditions, none of the possible interferents caused noticeable variation in the recovery of Cu(II), which was always higher than 95%. This result can be credited to the low rate of formation of the complexes metal-EBT in acid medium, which was already verified in the experiment where the effect of the pH was evaluated.

Analytical features of the method

The analytical curves employed in the quantification of Cu(II) in the final extracts were prepared by direct aspiration of aqueous solutions of Cu(II) in the range of 0.5-2.0 mg L^{-1} . It is represented by the following equation: $A = 0.044 [\text{Cu(II)}] + 0.001$, with a r^2 of 0.9995.

The limit of detection, derived from three times the standard deviation of the blank of the method, was $2.70 \mu\text{g L}^{-1}$.

The blank solution was obtained by digestion of the PUF after stirring with a solution containing 60 mg L^{-1} of EBT and 0.030 mol L^{-1} of HCl. In this condition, it was also possible to estimate the limit of quantification from ten times the standard deviation of the blank. The limit of quantification was $9.0 \mu\text{g L}^{-1}$. The limits of detection and quantification were calculated taking into account the preconcentration factor obtained by the application of the proposed procedure, which was 10. The intermediary precision of the method was also evaluated by analyzing a synthetic sample containing $50 \mu\text{g L}^{-1}$ for five consecutive days. In this case, the relative standard deviation of results was 1.8%.

The maximum retention capacity of the system was evaluated by a simple experiment in which 100 mL of solutions with different concentrations (2 to 15 mg L^{-1}) of Cu(II) (EBT concentration = 60 mg L^{-1} and $\text{pH} = 2.0$) were shaken for 30 min with 200 mg of PUF. The concentration of Cu(II) remaining in the solution was determined by FAAS and the amount of Cu(II) retained was calculated as the difference. From the data obtained in this experiment, it was possible to estimate that the maximum amount of Cu(II) that could be retained by the PUF was $752 \mu\text{g}$ (3.76 mg of Cu(II) per gram of foam). Also it was observed that the retention efficiency strongly decreased when solutions containing over 8 mg L^{-1} of Cu(II) were tested. Certainly, the maximum amount of Cu(II) retained was limited by the concentration of EBT added to the solution (60 mg L^{-1}), since the formation of Cu(II)-EBT complex is of fundamental importance in the adsorption process.

Application of the developed method

The developed method was applied in the determination of Cu(II) in five samples of water from different origins (tap water, mineral bottled water and seawater). A recovery test was employed to verify the accuracy of the proposed procedure by spiking the samples with 20 and $100 \mu\text{g L}^{-1}$ of Cu(II). The results obtained in the analysis of the samples are shown in the Table 2.

As it can be seen, the method was capable to quantify Cu(II) in four of the five samples, despite the low concentrations of this cation in the samples. The recovery percentages were between 99.4 and 107%, which proved the accuracy of the proposed procedure. Nevertheless, some points must be highlighted. Firstly, both EBT and HCl were added to the samples in a form that could not cause a significant variation of the volume. Therefore, 6 mg of EBT and 0.25 mL of concentrated HCl were directly added to the samples to provide final concentrations of these components in the samples close to those chosen in the optimization process.

Table 2. Results obtained in the analysis of the water samples employing the developed methodology. Values are expressed as mean \pm standard deviation (n = 3)

Sample	Cu(II) added / ($\mu\text{g L}^{-1}$)	Cu(II) found / ($\mu\text{g L}^{-1}$)	Recovery / %
S ₁ (tap water)	0	9.1 \pm 0.9	–
	100	110 \pm 1	101 \pm 1
S ₂ (mineral water)	0	11.3 \pm 1.7	–
	20	32.7 \pm 2.1	107 \pm 7
S ₃ (mineral water)	0	16.3 \pm 1.8	–
	20	36.3 \pm 1.5	100 \pm 4
S ₄ (mineral water)	0	9.2 \pm 1.4	–
	20	30.1 \pm 2.4	104 \pm 8
S ₅ (seawater) ^a	0	< LOQ	–
	100	99.4 \pm 1.8	99.4 \pm 1.8

^aThe conditions used in the analysis of the seawater were different from the conditions optimized. In this case, 400 mg of PUF were employed and the concentration of EBT was 160 mg L⁻¹. LOQ: limit of quantification.

Secondly, the satisfactory results obtained in the determination of Cu(II) in seawater only could be achieved after increasing the mass of PUF and the concentration of EBT in solution. Using the optimized conditions, the recovery was low, probably because of the effect of the salinity on the extraction of Cu(II). The mass of PUF and the concentration of EBT used were increased to 400 mg and 120 mg L⁻¹, respectively.

Conclusions

The method proposed in this work is a good option for the determination of Cu(II) in waters by FAAS when the analyte is found at trace level. The preconcentration procedure was simple, fast and used low-cost reagents and materials such as EBT and PUF, respectively.

The acid dissolution of the adsorbent was employed with success for the removal of Cu(II) from the PUF and can be further employed in other procedures as an alternative to the conventional elution with solvents or acid solutions.

Finally, the use of EBT as complexing agent for the adsorption of metals onto PUF showed to be efficient and it can be employed in other range of pH for the non-selective and multielemental separation/preconcentration procedures.

Acknowledgments

The authors are grateful to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Fundação Carlos Chagas de Amparo a Pesquisa do Estado

do Rio de Janeiro (FAPERJ) for the grants and fellowships and for financial support.

References

- Braun, T.; Navratil, J. D.; Farag, A. B.; *Polyurethane Foam Sorbents in Separation Science*, 1st ed., CRC Press: Boca Raton, FL, USA, 1985.
- Bowen, H. J. M.; *J. Chem. Soc., A* **1970**, 7, 1082.
- Braun, T.; Abbas, M.N.; *Anal. Chim. Acta* **1982**, 134, 321.
- Palagyi, S.; Braun, T.; *J. Radioanal. Nucl. Chem.* **1992**, 163, 69.
- Schroeder, S. G.; Chow, A.; *Talanta* **1992**, 39, 837.
- Jesus, D. S.; Cassella, R. J.; Ferreira, S. L. C.; Costa, A. C. S.; Carvalho, M. S.; Santelli, R. E.; *Anal. Chim. Acta* **1998**, 366, 263.
- Cassella, R. J.; Santelli, R. E.; Branco, A. G.; Lemos, V. A.; Ferreira, S. L. C.; Carvalho, M. S.; *Analyst* **1999**, 124, 805.
- Ferreira, S. L.C.; Santos, H. C.; Jesus, D. S.; *Fresenius J. Anal. Chem.* **2001**, 369, 187.
- Cassella, R. J.; Garrigues, S.; Santelli, R. E.; de la Guardia, M.; *Analyst* **2000**, 125, 257.
- El-Shahawi, M. S.; *J. Chromatogr., A* **1997**, 760, 179.
- El-Shahawi, M. S.; *Chromatographia* **1993**, 363, 318.
- Schumack, L.; Chow, A.; *Talanta* **1987**, 34, 957.
- Baldez, E. E.; Robaina, N. F.; Cassella, R. J.; *J. Hazard. Mater.* **2008**, 159, 580.
- El-Shahawi, M. S.; Al-Daheri, S. M.; *Anal. Chim. Acta* **1996**, 320, 277.
- Sant'Ana, O. D.; Jesuino, L. S.; Cassella, R. J.; Carvalho, M. S.; Santelli, R. E.; *J. Braz. Chem. Soc.* **2004**, 15, 96.
- Ras, M. R.; Borrull, F.; Marc, R. M.; *J. Sep. Sci.* **2009**, 32, 1051.
- Burham, N.; *Desalination* **2009**, 249, 1199.
- Azeem, S. M. A.; Arafa, W. A. A.; El-Shahat, M. F.; *J. Hazard. Mater.* **2010**, 182, 286.
- Burham, N.; Abdel-Azeem, S. M.; El-Shahat, M. F.; *Int. J. Environ. Anal. Chem.* **2011**, 91, 197.
- Lemos, V. A.; Santos, L. N.; Alves, A. P. O.; David, G. T.; *J. Sep. Sci.* **2006**, 29, 1197.
- Sant'Ana, O. D.; Jesuino, L. S.; Cassella, R. J.; Carvalho, M. S.; Santelli, R. E.; *J. Braz. Chem. Soc.* **2003**, 14, 728.
- Sant'Ana, O. D.; Jesuino, L. S.; Cassella, R. J.; Carvalho, M. S.; Santelli, R. E.; *Sep. Sci. Technol.* **2004**, 39, 2695.
- Anthemidis, A. N.; Zachariadis, G. A.; Stratis, J. A.; *Talanta* **2002**, 58, 831.
- Beltyukova, S. V.; Nazarenko, N. A.; Tsygankova, S. V.; *Analyst* **1995**, 120, 1693.
- Inczédy, J.; *Analytical Applications of Complex Equilibria*, 1st ed.; Ellis Horwood Limited, John Wiley & Sons: Budapest, Hungary, 1976.
- Masoud, M. S.; Hammud, H. H.; Beidas, H.; *Thermochim. Acta* **2002**, 381, 119.

27. Schumack, L.; Chow, A.; *Talanta* **1987**, *34*, 957.
28. Gough, K. M.; Gesser, H. D.; *J. Chromatogr.* **1975**, *115*, 383.
29. Fong, P.; Chow, A.; *Talanta* **1992**, *39*, 497.
30. El-Shahawi, M. S.; *Talanta* **1994**, *41*, 1481.
31. El-Shahawi, M. S.; Kiwan, A. M.; Al-Daheri, S. M.; Saleh, M. H.; *Talanta* **1995**, *42*, 1471.
32. El-Shahawi, M. S.; Al-Daheri, S. M.; *Anal. Chim. Acta* **1996**, *320*, 277.

Submitted: January 7, 2013

Published online: June 25, 2013