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Article

Copper, Zinc and Manganese Determination in Saline Samples Employing FAAS After Separation and Preconcentration on Amberlite XAD-7 and Dowex 1X-8 Loaded with Alizarin Red S

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Dois procedimentos foram comparados para separação e pré-concentração de traços de cobre, zinco e manganês em amostras salinas. Os métodos basearam-se na adsorção dos íons metálicos sobre duas fases sólidas obtidas por impregnação de uma resina não-iônica Amberlite XAD-7 e uma resina aniônica Dowex 1X8-50 com o reagente vermelho de alizarina S (ARS), ácido nítrico foi utilizado para re-extrair os cátions das fases sólidas, os quais foram determinados por FAAS. Para o sistema Amberlite XAD-7/ARS, Mn, Cu e Zn foram quantitativamente retidos, na faixa de pH de 8,5 a 10,0, para uma massa de 0,50 g da fase sólida, após 5 min de agitação e uma massa total de até 200 μg de cada metal. Os elementos foram eluídos com 5 mL de HNO_3 3 mol L^{-1}, com recuperação ≥ 95%, obtendo-se fator de pré-concentração de até 50 vezes para Zn e de 10 vezes para Mn e Cu. Para o sistema Dowex 1X8-50/ARS, Cu, Mn e Zn foram quantitativamente retidos, na faixa de pH de 8,1 a 9,0 e Zn em pH 8,1, usando uma massa de 0,75 g da fase sólida, após 90 min de agitação e uma massa total de até 50 μg de cada metal. Os elementos foram eluídos com 20 mL de HNO_3 2 mol L^{-1}, obtendo-se fator de pré-concentração de até 5 vezes para Cu e Zn. A precisão dos procedimentos foi estabelecida pela medida de 10 replicatas com 250 μg L^{-1} de cada íon e os desvios padrão relativos foram de 0,2% (Cu), 0,4% (Mn), e 0,4% (Zn), para ARS-XAD7 e 0,3% (Cu), 0,5% (Mn), e 0,3% (Zn), para ARS-Dowex. Os procedimentos propostos foram aplicados na determinação de Mn, Cu e Zn em solução fisiológica e água do mar da cidade de Salvador/BA. Testes de recuperação com adição de 5 mg dos metais às amostras revelaram eficiência no que diz respeito à exatidão e a precisão dos procedimentos propostos, com recuperação quantitativa (≥ 95%).

Two procedures have been proposed and compared for separation and preconcentration of trace amounts of manganese, copper, and zinc in saline samples. The procedures are based in the use of Amberlite XAD-7 and an anion-exchanger Dowex 1X8–50 loaded with Alizarin Red S (ARS). In order to obtain quantitative recoveries of metal ions, various experimental parameters such as pH, shaking time, sample volume, amounts of solid phase, effects of concomitants, capacity and cations desorptions from solid phases were optimized. For Amberlite XAD-7 impregnated with ARS (XAD 7-ARS), Mn, Cu, and Zn were quantitatively retained, in the pH range 8.5-10.0, by using 0.50 g of solid phase, stirring time of 5 min and a total mass up to 200 μg of each cation. The sorbed elements were subsequently eluted with 5 mL of 3 mol L^{-1} HNO_3, with recovering over 95%, and a fifty-fold preconcentration factor for Zn and a ten-fold preconcentration factor for Mn and Cu were obtained. For Dowex 1X8–50 impregnated with ARS (Dowex-ARS), Cu and Mn were quantitatively retained in the pH range 8.1 to 9.0, and Zn pH 8.1, by using 0.75 g of solid phase, 90 min of stirring time and a total mass up to 50 μg of each cation. The sorbed elements were subsequently eluted with 20 mL of 2 mol L^{-1} HNO_3, and a five-fold preconcentration factor to Cu and Zn was obtained. The precision of the procedure was determined by running 10 replicate samples, each one containing 250 μg L^{-1} of each element and the relative standard deviations were 0.2% (Cu), 0.4% (Mn), and 0.4% (Zn), to XAD 7-ARS and 0.3% (Cu), 0.5% (Mn), and 0.3% (Zn), to Dowex-ARS. The procedures were used for determining of Mn, Cu, and Zn in physiological solutions and seawater samples, from Salvador-Bahia. The analyte addition technique was used and the recoveries obtained (≥ 95%) revealed that the proposed procedure shows good accuracy and precision.

Keywords: preconcentration, solid-liquid extraction, Amberlite XAD-7, Dowex 1X8-50, alizarin red S, saline samples

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Introduction

The use of solutions with variable saline concentrations for man is indispensable for the industrial and physiologic activities, especially in clinical Chemistry. Solutions of NaCl 0.9% m/v are used as physiologic solution, because it reflects the isotonic composition of the biologics fluids of the human body. The determination of metals in this sample is very important because contamination of sodium salts and water can complicate the conditions of the patients that use dialysis solutions.[1] The determination of Mn, Cu, and Zn in natural waters is also important whereas these trace elements present in the matrix constitute an environmental problem and there is a lack of information on the behavior and toxic potential of these metals on the metabolism of living organisms.[2] Copper is an essential element for human body, its discovery in human brain in 1921, was important to establish its functions in the body: oxygen and electrons transport, constituent of enzymes to redox reactions and involvement in the mobilization of iron to hemoglobin synthesis.[3] Zinc, essential trace element for man, has been reported since 1934.[4] It is associate in the insulin production, in the composition of more 90 enzymes related with acid-base catalysis, and in DNA and RNA synthesis. The manganese is associated with cartilages and bones formation.[5-7]

Atomic absorption spectrometry is nowadays the most common method for trace metal determination in various materials. However the flame atomic absorption spectrometric (FAAS) determination of trace metal ions in high saline samples, such as seawater, is difficult due to various factors, particularly the low level of metal content and the high salt content of the matrix.[8] Thus, trace determination in saline solutions always needs a prior separation and preconcentration steps. Several procedures extensively used for separation and preconcentration include liquid-liquid extraction and solid phase extraction. However, solvent extraction suffers with problems for handling of large sample volume, mutual solubility of two phases, and emulsion formation. Consequently, in the last decade use of chelating resins for metal enrichment has increased very significantly.[9-19] Their advantages include good selectivity, high preconcentration factor, easy regeneration for multiple sorption-desorption cycles and good reproducibility in the sorption characteristics.

Alizarin Red S (sodium1,2-dihydroxyanthraquinone-3-sulfonate, ARS) reacts with various metal ions to form anionic chelates, which are not extractable into organic solvents. ARS was studied for separation and preconcentration of Al, Cu, Pb, Cd, Zn, and Ni in different matrices, such as alloys, biological samples and environmental samples.[20-22] Therefore the potential use of ARS impregnated in resins has been scarcely explored for analytical procedures employing separation and preconcentration.

The aim of this work was to explore the possibility of the application of a chelating resins obtained by immobilization the reagent alizarin red S (ARS) on nonionic polymer sorbent Amberlite XAD-7 and anion exchanger Dowex 1X8-50 for manganese, copper, and zinc separation and preconcentration from saline samples. The sorbed elements are subsequently eluted with nitric acid and determined by FAAS. The conditions have been optimized and the methods applied for the determination of copper, zinc, and manganese in physiological solutions and seawater samples.

Experimental

Reagents

All reagents were of analytical reagent grade. Double distilled and deionized waters were used for the preparations of solutions. The laboratory glassware was kept overnight in a 10% v/v nitric acid solution. Before use, the glassware was washed with deionized water and dried in a dust-free environment.

Metal stock solutions were prepared from Merck standard solutions to a final concentration of 1.000 g L^{-1}. Reference solutions were daily prepared by diluting aliquots with pure water and acidified with nitric acid. Buffer solutions were glycine/ hydrochloric acid adjusted at pH 3, acetate buffer at pH 4 to 6, tris-HCl buffer at pH 7 to 8, and ammonia buffer at pH 8.5 to 10. Acid solutions for study of the eluents were nitric, hydrochloric and sulphuric acids (Merck) at different concentrations prepared by suitable dilution of the respective concentrated acids in deionized water. The solutions for study of concomitants effects were prepared in different percentage (m/v) of Na^+, K^+, Ca^{2+}, Mg^{2+} e Ba^{2+}, by dissolving their respective salts in the chloride, sulphates, and phosphoric forms. Solid phase was prepared with ARS (Merck), Amberlite XAD-7 (surface area, 450 m^2 g^{-1}; pore diameter, 450 Å and bead size, 20-60 mesh) and Dowex 1X8-50 was purchased from Aldrich (Milwaukee, USA).

Apparatus

A flame atomic absorption spectrometer (Varian, Australia, model 220) employing air-acetylene flame was used for atomic absorption spectrometric measurements. The instrumental and operational parameters are showed in Table 1 and the pH value was measured with a PROCYON

PHD-10 digital pH meter supplied with a combined glass-calomel electrode.

Table 1. FAAS: Instrumental and operational parameters

Parameter	Cu	Zn	Mn
Wavelength (nm)	324.8	213.9	279.5
Current lamps (mA)	4	5	5
Spectral resolution (nm)	0.5	1.0	0.2
Reference solutions (μg mL^{-1})	0 – 1.2	0 – 1.0	0 – 1.2

Preparation and characterization of chelating resins

Amberlite XAD-7 and Dowex 1X8-50 were treated with an ethanol-HCl-water (2:1:1) solution overnight. Later on the resin was rinsed with deionized water until pH neutral and kept in desiccator with silica gel for 24 h. After dried, 10.0 g of Amberlite XAD-7 were weighed with 0.50 g of ARS and transferred to an Erlenmeyer containing 250 mL of deionized water. This mixture was stirred for 3 h with a magnetic stirrer, vacuum filtered using a Buckner funnel and filter paper (Framex, fast filtration, 0.00007% ash) and kept in desiccators with silica gel for 24 h. The Dowex-ARS solid phase was similarly prepared. Chelating resins were characterized by IR spectra.

Recommended procedure for separation and pre-concentration – XAD 7- ARS resin

Sample volumes from 10 to 50 mL containing up to 200 μg of each cation were transferred to plastic vessels. It was added 10 mL of pH 9.0 ammonium buffer solution and 0.5 g of the solid phase. The vessel was closed and kept under mechanical stirring for 5 min. The mixture was filtered through a filter paper and the liquid phase was discharged. Solid material retained onto filter paper was washed with 5 mL of 3 mol L^{-1} nitric acid. Metals ions extracted were then directly determined by FAAS. The same procedure was applied to blanks. An analytical curve prepared in 3 mol L^{-1} nitric acid was used in order to avoid matrix effects.

Recommended procedure for separation and pre-concentration - Dowex-ARS resin

Sample volumes from 50 to 200 mL containing up to 50 μg of each cation were transferred to plastic vessels. It was added 10 mL of pH 8.1 ammonium buffer solution and 0.75 g of the solid phase. The vessel was closed and kept under mechanical stirring for 90 min. The mixture was filtered through a filter paper and the liquid phase was discharged. Solid material retained onto filter paper was washed with 20 mL of 2 mol L^{-1} nitric acid. Metals ions extracted were then directly determined by FAAS. The same procedure was applied to blanks. An analytical curve prepared in 2 mol L^{-1} nitric acid was used in order to avoid matrix effects.

Results and Discussion

In order to obtain quantitative recoveries of Mn, Cu, and Zn on XAD 7-ARS and Dowex-ARS resins the separation and preconcentration procedures were optimized using an univariate approach for various experimental parameters such as characterization of solid phases, pH, stirring time, sample volume, amounts of solid phase, sorption capacity, and cations desorption from solid phase and concomitants effect.

Characterization of solid phases - IR spectra Amberlite XAD-7 and Dowex 1x8-50 loaded with Alizarin Red-S

The chelating resins were characterized employing Fourier transform infrared spectrometry (FTIR). The characteristic IR bands (in cm^{-1}) for XAD 7-ARS resin were: 3503 and 1444 (OH vibrations); 1656 (1,4-quinone stretching); 1348 (>S=O stretching); and 1275 (>C-O stretching). For ARS loaded Dowex 1X8-50, the IR spectrum was analogous but lower intensities and deformation bands due to impregnating process agent chelating-resin (ion exchange) were observed. Because of the absence of ion-exchange sites in Amberlite XAD-7 structure, this sorbent is more able to retain molecule of ARS. The occurrence of five bands further supports the loading of the chelating agent on the resins.

Effect of pH on Mn, Cu, and Zn sorption

Effect of pH on the chelating efficiency of XAD 7-ARS and Dowex-ARS for manganese, copper, and zinc was tested by batch experiments using 25 mL of aqueous solutions containing 25 μg of metal ions and 1.0 g of the resins. The pH of the solutions was varied and adjusted in the range 3.0-10.0. Recoveries (%) of Cu(II), Mn(II), and Zn(II) as a function of pH for the XAD 7-ARS and Dowex-ARS resins are shown in Figures 1 and 2, respectively. The results for XAD 7-ARS resin demonstrated that maximum extraction (over 95% for all cations) is achieved for pH ranging from 8.5 to 10.0. For the Dowex-ARS resin, maxima recoveries for Mn and Cu were 8.1 to 9.0, respectively, and for Zn was pH 8.1. In subsequent studies, the pH was maintained at 9.0 and 8.1, using an ammonium

buffer, for XAD 7-ARS and Dowex-ARS resins, respectively.

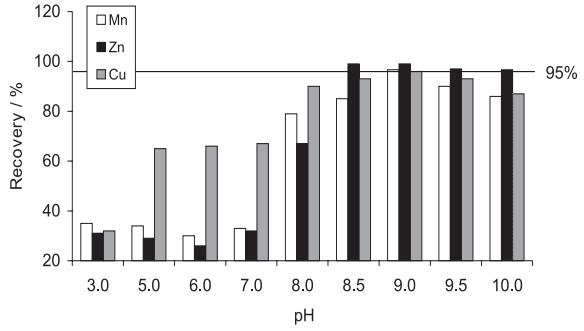

Figure 1. Effect of pH on cations extraction by XAD 7-ARS resin**.** Mass of each cation: 50.0 μg. Sample volume: 25 mL. Phase solid mass: 1 g with 0.5% (m/m) ARS. Shaking time: 30 min. Back extraction: 2 extractions with 25.0 mL HNO_3 6 mol L^{-1}.

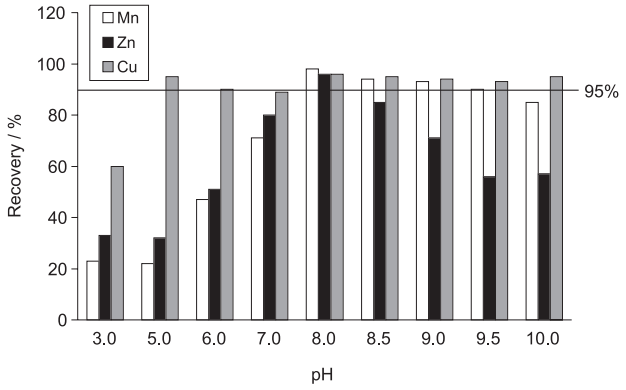

Figure 2. Effect of pH on cations extraction by Dowex-ARS resin**.** Mass of each cation: 50.0 μg. Sample volume: 25 mL. Phase solid mass: 1 g with 0.5% (m/m) ARS. Shaking time: 30 min. Back extraction: 2 extractions with 25.0 mL HNO_3 6 mol L^{-1}.

Effect of shaking time

For determining the effect of the reaction time on the rate of loading of Cu(II), Mn(II), and Zn(II) on the solid phases, the chelating resins beads (1.0 g) were stirred with 50 mL de solution containing 10 mL ammonium buffer and all the metal ions (50 μg of each) at room temperature from 1 to 60 min for XAD 7-ARS resin and from 1 to 120 min for Dowex-ARS resin. Results demonstrated that for the XAD 7-ARS system, the shaking time required for quantitative sorption was 5 min. The Dowex-ARS resin showed a behavior different, with maximum recoveries obtained only at time ≥ 60 min for Mn and 90 min for Cu and Zn. However, 90 min was preferred to further experiments for obtaining the simultaneous separation and preconcentration of the metallic ions. The large difference in the shaking time between the two systems can be explained by the impregnation process of the Dowex 1X8-50 with ARS, because in the value of pH established it can occurs stereo hindrance between resonance of the aromatic ring and oxygen atoms of the ARS, making the complexation of metallic ions difficult.[23] This was not observed with XAD 7-ARS resin because the impregnation process occurs by physical adsorption.

Choice of eluent

Solutions of sulfuric, nitric, and hydrochloric acids in different concentrations (0.5; 1.0; 2.0; 3.0; 5.0; and 7.0 mol L^{-1}) and volumes (1-50 mL) were tested to desorb Mn, Cu, and Zn from solids phases. It was essential to select an eluent that could also be used for FAAS measurements without problems. The best results for quantitative recoveries of the metallic ions were obtained using nitric acid as eluent. It was found that 5 mL of 3.0 mol L^{-1} HNO_3 and 20 mL of 2.0 mol L^{-1} HNO_3 were sufficient for quantitative (>95%) elution of Mn, Cu, and Zn, in a single step, in the XAD 7-ARS and Dowex-ARS resins, respectively.

Influence of volume of aqueous phase

Since the volume of solid phase was small compared to the aqueous phase, it was important to study the effect of the latter on the separation and preconcentration of Mn(II), Cu (II), and Zn (II). The volume of the aqueous phase was varied from 10 to 1000 mL, and the retention was found to be quantitative when the volume of the aqueous phase did not exceed 100 mL, for determination of Zn and Cu using Dowex-ARS resin; and 50 mL for determination of Mn, Cu, and Zn using XAD 7-ARS resin.

Effect of mass of solid phase

The mass of solid phases were varied from 0.1 to 1.0 g under optimum conditions. Results demonstrated that 0.50 g and 0.75 g, respectively, of XAD 7-ARS and Dowex-ARS resins, were sufficient for quantitative retention of Mn(II), Cu(II), and Zn(II).

Sorption capacity of the solid phases

Solid phase sorption capacity was also assessed with a multielemental solution. The sorption capacity of the solid phases, XAD 7-ARS and Dowex-ARS resins, for Mn, Cu, and Zn was determined using parameters optimized and a set of solutions containing different amounts of metallic ions in the range of 5-1000 μg. Results demonstrated that 0.50 g of XAD 7-ARS resin had a capacity to retain up to

500 μg of Mn(II), and up to 200 μg of Cu(II) and Zn(II). It was observed that 0.75 g of solid phase Dowex-ARS, was efficient to retain up to 50 μg of each one of the cations.

Effect of electrolytes

The effect of NaCl, KCl, $BaCl_2$, $CaCl_2$, Na_2SO_4, $MgCl_2$ and Na_3PO_4 on the sorption of Mn(II), Cu(II), and Zn(II) in the proposed systems was also studied. A set of solutions containing varying amount of electrolyte (0.5; 1.0; 3.0; and 5.0% m/v) was taken and the recommended procedures applied. Various amounts of matrix ions were added to a solution containing fixed amounts of analytes (50 mg of Mn(II), Cu(II), and Zn). Phosphate interferes in the sorption of Zn(II) in all proportions, due to precipitation losses of Zn; the other electrolytes did not interfere up to 5% m/v. For Cu(II), the presence of NaCl, Na_2SO_4, Na_3PO_4, and KCl did not interfere in the determination of the metal until a concentration of 5.0% m/v. Mg^{2+}, Ba^{2+} and Ca^{2+} interfered in all proportions. For Mn(II), Na_2SO_4, Mg^{2+} and Ba^{2+} were tolerated until a concentration of 5.0% m/v, 0.5% m/v and 3.0% m/v, respectively, and Ca^{2+} interfere considerably.

Solid phases stability

Adsorption and desorption were repeated on the same solid phases and adsorptive capacity was estimated after each cycle of operation. The capacity of the XAD 7-ARS resin was also found to be practically constant (within 3-4%) after repeated use more than six times. For the Dowex-ARS resin the results indicated that this could be used only one time.

Analytical figures of merit and application

The accurate determination of Mn(II), Cu(II), and Zn(II) at low concentration levels in seawater and physiological solutions after separation and preconcentration requires low and reproducible blanks. Absolute blanks, based on the analysis of separate concentrates from different volumes of ultra pure water were submitted to the separation and preconcentration procedures. The characteristic data for the performance of the separation and preconcentration systems are summarized in Table 2. The detection and quantification limit (LOD and LOQ) for Mn, Cu and Zn were determined employing the procedures to blank solutions (nitric acid in appropriate concentration). The limit of detection (3s/slope of 30 measurements of blank, where s is the standard deviation of blank) and the limit of quantification (10s/slope of 30 measurements of blank) were studied. The results of the LD and LQ for the XAD 7-ARS and Dowex-ARS resins, are presented in Table 2. The precision of the procedure was determined by running 10 replicate samples, each one containing 250 μg L^{-1} of each element and the relative standard deviations were 0.2% (Cu), 0.4% (Mn), and 0.4% (Zn), to XAD 7-ARS e 0.3% (Cu), 0.5% (Mn), and 0.3% (Zn), to Dowex-ARS.

The applicability of two resins was tested for seawater and physiological solutions samples. The recommended procedures were investigated by addition of 5.0 μg of Mn, Cu, and Zn to seawater, from Salvador city, Bahia-Brazil, and physiological solutions samples carried out followed by analysis with the developed methods. Results are presented in Tables 3 and 4. Application of a t-test (at the 95% confidence level) shows no significant difference between the added recovered contents using both experimental procedures. Recovery values were always higher than 95%, confirming the accuracy of the procedure and the absence of matrix effects. Manganese, Cu, and Zn contents determined in seawater are lower than the allowed values (CONAMA[24]) which establishes, in the 1986 Resolution, the maximum values of the substances potentially harmful to the man in saline waters. For Mn, Cu, and Zn, the maximum values are 0.10, 0.05, and 0.17 μg mL^{-1}, respectively.

Table 2. Comparison of optimized parameters for the two systems studied

Parameters	Dowex-ARS	XAD 7-ARS
pH value	8.1	9.0
HNO_3 (mol L^{-1}) for elution	2.0	3.0
HNO_3 (mL) for elution	20.0	5.0
Loading time (min)	90	5
Quantity of solid phase (g)	0.75	0.50
Adsorptive capacity (mg g^{-1})	50	Mn: 500 ; Zn and Cu: 200
Preconcentration factor	Zn and Cu: 5	Zn: 50; Mn and Cu: 10
Limit of detection (μg L^{-1})	Mn: 25; Zn 23; and Cu: 9	Mn: 32; Zn 29; and Cu: 10
Limit of quantification (μg L^{-1})	Mn: 82; Zn 76; Cu:29	Mn: 105; Zn 98; Cu: 35

Table 3. Determination of Mn, Cu, and Zn in saline samples using XAD 7-ARS resin. Mean and standard deviations (n = 3)

Samples	Cu (μg mL^{-1})	Zn (μg mL^{-1})	Mn (μg mL^{-1})
Physiological solution 1	0.022 ± 0.001 (97%)[a]	0.028 ± 0.002 (96%)[a]	0.026 ± 0.001 (97%)[a]
Physiological solution 2	0.019 ± 0.001 (97%)[a]	0.021 ± 0.004 (95%)[a]	0.024 ± 0.002 (96%)[a]
Ondina seawater	0.060 ± 0.001 (97%)[a]	0.110 ± 0.004 (97%)[a]	0.123 ± 0.003 (98%)[a]
Rio Vermelho seawater	0.053 ± 0.001 (97%)[a]	0.092 ± 0.003 (99%)[a]	0.117 ± 0.001 (96%)[a]
Porto da Barra seawater	0.061 ± 0.001 (95%)[a]	0.112 ± 0.002 (99%)[a]	0.115 ± 0.002 (98%)[a]

[a]% Recovery (spiking: 5.0 mg of Mn, Cu, and Zn).

Table 4. Determination of Mn, Cu, and Zn in saline samples using Dowex-ARS resin. Mean and standard deviations (n = 3)

Samples	Cu (μg mL^{-1})	Zn (μg mL^{-1})	Mn (μg mL^{-1})
Physiological solution 1	0.020 ± 0.002 (98%)[a]	0.035 ± 0.004 (99%)[a]	0.026 ± 0.003 (95%)[a]
Physiological solution 2	0.018 ± 0.001 (96%)[a]	0.034 ± 0.002 (99%)[a]	0.022 ± 0.002 (95%)[a]
Ondina seawater	0.059 ± 0.002 (95%)[a]	0.095 ± 0.003 (101%)[a]	0.118 ± 0.002 (95%)[a]
Rio Vermelho seawater	0.061 ± 0.001 (96%)[a]	0.085 ± 0.004 (100%)[a]	0.118 ± 0.002 (95%)[a]
Porto da Barra seawater	0.051 ± 0.001 (95%)[a]	0.108 ± 0.003 (96%)[a]	0.112 ± 0.001 (95%)[a]

[a]% Recovery (spiking: 5.0 μg of Mn, Cu, and Zn).

Conclusions

The present paper is focused on the analytical problem of trace analysis of saline matrices by FAAS, and the fact that Mn, Cu, and Zn are trace constituents, in clinical and environmental samples. Two procedures using chelating resins obtained by modification of nonionic polymer sorbent Amberlite XAD-7 and anion exchanger Dowex 1X8-50 with Alizarin Red S are proposed for separation and preconcentration of Mn, Cu, and Zn from saline matrices. The procedures developed are simple and efficient. The system XAD 7-ARS presented some advantages due to rapid kinetic, low consumption of reagents and eluent, good stability and a good enrichment factor (up to 50x for Zn). The sorption capacity and preconcentration factor of alizarin red S loaded in Amberlite XAD-7 are higher than the alizarin red S loaded in Dowex 1X8-50. Furthermore, the elution step does not involve the use of organic solvents as others procedures. The addition recovery experiments showed that the proposed procedures had proper accuracy. The proposed method is simple and suitable for the separation and determination of Mn, Cu, and Zn in saline samples.

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