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Quantitative separation of zinc traces from cadmium matrices by solid-phase extraction with polyurethane foam

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Abstract

A system for separation of zinc traces from large amounts of cadmium is proposed in this paper. It is based on the solid-phase extraction of the zinc in the form of thiocyanate complexes by the polyurethane foam. The following parameters were studied: effect of pH and of the thiocyanate concentration on the zinc extraction, shaking time required for quantitative extraction, amount of PU foam necessary for complete extraction, conditions for the separation of zinc from cadmium, influence of other cations and anions on the zinc sorption by PU foam, and required conditions for back extraction of zinc from the PU foam. The results show that zinc traces can be separated from large amounts of cadmium at pH 3.0 ± 0.50, with the range of thiocyanate concentration from 0.15 to 0.20 mol l^{-1}, and the shaking time of 5 min. The back extraction of zinc can be done by shaking it with water for 10 min. Calcium, barium, strontium, magnesium, aluminum, nickel and iron(II) are efficiently separated. Iron(III), copper(II) and cobalt(II) are extracted simultaneously with zinc, but the iron reduction with ascorbic acid and the use of citrate to mask copper(II) and cobalt(II) increase the selectivity of the zinc extraction. The anions nitrate, chloride, sulfate, acetate, thiosulphate, tartarate, oxalate, fluoride, citrate, and carbonate do not affect the zinc extraction. Phosphate and EDTA must be absent. The method proposed was applied to determine zinc in cadmium salts using 4-(2-pyridylazo)-resorcinol (PAR) as a spectrophotometric reagent. The result achieved did not show significant difference in the accuracy and precision (95% confidence level) with those obtained by ICP–AES analysis. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Zinc separation; Solid-phase extraction; Polyurethane foam; Cadmium matrices

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1. Introduction

Zinc is frequently present at trace level in cadmium and their compounds. However, the spec-

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trophotometric determination of this element in these matrices is troublesome because many of the chromogenic reagents proposed also react with cadmium.

Numerous methods have been published for such determination. However, they are not simple and usually require extensive and laborious steps for the separation of zinc from cadmium, using procedures which involve: liquid–liquid extraction [1–6] of zinc or cadmium, ion exchange [7,8], and precipitation [9].

This paper proposes a method for the separation and determination of zinc in cadmium matrices based on solid-phase extraction (SPE) of zinc in the form of thiocyanate complexes by the polyurethane foam (PU foam).

The PU foam has been used as a solid sorbent on a wide variety of inorganic and organic compounds from different media. It was first proposed by Bowen [10] in 1970. Braun [11–13] and Palagyi [14] have described reviews about the use of PU foam in procedures of separation and preconcentration.

The use of PU foam for zinc extraction has been proposed by several authors [15–18]. The extraction mechanism of the zinc by the PU foam in the form of thiocyanate complexes has been studied by Moody et al. [15]. Maloney et al. [16] have proposed a procedure for simultaneous extraction of zinc, cobalt(II), iron(III) and cadmium(II) from thiocyanate medium by PU foam. Nickel is not extracted. Braun and Abbas [17] have proved that zinc, mercury and indium are extracted quantitatively by PU foam in the form of thiocyanates complexes. Hamza et al. [18] have used PU foam treated with dithizone for the extraction of zinc and bismuth.

Zinc(II) reacts instantaneously with 4-(2-pyridylazo)-resorcinol (PAR) [19,20] in the range of pH from 9.0 to 10.0, forming a complex with maximum absorption at 496 nm and molar absorptivity of 8.30×10^4 l mol^{-1} cm^{-1}. Cadmium(II) also reacts with PAR, forming a complex with absorption maximum at 510 nm and molar absorptivity of 8.12×10^4 l mol^{-1} cm^{-1}.

2. Experimental

2.1. Apparatus

Spectrophotometric measurements were made using a Varian Cary 1E spectrophotometer with matched 1.00-cm quartz cells.

An Applied Research Laboratories model 3410 minitorch sequential inductively coupled plasma spectrometer with an IBM PC-AT computer was used for ICP-AES analysis.

A Rigaku-B3 wavelength dispersive X-ray fluorescence spectrometer, with a rhodium tube operated at 40 kV and 30 mA, a LiF crystal, and a scintillation counter was used.

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.

2.2. Reagents

All reagents were of analytical-reagent grade unless otherwise stated. Doubly distilled water was used to prepare the solutions. The nitric acid and hydrochloric acid were of Suprapur quality (Merck). The laboratory glassware was kept overnight in a 5% nitric acid solution. Before being used the glassware was washed with doubly distilled water and dried in a dust-free environment.

Zinc solution (10.00 μg ml^{-1}) was prepared by diluting a 1000.00 μg ml^{-1} zinc solution (atomic absorption Aldrich) using a 5% hydrochloric acid solution.

Potassium thiocyanate solution (1.0 mol l^{-1}) was prepared by dissolving the reagent (Carlo Erba) in doubly distilled water.

Masking solution containing citrate and acid ascorbic (1.6%) was prepared by dissolving its sodium salts (Merck) in doubly distilled water.

4-(2-Pyridylazo)resorcinol solution (0.05% m/v) was prepared by dissolving a monosodium reagent (Merck) in doubly distilled water.

Buffer solution (pH 10.0) was prepared by mixing 42.0 g of di-sodium hydrogen carbonate and 53.0 g of sodium carbonate in 1 l of doubly distilled water.

Polyurethane foam: a commercial, open cell, polyether-type PUF (Vulcan of Brazil, VCON 202, 42% resilience and 10–12 cells/linear cm) was broken into small particles in a blender with doubly distilled water and used as described by Carvalho [21–23].

2.3. Separation procedure

It was added into a polypropylene flask the following reagents: 10.00 ml of zinc(II) cation solution in the mass range of 1.0–60.0 μg, 5.00 ml of 1.0 mol l^{-1} thiocyanate solution and 10.00 ml buffer solution. It was mixed and added the mass of 60 mg of comminuted PU foam (previously treated with 0.20 mol l^{-1} thiocyanate solution). Then the system was stoppered and mechanically shaken for 5 min. The PU foam was collected by vacuum filtration (filter paper $\phi = 2.0$ cm), washed with 0.2 mol l^{-1} KSCN solution, transferred to another polypropylene flask where zinc was, then, back extracted with 10.00 ml of doubly distilled water, after shaking for 10 min.

2.4. Spectrophotometric determination of zinc using PAR reagent

The following reagents were added into a volumetric standard flask of 10 ml: zinc(II) solution in the mass range of 0.40–10.0 μg, 2.50 ml of carbonate buffer and, 1.00 ml of PAR solution. Then, it was filled up with doubly distilled water and its absorbancy was measure at 496 nm.

3. Results and discussion

3.1. Effect of pH on the zinc sorption

The pH effect on the zinc sorption was studied. The results show that the extraction was maximum and constant in the range of pH from 2.0 to 10.0 as it can be seen in Fig. 1. The pH control was done using acetate buffer with pH 3.75–5.75, borate buffer pH 8.0 and carbonate buffer with pH 10.0. For pH 2.0, 3.0, and 12.0, solutions of hydrochloric acid and sodium hydroxide were used, respectively. The procedure proposed recommends the extraction with the pH solution at 3.0 ± 0.5 because in such pH, cadmium is not extracted by the PU foam. At pH higher than 5.0, cadmium can also be extracted by the PU foam in the form of thiocyanate complexes.

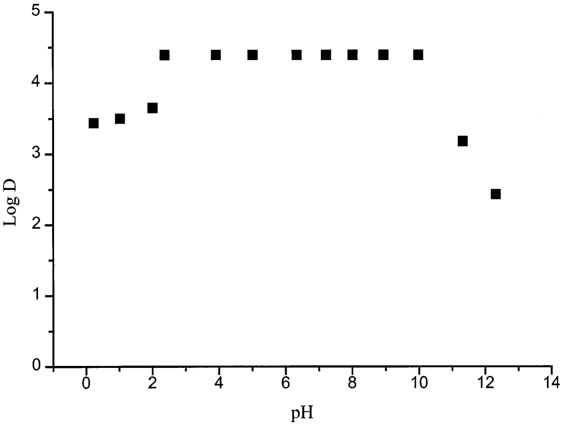

Fig. 1. Effect of pH on the zinc extraction.

3.2. Effect of the thiocyanate concentration on the zinc extraction

In order to test the thiocyanate concentration required for a quantitative extraction, 10.00 μg of zinc was extracted by PU foam changing the thiocyanate concentration from 0.02 to 2.00 mol l^{-1}. The results in Fig. 2 show that the extraction efficiency increases when the thiocyanate concen-

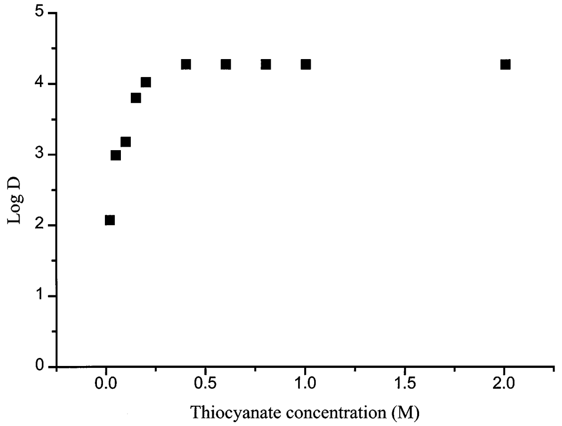

Fig. 2. Effect of thiocyanate concentration on the zinc extraction.

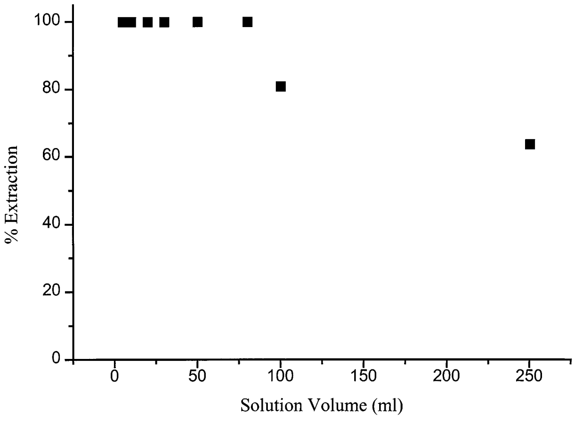

Fig. 3. Effect of the solution volume on the zinc extraction.

tration reaches a constant value over 0.15 mol l^{-1} KSCN, in which the system has the highest distribution coefficient ($D \geq 10^4$).

3.3. Effect of the solution volume on the zinc extraction

In order to evaluate the effect of the solution volume on the efficiency of zinc extraction were prepared several solutions with variable volumes of (5, 10, 25, 50, 80, 100, and 250 ml). All of them contained a fixed mass of 10.00 μg of zinc and the thiocyanate concentration of 0.20 mol l^{-1}. Then, zinc was extracted by using 55 mg of PU foam. The system was shaken for 10 min. The results show that the extraction was constant and quantitative for solutions in the range of volume from 5 to 80 ml. It can be seen in Fig. 3.

3.4. Effect of shaking time

The effect of the shaking time on the extraction efficiency was studied. The results show that 3 min are enough for a quantitative extraction of 10.00 μg of zinc and the thiocyanate concentration of 0.20 mol l^{-1}. In the procedure proposed, 5 min is recommended to guarantee a maximal extraction.

3.5. Amount of PU foam necessary for complete extraction

The effect of the amount of PU foam on the zinc extraction was also evaluated. It was found that 55 mg of PU foam is required as the minimal mass for a quantitative extraction of 60.00 μg of zinc.

Thus, PU foam in the range of mass from 55 to 65 mg is recommended to guarantee a complete extraction. This test was done using PU foam with a sorption capacity of 0.016 mmol of zinc/g of PU foam determined by the sorption isotherm [23].

3.6. Back extraction of zinc

Several solutions were tested for zinc back extraction by PU foam. The results show that zinc can efficiently be recovered using 10 ml of doubly distilled water, or 10 ml of ethanol solution (10% v/v), or 10 ml of nitric acid solution 0.10 mol l^{-1}, or 10 ml hydrochloric acid solution 0.10 mol l^{-1}. The back extraction with water was chosen because it was more convenient for spectrophotometric measurements. The carbonate buffer showed a poor result. Cadmium complexes are not back extracted with water and, in this case, a nitric acid solution must be used.

3.7. Zinc separation from cadmium

Zinc can be separated from large amounts of cadmium. However, at pH higher than 5.0 and the thiocyanate concentration up to 0.30 mol l^{-1}, cadmium in the form of thiocyanate complexes can also be extracted by the PU foam. Thus, the pH recommended for the separation of zinc from cadmium, is at 3.0 ± 0.50 and thiocyanate must be in the range of concentration from 0.15 to 0.20 mol l^{-1}. Table 1 show the pH effect on the separation of zinc from cadmium.

In order to test the separation procedure efficiency for spectrophotometric determination of zinc with PAR reagent, several amounts of zinc (2.00, 4.00, 8.00, 12.00, and 16.00 μg) were mixed with 1000.00 μg of cadmium(II) and the procedure proposed in Section 2 was applied. The

Table 1
Separation of zinc (10.00 μg) in the presence of several amounts of cadmium

Cadmium present (μg)	Zinc extracted at pH 3.00	Cadmium extracted at pH 3.00	Zinc extracted at pH 5.0	Cadmium extracted at pH 5.0 (μg)
200.00	99%	<LD	99%	45.88 (22.94%)
500.00	98%	<LD	98%	72.39 (14.48%)
1000.00	99%	<LD	98%	199.0 (19.90%)
2000.00	98%	6.66 (0.33%)	90%	315.50 (15.78%)
3000.00	94%	11.59 (0.38%)	87%	358.10 (11.94%)
5000.00	90%	31.29 (0.63%0	85%	870.00 (17.40%)

LD, detection limit. PU foam amount: 60 mg [SCN–]: 0.20 mol l^{-1}.
Zn and Cd were back extracted with nitric acid solution and determined by ICP–AES.

amount of zinc recovered was plotted on the *y*-axis and the amount of zinc added on the *x*-axis. The linear equation resulted in the followings data: the angular coefficient was 1.022 ± 0.033 and the linear and correlation coefficient were 0.044 ± 0.125 and 0.9997, respectively. These data show the separation efficiency of the method proposed.

3.8. Separation of zinc from other elements

Solutions containing 10.00 μg of zinc(II) and different amounts of several cations were prepared and the efficiency of the separation procedure was tested. The results show that at pH 3.0 and thiocyanate concentration of 0.20 mol l^{-1}, 10 μg of zinc can be perfectly separated from 5.0 mg of the followings ions: aluminum(III), calcium(II), magnesium(II), strontium(II), iron(II), nickel(II), and barium(II). Iron(III), copper(II), cobalt(II), and zinc(II) are extracted simultaneously. However, the iron(III) reduction with ascorbic acid and the use of citrate to mask copper(II) and cobalt(II) increase the selectivity of the zinc separation. Mercury(II), gallium(III) and lead(II) ions are also extracted by the PU foam in this medium. Nevertheless, these ions are not back extracted with water. The anions nitrate, chloride, sulfate, acetate, tartarate, thiosulphate, oxalate, fluoride, citrate, and carbonate do not affect the zinc extraction by the PU foam. Phosphate and EDTA must be absent. In this experiment all determinations of those elements were done using ICP–AES analysis and/or X-ray fluorescence spectrometry to measure directly metal thiocyanate complexes on the PU foam.

3.9. Application

The analytical curves for the zinc(II)–PAR system was done according to the procedure described in Section 2. The system showed a calibration sensitivity [24] of 1.355 ml μg^{-1} for a dynamic interval of application from 60 ng ml^{-1} to 1.00 μg ml^{-1}, detection limit of 20 ng ml^{-1} and a variation coefficient of 0.84%.

The analytical characteristics of the separation procedure are summarized in the Table 2. They were done based on the zinc extraction from 0.20 mol l^{-1} thiocyanate solutions at pH 3.0.

The method proposed was applied to zinc determination in several cadmium salts. The accuracy and precision achieved were not significantly different from 95% confidence level those obtained by ICP–AES analysis (Table 3).

Table 2
Analytical characteristics of the system Zn(II)–0.2 M KSCN–PU foam

Distribution coefficient	1.04×10^4 (l Kg^{-1})
Shaking time for extraction	5 min
Time for back extraction (water)	10 min
Sorption capacity of the PU foam	0.016 (mmols g^{-1})
Recovery range	98–101%
Coefficient of variation	1.35%

Table 3
Zinc determination in cadmium salts

Samples	Zn found (mg g^{-1} salt)	
	Proposed method	ICP method
$CdSO_4 \cdot 8/3H_2O$	1.96 ± 0.01	2.05 ± 0.02
$CdSO_4 \cdot 8/3H_2O$	3.90 ± 0.02	4.09 ± 0.04
$Cd(H_3CCOO)_2 \cdot 2H_2O$	5.57 ± 0.01	5.63 ± 0.09

4. Conclusions

Zinc can be easily extracted by the PU foam in a wide range of pH and large thiocyanate concentration. However, for the separation of zinc from cadmium the pH and the thiocyanate concentration are critical.

The zinc recovered from PU foam with water is ideal for application of the analytical technique of determination used.

The pH and thiocyanate concentration control as well as the use of masking agents allowed an efficient and simple zinc separation procedure from many others elements.

The solid-phase extraction has two typical advantages over the solvent extraction: avoiding the manipulation of organic solvents, which are frequently toxic and eliminating common problem of emulsions. The PU foam is also commercially available at low price.

The separation method proposed is opportune, considering that the spectrophotometric determination of zinc traces in cadmium matrices is troublesome, could be also applied for determination of zinc by other analytical methods.

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