Separation and Preconcentration of Cobalt after Sorption onto Amberlite XAD-2 Loaded with 2-(2-Thiazolylazo)-*p*-cresol

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Analytical chemists frequently receive samples that cannot be analyzed in the natural state, due to the presence of interferences and/or inadequate sensibility of the available analytical methodology. Previous steps for separation and enrichment are almost always necessary, and many procedures have been proposed. The process, involving extraction in solid phase, has received more acceptance due to a number of possible advantages, including the availability and easy recovery of the solid phase, attainability of large preconcentration factors and the facility for separation and enrichment using systems with continuous flow. Besides, they usually do not need organic solvents, which may be toxic. For cobalt adsorption determination, several procedures have been proposed involving polyurethane foam¹, activated carbon^{2,3}, Amberlite XAD-4 resin^{4,5}, naphthalene⁶ and C₁₈-bonded silica gel column;^{7,8} other techniques as coprecipitation using indium hydroxide as collector⁹, liquid-liquid extraction¹⁰ and cobalt separation as complex and filtration with a membrane filter.^{11,12}

Isshiki and Nakayama¹³ examined the selective concentration of trace amounts of cobalt in seawater using 14 ligands, such as 2-(2-thiazolylazo)-*p*-cresol and 2-(2-thiazolylazo)resorcinol, and two XAD resins (styrene polymer and acrylate polymer types). They concluded that the combination of TAR and XAD-4 is the most preferable choice. In their system, complexes of coexisting metals were eluted with 1 mol dm⁻³ hydrochloric acid solution, and the cobalt complex was then eluted with a methanol-chloroform mixture.

2-(2-Thiazolylazo)-*p*-cresol (TAC) is a reagent proposed for the determinations of metal cations. In our laboratory, it has been used for the spectrophotometric determination of nickel¹⁴, lead¹⁵, indium¹⁶, titanium¹⁷ and vanadium;¹⁸ it has also been proposed as a complexing agent in the separation processes for the determination of nickel¹⁹ and iron²⁰ by using ICP-AES. This paper proposes an analytical procedure for the determination of trace cobalt in saline matrices by ICP-AES,

using a column containing Amberlite XAD-2 resin loaded with TAC for preconcentration and separation. This method does not require toxic chloroform as an eluent.

Experimental

Apparatus

An Applied Research Laboratories (Model 3410) minitorch sequential inductively coupled plasma spectrometer with an IBM PC-AT computer was used. The emission measurements were made using the conditions given in Table 1. A 300 ANALYSER pH meter was used to measure the pH values.

Reagents

All reagents were of analytical reagent 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 5% nitric acid solution.

Cobalt(II) solution (5.00 µg cm⁻³): prepared by diluting a 1000 µg cm⁻³ cobalt solution (atomic absorption Aldrich) using a 5% hydrochloric acid solution.

TAC solution (0.05%): prepared by dissolving 0.10 g

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 dm ³ min ⁻¹
Auxiliary gas flow rate	0.8 dm ³ min ⁻¹
Aerosol carrier gas flow rate	0.8 dm ³ min ⁻¹
Solution uptake rate	2.5 cm ³ min ⁻¹
Wavelength	238.896 nm
Signal integration time	5 s
Integration for determination	3

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TAC (Aldrich) in 200 cm³ of ethanol.

Borate buffer solution (pH 8.5): prepared by dissolving 19.05 g of sodium tetraborate 10 hydrate in 1000 cm³ of deionized water and pH adjusted with 10% hydrochloric acid solution.

Preparation of Amberlite XAD-2 column loaded with TAC

XAD-2 was treated with an ethanol:hydrochloric acid:water (2:1:1) solution over night. Then, the resin was rinsed with deionized water until the pH of the supernatant water became neutral, and was then dried in an oven at temperature of 110°C for 3 h. The packing of the column must be done using ethanol as eluent, because with water the beads of resin float.

The resin was saturated with the reagent by elution of 5.0 cm³ of a 0.05% TAC solution in ethanol at a flow rate of 0.50 cm³ min⁻¹. Later it was rinsed with water until any excess reagent was eliminated from the resin. All of the experiments were performed in glass columns (0.40 cm internal diameter and 15 cm length) containing 0.50 g of XAD-2. Before sample loading, the column must be preconditioned by passing buffer solution. The column could be used repeatedly for at least seven times.

Procedure for the sorption of cobalt on the column

Transfer 25 to 500 cm³ of sample solution containing cobalt ions in the range of 0.10 to 110.0 µg into a beaker, and add 10 cm³ of the pH 8.5 buffer solution. This solution must be passed through the column at a flow rate of 1.50 cm³ min⁻¹. After passing this solution, the column is rinsed with 10 cm³ of deionized water. The adsorbed cobalt chelate on the column is eluted with 5.0 cm³ of 3 mol dm⁻³ hydrochloric acid solution, at a flow rate of 1.0 cm³ min⁻¹. The eluent is collected in a 5 cm³ volumetric flask and the cobalt is determined by ICP-AES technique.

Results and Discussion

Complex formation studies

Cobalt(II) ions in an alkaline pH region react with TAC adsorbed onto Amberlite XAD-2 resin, to form a complex, which readily oxidized to cobalt(III) chelate by dissolved oxygen in water, as occur in another reactions of cobalt(II) ions.^{8,21} A complementary study revealed that cobalt(II) ions are not retained in a column loaded with TAC in the presence of reducing agents, such as ascorbic acid and hydroxylammonium chloride. In aqueous solution the cobalt(III) complex has green coloration and an absorption maximum at 576 nm.

Determination of the optimum conditions for cobalt sorption

A study of the pH effect on the sorption of cobalt(II) ions showed that the recovery of cobalt is maximum

and quantitative in a pH range of 8.0 to 10.0. The effect of the flow rate on cobalt sorption was also examined, by varying the flow rate from 0.30 to 2.0 cm³ min⁻¹. The cobalt(III) retention on the resin is complete, only with a flow rate equal to or lower than 1.50 cm³ min⁻¹. A study of the volume effect of the aqueous phase demonstrated that the cobalt adsorption is quantitative for a solution volume in the range of 25 to 500 cm³. The electrolytes presence don't influence the cobalt sorption. The cobalt extraction of 100 cm³ solution was quantitative, even in the presence of 30% sodium chloride or 30% potassium nitrate. The sorption capacity of the Amberlite XAD-2 resin loaded with TAC was determined using a column containing 0.50 g of loaded resin. The resin had a sorption capacity of 3.75 µmol of cobalt per gram of XAD-2 resin. In condition of maximum adsorption, distribution coefficient was higher than 1.0×10⁴ dm³ kg⁻¹.

Cobalt desorption from XAD-2 resin

In order to determine the cobalt desorption from the resin, 5.0 cm³ of hydrochloric acid with concentrations of 0.50, 1.0, 2.0 and 3.0 mol dm⁻³ was used. The desorption was quantitative (>95%) for solutions with concentrations equal to or higher than 3.0 mol dm⁻³. Another study revealed that 0.50 cm³ of 3.0 mol dm⁻³ hydrochloric acid is sufficient for quantitative desorption.

Characteristics of the proposed procedure

The proposed procedure can be applied to the preconcentration and separation of cobalt, in the range of 0.10 to 110.0 µg, contained in a solution volume of 25 to 500 cm³, by using of 0.50 g of Amberlite XAD-2 resin loaded with TAC reagent. A calibration graph for cobalt determination by ICP-AES (0 – 2.0 µg cm⁻³) was obtained using solutions prepared from a 1 mg cm⁻³ stock solution. The limit of detection was 12 µg dm⁻³ and the correlation coefficient was 0.9996. The precision of the method, evaluated as the relative standard deviation obtained after analyzing a serie of six replicates, was 1.29% to 10.0 µg of cobalt contained in a solution volume of 25 cm³.

Cobalt determination in saline matrices by ICP-AES

Cobalt is a metal frequently analyzed by ICP-AES. However, the use of this technique for the determination of metal traces in saline matrices is problematic.^{22,23} Thus, the proposed method was applied for cobalt determination in alkaline salts. A volume of 100 cm³ of 30% solution salts was used for cobalt determination. The obtained recovery, measured through the addition technique of a standard, revealed that the proposed procedure is accurate. The results are given in Table 2.

One of advantages of the proposed procedure in relation to the method developed by Isshiki and Nakayama¹³ is in the use of a 3.0 mol dm⁻³ hydrochloric

Table 2 Determination and recovery of cobalt in saline samples

Sample	Mass of added cobalt per gram of salt/ng	Cobalt found ^a /ng g ⁻¹	Recovery
NaCl	0	31.7±2.1	100.4%
	100	132.1±5.2	
NaNO ₃	0	23.0±2.0	100.7%
	100	123.7±7.2	
KCl	0	6.8±1.6	102.0%
	100	108.8±4.9	

a. At 95% confidence level.

ric acid solution in substitution of the methanol-chloroform mixture, during the step of cobalt desorption. In the Isshiki and Nakayama¹³ procedure, the ligands are eluted together with the cobalt(III) complex. In this study, the use of a column loaded with TAC and the desorption step with 3.0 mol dm⁻³ hydrochloric acid solution allowed the application of the TAC-XAD2 system in procedures for cobalt preconcentration by using the flow injection analysis technique.

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