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Research Article

Separation and Preconcentration of Cobalt Using a New Schiff Base Derivative on Amberlite XAD-7

In this study, a new solid-phase extraction procedure has been developed for preconcentration and determination of Co ions in different water samples by flame atomic absorption spectrometry (FAAS). Cobalt was preconcentrated as *N,N′*-bis(pyridine-2-yl-methyl)benzene-1,4-diamine (Co-BPMBDA) from sample solutions using a column containing Amberlite XAD-7 and was determined. In order to achieve the best performance for the method, effects of several parameters such as pH, concentrations of ligand, sample flow rate, eluent, and matrix ions on the method efficiency were investigated. Under optimum conditions, the preconcentration factor was found to be 200 for 1000 mL waters samples. Detection limit based on the $3S_b$ criterion was calculated as 0.24 μg/L for 100 mL of sample solution and relative standard deviation was found to be 1.8%. The method was applied to determine the trace amounts of cobalt in water samples.

Keywords: Amberlite XAD-7; Cobalt; Preconcentration; FAAS; Solid-phase extraction

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1 Introduction

Cobalt is an important element for industry and for biological systems. Cobalt is present in vitamin B_{12} and is an essential micronutrient for all living systems [1]. Drinking water, food, and inhalation are common ways of cobalt contamination for living organisms. The deficiency of cobalt in human and animal bodies results in anemia [2], while large amounts of cobalt causes to toxic effects (mechanism to fail in asthma, kidney and liver disorders, heart growth and expansion, sinus tachycardia), usually after occupational exposure to cobalt dust (cobalturia, cobaltemia) [3, 4].

There are two main alternative sources of cobalt for aquatic environment: Natural sources and anthropogenic sources. The natural sources include volcanic emissions, the weathering of rocks by the action of water and decomposition of plant waste. The main human-related sources of cobalt to aquatic environment are sewage and industrial waste [5].

Since one of the routes of incorporation of cobalt into the human body is by ingestion, its determination in drinking water, food, and environmental samples such as soil and dust becomes very important [6].

Several analytical techniques including electrothermal atomic absorption spectrometry (ETAAS) [7], inductively coupled plasma optical emission spectrometry (ICP-OES) [8], inductively coupled plasma mass spectrometry (ICP-MS) [9], flame atomic absorption spectrometry (FAAS) [10], and high performance liquid chromatography (HPLC) [11, 12] have been devised for the determination of cobalt in different matrixes.

Due to the high complexity of the matrixes and the low level of cobalt ions in the aquatic samples, separation, and preconcentration step prior to cobalt analysis are needed [13, 14]. There are many methods for preconcentration such as, coprecipitation, solvent extraction, electrochemical deposition, membrane extraction, and solid-phase extraction [15–17]. Solid-phase extraction (SPE) has become a preferred method at enrichment of many metal ions prior to their analysis by FAAS and other techniques. Trace elements are converted to their chelates or inorganic complex with appropriate ligand and are retained by various adsorbents. Schiff bases play a central role as chelating ligands in main group and transition metal coordination chemistry [18]. Transition metal complexes of tetradentate Schiff-base ligands find applications as models in materials chemistry [19].

In this study as a Schiff bases, *N,N′*-bis(pyridine-2-yl-methyl)benzene-1,4-diamine (BPMBDA) was used for the first time as chelating agent, for separation and enrichment. This Schiff bases is an important indicator and complexing agent for metal ions [20] and the reaction scheme of its synthesis is shown in Scheme 1.

In the present work, a novel method was developed for the determination of trace amount of cobalt by using FAAS in different water samples. Co(II)-BPMBDA chelates can be adsorbed on XAD-7 in column and optimum experimental conditions for cobalt recovery were investigated. Analytical parameters such as precision and

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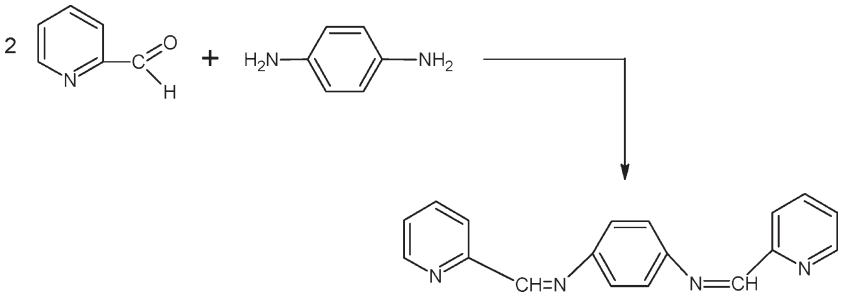
Abbreviations: **BPMBDA**, *N,N′*-bis(pyridine-2-yl-methyl)benzene-1,4-diamine; **FAAS**, flame atomic absorption spectrometry; **LOD**, limit of detection.



Scheme 1. Synthesis of BPMBDA.

accuracy of the method have also been determined. The developed method has been successfully used to determine the cobalt in various samples.

2 Experimental

2.1 Apparatus

A Perkin Elmer Analyst model 700 (Shelton, CT, USA) FAAS with a Perkin Elmer cobalt hollow cathode lamp and a deuterium background corrector, at respective resonance line using an air–acetylene flame was used. The instrumental parameters were as follows: wavelength 240.7 nm, lamp current 7.5 mA, and bandpass 0.2 nm. All instrumental settings were those recommended in the manufacturer's manual.

2.2 Reagents and Solutions

High purity deionized water (resistivity 18.2 MΩ cm) obtained by a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used throughout this work. All reagents used were of analytical grade. Amberlite XAD-7 (surface area 450 m^2/g and bead size 20–40 mesh) was obtained from Aldrich (Milwaukee, USA). BPMBDA was obtained from Firat University, Inorganic chemistry division. Standard BPMBDA solution of 0.04% w/v was prepared by dissolving 0.02 g of BPMBDA (99.9% purity) in 50 mL mixture of methanol–water (60:40% v/v). Metal solutions were prepared by diluting the atomic absorption standard solutions (1000 ± 2 mg/L). Standard metal solutions and other chemical reagents were purchased from Merck (Darmstadt, Germany). All chemicals were used without further purification. The glassware used were washed with 1.0 mol/L HNO_3, ethanol and thoroughly washed with distilled water. Amberlite XAD-7 was removed prior to its use by washing it thoroughly with 1 mol/L NaOH, water and 4 mol/L HCl, respectively. Afterwards, it was washed with deionized water.

2.3 Preparation of Adsorption Column

A glass column (10 cm length and 0.8 cm internal diameter) was prepared by placing a small portion of cleaned glass wool as a plug at one end of the column holding a certain amount (0.5 g) of adsorbent. Then, another small glass-wool plug was inserted onto the tap of the adsorbent, as described in ref. 21. This system was cleaned with water, methanol, 2 mol/L HCl and 2 mol/L HNO_3 solutions by following given order.

2.4 Test Studies for Solid-Phase Extraction

The given procedure was checked with standard test solutions. The standard test solutions were prepared as follows: 5 mL of 1.0 mg/L of Co(II) standard solution was added to 2.5 mL of standard BPMBDA solution (0.04% w/v) and mixed with 2 mL of buffer solution in a volumetric flask. Citrate buffer (0.1 mol/L) for the pH range of 2.0–3.0, acetate buffer (0.1 mol/L) for the pH range of 3.0–6.0, phosphate buffer (0.1 mol/L) for the pH range of 6.8–9.0, and ammonia buffer (0.1 mol/L) for the pH range 8.0–12.0 were used. Afterwards, final volume of sample was completed to 50 mL with distilled water. Before use, the column was preconditioned with blank solution containing buffer solution having suitable working pH. In all experiments, the standard test solutions were kept at 30 min in order to form complexes of desired metal ion. Then, this solution was permitted to flow through the column under gravity at flow rate of 3 mL/min. The retained cobalt ions were eluted with 5 mL of 2 mol/L HNO_3 in ethanol solution that has a flow rate of 5 mL/min. Cobalt was analyzed by using proposed method in direct calibration curve by FAAS. A blank solution was also run under the same conditions without adding any cobalt.

2.5 Analysis of Water Samples

A tap water sample was collected from Elazig city line, a commercial natural drinking water and mineral water collected from local market in Elazig, Turkey. These samples were filtered by using Whatman filter paper (No. 40), then 2.5 mL of standard BPMBDA solution and phosphate buffer (pH 7.0) solutions were added then passed through the column which contains Amberlite XAD-7 resin. After elution process, samples were analyzed by FAAS.

3 Results and Discussion

3.1 Effect of pH of the Aqueous Solution on the Recovery of Cobalt

To determine the optimum pH range for sorption of cobalt ions, seven standard sample solutions having pH in the range of 2.0–10.0 were passed through columns. The cobalt ions was stripped with 5 mL of 2 mol/L HNO_3 in ethanol solutions and determined by FAAS as described in the proposed procedure. Effect of the pH value on the recovery values are summarized in Fig. 1. As shown in the figure, the optimum recoveries were found between the pH values of 6.5 and 7.5. Therefore, pH 7.0 was chosen as an optimum pH in phosphate buffer for analytical determination of cobalt in further studies.

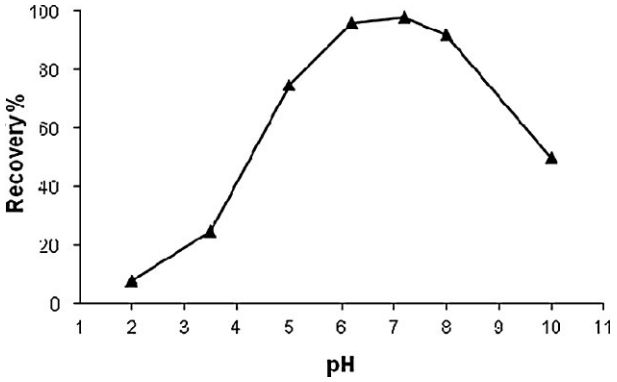


Figure 1. The effect of pH on the recovery of cobalt (sample volume: 50 mL, amount of cobalt: 5 μg, eluent: 5 mL of 2 mol/L HNO_3 in ethanol solution, flow rate of sample: 3 mL/min, sorbent: 500 mg, $N = 3$).

3.2 Effect of Ligand Amount

In recent studies, ligands were used widely in adsorption process because of their high affinity to metal ions. In this study BPMBDA that contains imine residues as an organic functional group which provides various numbers of different potential binding sites for metal ion under investigation was used as ligand.

Effect of the amount of BPMBDA on recovery values of method was studied. For this purpose, different amounts of BPMBDA in the range from 0.2 to 4.0 mg were added to different test solutions each contains 5.0 μg of Co(II) and these solutions were passed through Amberlite XAD-7 column. The results are given in Fig. 2. As can be seen from this figure, when BPMBDA was used the adsorption of cobalt ions on Amberlite-XAD-7 resin was stimulated and this effect increased the performance of proposed method. Quantitative recoveries were obtained for Co(II) ions when the amount of BPMBDA was 0.5 mg or higher. At amount of BPMBDA less than 0.5 mg, the recovery was below 95%. As a result, 1.0 mg of BPMBDA was added to the solutions in further works.

3.3 Effect of Sample Volume

Optimization of the sample volume is one of the important parameter in this kind of studies. So the influence of the sample volume on recovery values was examined on XAD-7 column at a 3.0 mL/min flow rate. For this purpose: 50, 100, 250, 500, 750, and 1000 mL of the sample solutions each contains 2.5 μg of cobalt were passed through the column at the optimum conditions. The results are given in Fig. 3. The recovery of cobalt was found to be quantitative (>95%) for the sample volume up to 1000 mL. By analyzing 5 mL of the final solution after preconcentration of 1000 mL of sample solution, an enrichment factor of 200 was found.

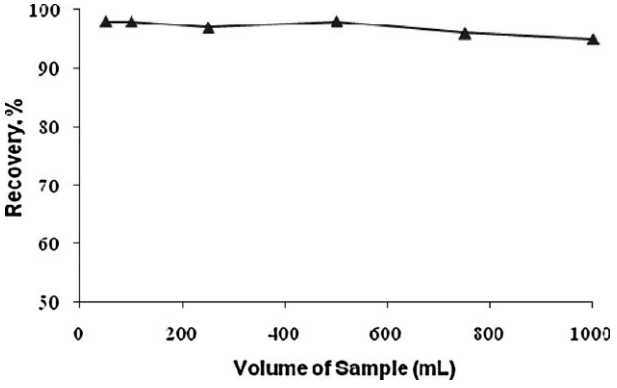


Figure 2. The effect of BPMBDA amount on the recovery of cobalt (sample volume: 50 mL, amount of cobalt: 5 μg, eluent: 5 mL of 2 mol/L HNO_3 in ethanol solution, flow rate of sample: 3 mL/min, pH: 7.0, sorbent: 500 mg, $N = 3$).

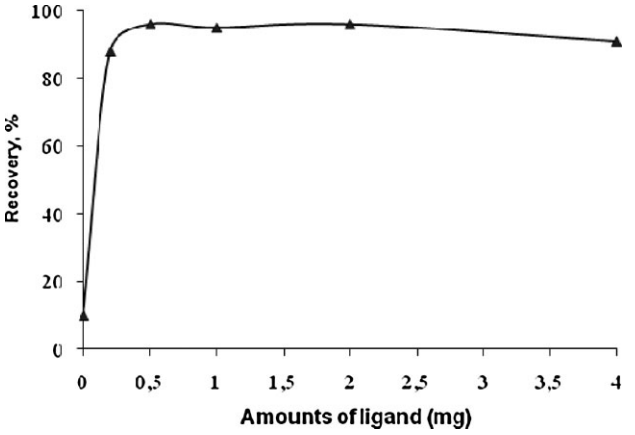


Figure 3. The effect of sample volume on the recovery of cobalt (amount of cobalt: 2.5 μg, eluent: 5 mL of 2 mol/L HNO_3 in ethanol solution, flow rate of sample: 3 mL/min, pH: 7.0, sorbent: 500 mg, $N = 3$).

3.4 Effect of Flow Rate

After sample volume optimization, the effects of flow rate on the adsorption of cobalt were investigated. To obtain maximum recoveries for cobalt, different flow rates were tested in optimum conditions. As shown in Fig. 4, it was found that the suitable value for the flow rate of the solution was in the range of 1–3 mL/min. Therefore, an optimum flow rate of 3 mL/min was selected as the working solution flow rate to decrease the analysis time.

3.5 Choice of Eluent Agents

Recovery values in desorption process depend strongly on physical and chemical properties of adsorbent and eluent reagents. Besides these factors, it also depends on electrical charge, polarity, size of

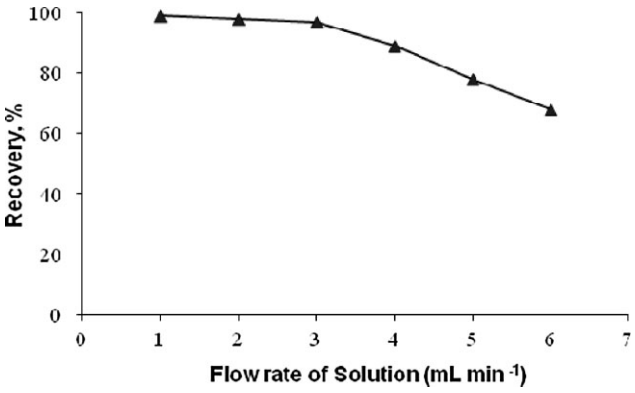


Figure 4. The effect of solution flow rate on the recovery of cobalt (sample volume: 50 mL, amount of cobalt: 5 μg, eluent: 5 mL of 2 mol/L HNO_3 in ethanol solution, pH: 7.0, sorbent: 500 mg, $N = 3$).

Table 1. The effect of eluent types on the recovery of cobalt (sample volume: 50 mL, amount of cobalt: 5 μg, flow rate of sample: 3 mL/min, pH: 7.0, sorbent: 500 mg, $N = 3$).

Eluent	Recovery (%)[a)]
2 mol/L HCl, 5 mL	90 ± 1
2 mol/L HCl, 10 mL	93 ± 3
3 mol/L HCl, 5 mL	96 ± 2
2 mol/L HNO_3, 5 mL	93 ± 1
3 mol/L HNO_3, 5 mL	94 ± 2
2 mol/L HNO_3, 5 mL (in ethanol)	99 ± 2
2 mol/L HNO_3, 7 mL (in ethanol)	99 ± 3
5 mL ethanol	27 ± 1

a) Mean ± standard deviation for three repeated measures.

adsorbed species, interactions with eluent, and unbalanced forces of adsorbed species on the surface of adsorbent. Therefore, mixtures of organic solvent (i.e., methanol, ethanol, acetone, etc.) with inorganic acids, as an alternative solution of inorganic acids are needed to evaluate the satisfactory recovery values. In order to choose a proper eluent for retained cobalt ions, different eluting agents such as, HCl, HNO_3, and ethanol were tested. The experimental results show that maximum recovery for cobalt was observed when 5 mL of 2 mol/L HNO_3 in ethanol was used. The effects of various eluent on recoveries of cobalt are summarized in Tab. 1.

3.6 Effect of Resin Amount

The amount of resin for metal recovery is also another important factor on the column studies for the quantitative recoveries of desired metal. Effect of the amount of solid-phase on the sorption of metal ions at optimum pH was investigated in the range 300–800 mg (Fig. 5). The results showed that the optimum amount of sorbent was found in the range from 500 to 700 mg for maximum extraction of cobalt. Therefore, 500 mg of resin has been used for subsequent experiments because of easy elution and sufficient recovery in water samples.

Generally, recovery values increase with increasing amount of resin. But, to attain the expected increase in recovery values with increasing amount of resin, the volume of the eluent should be increased in same ratio [22]. Because of this statement, decrease in recovery values was obtained for the experiments in which resin amount was higher than 700 mg when the volume of eluent was held constant at 5 mL.

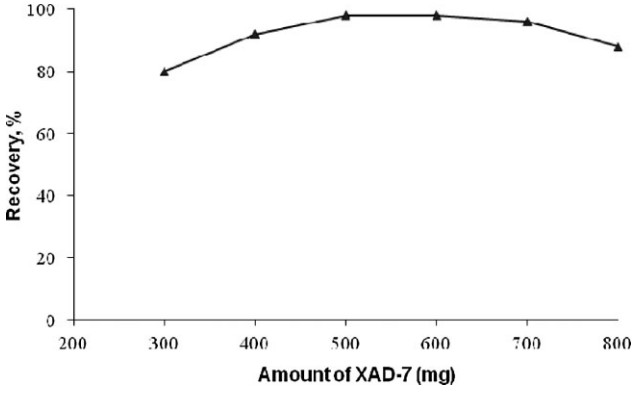


Figure 5. The effect of XAD-7 amount on the recovery of cobalt (sample volume: 50 mL, amount of cobalt: 5 μg, eluent: 5 mL of 2 mol/L HNO_3 in ethanol solution, flow rate of sample: 3 mL/min, pH: 7.0, $N = 3$).

3.7 Matrix Effect

The influence of possible matrix ions in the water samples and some metals was also examined. The effect of potential interfering ions on the determination of cobalt was investigated by adding known concentrations of each ion into the solution containing analytes and then determined. The results are given in Tab. 2. These recovery values showed that normally present ions in water have no significant interferences on the extraction and determination of cobalt in sample solutions.

3.8 Analytical Features

Analytical figures of merit were evaluated for the determination of cobalt according to the proposed procedure at optimum conditions. The linear range of calibration graph was found to be 0.2–5.0 μg/mL with $R^2 = 0.9964$, for standard cobalt solutions. The calibration equation was as follows: $A = 0.0812\,C - 0.0082$, where A is absorbance and C is cobalt concentration (μg/mL). The precision of the method was investigated at optimum conditions mentioned above. The mean recovery for ten determinations was 98.4%. As can be seen, the precision of the method is very good. The relative standard deviation of recovery values was found to be 1.8%.

The detection limit of this method was calculated after application of the preconcentration procedure to the 100 mL of blank solutions. The limit of detection (LOD) for cobalt based on three times the standard deviations of the blank ($N = 10$) was calculated as

Table 2. The effect of some ions on the recovery of cobalt.

Interfering ions	Concentration (mg L^{-1})	Recovery[a)] (%)
K^+	50	95 ± 2
	100	96 ± 3
Na^+	100	98 ± 3
	500	97 ± 2
	1000	95 ± 2
Ca^{2+}	20	96 ± 4
	100	90 ± 2
Mg^{2+}	20	97 ± 3
	50	94 ± 2
Cl^-	100	102 ± 4
	400	97 ± 2
SO_4^{2-}	20	98 ± 3
	50	95 ± 2
Cu^{2+}	10	95 ± 3
	20	96 ± 2
Zn^{2+}	10	99 ± 3
	20	93 ± 1
Ni^{2+}	20	101 ± 2
Pb^{2+}	10	98 ± 3
	20	94 ± 1
Al^{3+}	20	97 ± 4
Fe^{3+}	10	99 ± 2
	50	104 ± 3
Cr^{3+}	20	96 ± 2
Cd^{2+}	10	94 ± 1

a) Mean ± standard deviation for three repeated measures.

Table 3. Comparison of enrichment factors and LOD for cobalt.

Solid-phase	Ligand	Enrichment factor	LOD (μg/L)	Sample volume (mL)	References
Styrene–ethylene glycol dimethacrylate polymer	5,7-Dichloroquinone-8-ol	200	2.0	1000	[23]
Silica gel	Polyethylene glycol	166.6	0.37	500	[24]
Amberlys 36	–	200	0.44	1000	[25]
Ambersorb 563	1-(2-Pyridylazo) 2-naphtol	125	0.21	250	[26]
Duolite XAD-761	PAR	150	0.36	600	[27]
Activated Carbon	Dithioxamide (rubeanic acid)	330	0.80	1650	[28]
MCI GEL CHP 20Y	2-(2-Quinolinil-azo)-4-methyl-1,3-dihydroxidobenzene	300	0.012	300	[29]
Amberlite XAD-7	BPMBDA	200	0.24	1000	Present paper

0.24 μg/L. These value shows that, developed method is suitable to determine the trace amount of cobalt in different water samples. The analytical performance of the method is comparable with the other preconcentration methods. Some comparative data about separation and preconcentration of cobalt are summarized in Tab. 3.

The proposed SPE method due to advantages such as: high enrichment factor (200), the sufficiently good recoveries (98.4), high tolerance limit of interfering ions, and low detection limit (0.24 μg/L) is a powerful tool for simple and sensitive determination of cobalt ions in water samples.

Statistical analysis of results obtained by proposed method and methods given in literature for 95% confidence level are given Tab. 4. The results of *F*-tests and the variances between three methods were found to be insignificant at 95% confidence level indicating that no significant differences exist between the precision of the three methods. As a result proposed method might be alternatives to the methods given in literature.

Table 4. Statistical analysis of results obtained by proposed method and methods given in literature for 95% confidence level.

Method	Mean recoveries, %	RSD, %	*N*	*F*-Test significance[a)]	*F* (tabulated)[a)]
Proposed	98.4	1.8	10	–	–
Ref. [25]	98.0	1.9	7	1.11	3.22
Ref. [28]	98.9	1.3	15	1.91	2.60

a) Given test values are the values between proposed method and literature given in the left-hand side of table.

Table 5. The determination of cobalt in water samples (initial volume: 750 mL).

Sample	Added (μg/L)	Found[a)]	Recovery, %
Mineral water A	–	ND	–
	4.0	4.2 ± 0.2 μg/L	105
Mineral water B	–	7.9 ± 0.8 μg /L	
	4.0	12.1 ± 0.9 μg/L	101.6
City line	–	3.6 ± 0.6 μg/L	–
	4.0	7.4 ± 0.8 μg/L	97.3
Natural water A	–	ND	
	4.0	3.9 ± 0.5 μg/L	97.5
Natural water B	–	1.8 ± 0.2 μg/L	
	4.0	6.0 ± 0.7 μg/L	103.4

ND, non determined.
a) Mean $\pm\, t\, s/\sqrt{N}$ with 95% confidence level.

3.9 Determination of Cobalt in Water Samples

The accuracy of proposed procedure was investigated through the recovery test in water samples in which known amount of analyte was added. After homogenizing the samples and applying the procedure, cobalt was determined by direct calibration method. Experimental results of spiked cobalt samples are given in Tab. 5. Calculated recoveries for waters were found between 97.3–105.0%.

4 Conclusion

In the present work, a simple, sensitive, safe, and reliable solid-phase extraction method was developed for the preconcentration of cobalt in different water samples. BPMBDA was firstly used as chelate derivatization reagent for enrichment and separation of cobalt ions. The cobalt-chelates were preconcentrated by XAD-7 resin and the enrichment factor of 200 was achieved. This method is able to detect the cobalt ions in the concentration level of micro gram per liter. Most foreign ions do not interfered with the determination. The developed method is good precision and accuracy. The method was successfully applied to determine cobalt ions in the water samples.

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The author has declared no conflict of interest.

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