Separation and Preconcentration of Cobalt(II) from Water Samples with Amberlite CG-120 Resin

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ABSTRACT: *A selective solid-phase extraction method has been developed for the preconcentration and separation of trace amounts of Co(II). The method was based on the adsorption of Co(II) ions on the Amberlite CG-120 resin. The adsorbed Co(II) ions on the resin were eluted by 4 mol/L HCl and then they were determined by Flame Atomic Absorption Spectrometry (FAAS). Various experimental conditions, such as pH, type and concentration of eluent, the flow rate of sample and eluent solution, amount of resin, and sample volume were investigated to obtain better sensitivity and effective separation of trace levels of the Co(II) ions. Moreover, the interference effects of some ions on the recovery of Co(II) were also investigated. The developed method was applied for the determination of Co(II) ions in drinking and wastewater samples. The enhancement factor (EF) and limit of detection (LOD) values were found to be 25-fold and 9.32 µg/L, respectively. The accuracy of the method was tested by the certified reference material of TMDA-70.2 Lake Ontario Water and there was a good agreement between found and certified values at a 95% confidence level.*

KEYWORDS: *Cobalt; Amberlite CG-120 resin; Solid-phase extraction; Water samples; FAAS.*

INTRODUCTION

Cobalt plays an important role for many vital processes, such as the blood formation, stimulation of hemoglobin synthesis, and the functioning of some vitamins, enzymes and hormones. Furthermore, it also affects the metabolism of some vitamins, such as ascorbic acid and vitamin B12 in a positive way [1,2]. While pernicious anaemia is associated with cobalt deficiency, the vasodilation, flushing, and cardiomyopathy are occurred by excessive intake of cobalt in the living creatures [3]. In general, its dietary intake for adults is ranged from 5 and 40 mg Co/day and its safe dietary supplements at ingested doses are between 200 and 1400 µg Co/day in the US and Europe [4]. Moreover, it is an also essential element in the industrial and military applications. Its main applications in industry are the production of glass, porcelain, ceramics and paint.

The discharged of industrial wastewater into rivers and used as irrigation water have caused to increase its

concentration in the soil, sediment and water [5]. Due to the use of cobalt in various industrial fields, it causes various toxic effects on all living organisms including plants, animals and microorganisms. Additionally, it can cause different significant illness, such as gastrointestinal tract, heart diseases, genotoxicity, neurotoxicological disorders and cancer in human. [6, 7]. Therefore, the accurate and efficient analytical methods should be developed to monitor its concentration especially at trace level in the food, water and environment samples [8].

In the literature, the determination of Co in the different real samples has been successfully carried out with different analytical techniques, such as Flame Atomic Absorption Spectrometry (FAAS) [9], Graphite Furnace Atomic Absorption Spectrometry (GFAAS) [1], Inductively Coupled Plasma Optical Emission Spectrometry (ICPOES) [10], Inductively Coupled Plasma Mass Spectrometry (ICPMS) [4] and energy dispersive X-Ray fluorescence spectrometry [11]. Among them, FAAS is still commonly used as an attractive alternative due to availability of the instrumentation in routine laboratory, its simplicity, relatively higher speed, precision and accuracy [12]. Because metal ions are generally found in the environmental samples at trace levels and environmental samples include highly matrix interferences, determination of them in such complex matrices lead to the development of some preconcentration and/or separation methods to enhance the sensitivity and selectivity of analyses [6, 13, 14], such as Dispersive Solid Phase Extraction (DSPE) [15], Solid-Phase Extraction (SPE) [16], Liquid-Liquid Micro Extraction (DLLME) [17], and Solvent Extraction [18].

Environmentally friendly-SPE method is widely used because of its some special features, such as simplicity, availability in in routine laboratory, low cost, easy to application, higher accuracy, precision, and sensitivity, lower consumption of reagents, reproducibility, and flexibility [16]. To date, different substances, such as Chromosorb 105 [19], Amberlyst®15 resin [20], Amberlyst 36 [21], Activated carbon [22] and Tween 80 coated alumina [12] have been used as SPE resins for the preconcentration and/or separation of Co. Along with these resins, functionalized resins have been also used for enrichment of Co in recent years. For example, SBA-15 was modified by 5-(4-imethylaminobenzylidene) rhodanin reagent and Co(II) ions were enriched by using this resin. Co(II) ions were adsorbed on resin in the pH range of 6.8–7.9. The developed method was used for determination of Co(II) ions in standard samples, water samples and agricultural products [23]. In another study, the coated alumina was selected as adsorbent for preconcentration of Co. The coated alumina resin was prepared by mixing alumina with Tween 80 (3%). This method was successfully applied for Co determination in some real samples, such as tobacco, brewed tea and water samples [12]. In another study, Amberlite XAD-4 was functionalized with 2-hydroxyacetophenone and it was used as adsorbent in SPE method. The characterization studies of functionalized Amberlite XAD-4 were performed by using infrared spectroscopy and scanning electron microscopy, respectively. Under optimum conditions, this method was employed for the enrichment and determination of Co(II) ions in sediment samples [24].

Previously, some studies were successfully conducted in our group for the quantitatively separation, preconcentration and determination of some metals, such as Cu, Mn, Cd and Ni from some samples with Amberlite CG-120 resin [25-28]. In the present work, we have also developed a simple analytical methodology using SPE method for the separation and/or preconcentration of Co(II) from drinking and waste water samples with Amberlite CG-120. In the detection step, FAAS was used. The effect of some chemical and physical variables, such as pH, type and concentration of eluent, flow rate of sample and eluent solution, resin amount, sample volume and interference effects were investigated and their optimum values were found to obtain better separation and/or preconcentration conditions for Co(II) determination. As far as we can ascertain, Amberlite CG-120 resin has not been used for separation, preconcentration and determination of Co(II). Furthermore, the optimized methodology was also applied for drinking and waste water samples. The accuracy of the method was also tested by the certified reference material of TMDA-70.2 Ontario Lake Water at a 95% confidence level.

EXPERIMENTAL SECTION
Reagents and Chemicals

All chemicals and solvents used were of analytical reagent grade. $18 M\Omega$ cm deionized water (Puris purification system, Expe-UP Series) was used throughout the work. A stock solution containing 1000 mg/L of Co was prepared by dissolving of $Co(NO_3)_2$. The standard

solutions (50 mg/L) were prepared by appropriate dilution of the stock solution (1000 mg/L) with deionized water. The stock solutions (1000 mg/L) of the cations used in the interference study were prepared from their salts supplied from Sigma-Aldrich, and Riedel-de Haen depend on interference elements. The used acid solutions are HNO_3 (65%, Merck), HCl (37%, Sigma-Aldrich) and $HClO_4$ (60%, Riedel-de Haen).

Apparatus

ATI Unicam 939 model atomic absorption spectrometer equipped with deuterium background correction and cobalt hollow cathode lamp was used for the determination of cobalt at a wavelength of 240.7 nm. The pH values were controlled with a pH-meter (Thermo Orion 3 Stars) supplied with a glass-combination electrode and an Memmert, UN-110 Model oven was used for the drying of all glass materials. In this study, the glass column whose volume, length and internal diameter were 250 mL, 15 cm and 0.8 cm, respectively was used for the separation and/or preconcentration of Co(II) before detection step.

Column preparation

Firstly, a small glass wool wad was placed at the bottom of the column and 0.3 g of Amberlite CG-120 resin was added on it. Then another portion glass wool wad was inserted onto the top of resin to avoid spills. Before use, the column was washed with ethanol, 1 mol/L HCl, 1 mol/L HNO_3, and deionized water, respectively. After each experiment, the prepared column was filled with deionized water to prevent drying of resin.

Collection and Preparation of Samples

In this study, the Co(II) ions were successfully separated, preconcentrated and determined in the drinking water samples supplied from Burdur city, Turkey province and the waste water supplied from Isparta city, Turkey province.

RESULTS AND DISCUSSION

In this study, some of the experimental parameters, such as the pH, concentration and type of eluent, eluent and sample flow rate, sample volume, and amount of resin were optimized for the quantitatively separation and/or preconcentration of Co(II) with the Amberlite CG-120 resin prior to FAAS detection.

pH effect

The pH is an important parameter affecting adsorption as the acidity of the environment affects the ability to compete for hydrogen ions and metal ions on available centers of the adsorbent surface. Therefore, adsorption studies were performed at different pH values in the range of 1-10. Firstly, the column was conditioned at working pH values. Then, 25 mL of synthetic solutions containing 50 µg Co(II) were also conditioned at the same pH and passed through the column. The adsorbed Co(II) ions on the Amberlite CG-120 resin were recovered with 10 mL of 4 mol/L HCl solution. The results for the recovery of Co(II) based on pH values were shown in Fig. 1. As shown in Fig. 1, even though the quantitative similar recovery was obtained for pH 1-5, pH 1 with the highest recovery was chosen as optimum pH value to prevent precipitation of metal ions occurred at high pH value and to easily dissolve some real samples.

Type and Concentration of Eluent

In the adsorption studies, it is necessary to determine the most suitable type of eluent and its concentration to ensure the quantitative recovery of Co(II). For this, a series of eluent solutions, such as 10 mL of 2 mol/L HNO_3, 2 mol/L HCl and 2 mol/L $HClO_4$ were used to find out suitable eluent type. The quantitative recovery was obtained with 10 mL of 2 mol/L HCl among these eluent solutions. Afterwards, various HCl concentrations between 2 mol/L and 4 mol/L of HCl were investigated in detail to obtain the highest recovery value for Co(II). It was found that as quantitative elution for Co(II) was achieved by using 4 mol/L HCl, this eluent was employed in all studies.

Flow rate of Sample and Eluent Solution

The sample and eluent flow rates should be optimized to obtain the highest recovery efficiency of analyte and the time of analysis. For this, the sample solution was passed through the column at a flow rate changing from 0.25 to 5 mL/min. As shown in Fig. 2, the quantitative recovery was obtained for all sample flow rates but 5 mL/min flow rate was chosen as the optimum value to shorten the analysis time. The solution flow rates were not increased more than 5 mL/min as the preconcentration factor was decreased due to the fact that Co(II) ions were not sufficiently
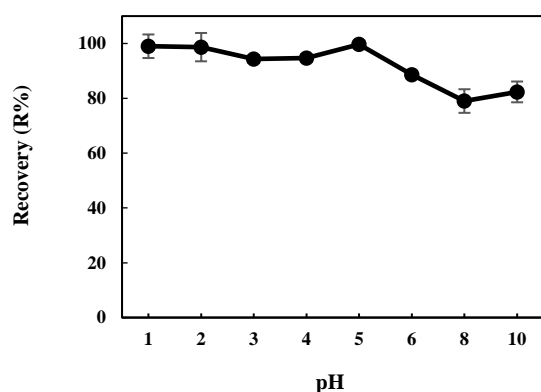
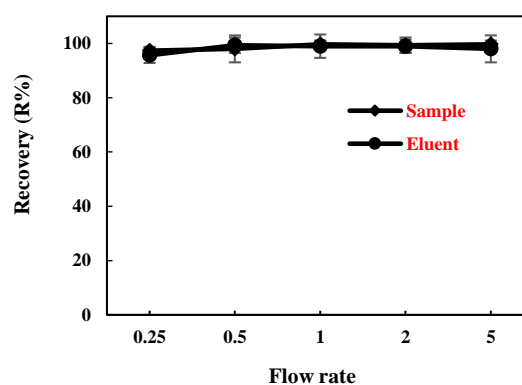*Fig. 1: The effect of pH on the recovery of Co(II).*

Fig. 2: The effect of sample and eluent flow rate on the recovery of Co(II).

adsorbed on the resin and it was difficult to control higher flow rates in our system. After optimum sample solution flow rate was determined, the eluent was passed through the column at a flow rate changing from 0.25 mL/min to 5 mL/min. The optimum eluent flow rate was also chosen as 5 mL/min for the same reason mentioned above.

Properties and characterization of Amberlite CG-120 resin

The selected resin in the SPE method is one of the most important parameters because its properties significantly influence the experimental results to obtain better separation and/or preconcentration. In this study, Amberlite CG-120 resin was used for separation and/or preconcentration of Co(II) in aqueous solution and its physical properties were given in Table 1.

The general adsorption mechanism between metal and resin was also shown in Fig. 3. As shown in Fig. 3, the target metal replaces with the sodium form during the interaction of the target metal in the solution with the resin.

Moreover, in this study, the surface morphology of the resin was determined by using Scanning Electron Microscopy (SEM). Additionally, the elemental composition of resin was also detected by Energy-Dispersive X-ray (EDX) spectrometry. The SEM image and EDX results of resin were given in Fig. 4

Resin Amount

The amount of the Amberlite CG-120 resin should be optimized in order to ensure effective adsorption of Co(II) ions on the resin. For this, the effects of different

amounts of Amberlite CG-120 resin varied from 0 to 0.5 g were investigated for Co(II) adsorption on resin. By the time the resin was higher than 0.5 g, the Co(II) ions adsorbed on the resin were not efficiently recovered by the eluent. As shown in Fig. 5, the quantitative recovery was obtained from 0.3 g to 0.5 g. Because the capacity of Amberlite CG-120 resin for Co(II) adsorption decreased when the amount of resin was less than 0.3 g due to insufficient number of adsorption sites., 0.3 g was chosen in further experiments to use less amount of resin.

Sample Volume

To obtain the highest enrichment factors, sample solution volumes ranged from 25 mL to 300 mL containing 50 µg Co(II) were passed through the Amberlite CG-120 resin. As shown in Fig. 6, the quantitative recovery for Co(II) was obtained for sample solution volumes ranged from 25 mL to 250 mL. When sample and eluent volumes were chosen to be 250 mL and 10 mL, respectively, the enrichment factor and limit of detection was found to be 25-fold and 9.32 µg/L, respectively.

Matrix Effect

For the real samples applications, as interfering ions present in high amounts in real samples affect the Co(II) signal to be determined as positively and/or negatively, their effects on Co(II) detection were investigated in this study. The tolerance limits for interfering ions on the Co(II) recovery were given in Table 2. There was no obvious influence on the recovery of Co(II) for Mn(II), Mg(II) and Al(III) up to 100-fold, and for Zn(II), Cu(II)

Research Article

Table 1: Physical properties of Amberlite CG-120 resin [29, Manufacturer Information].

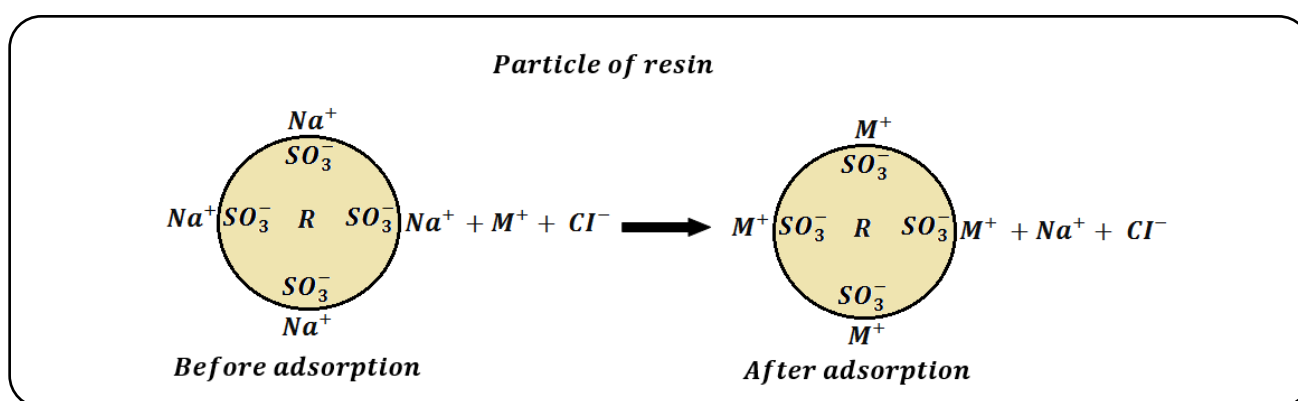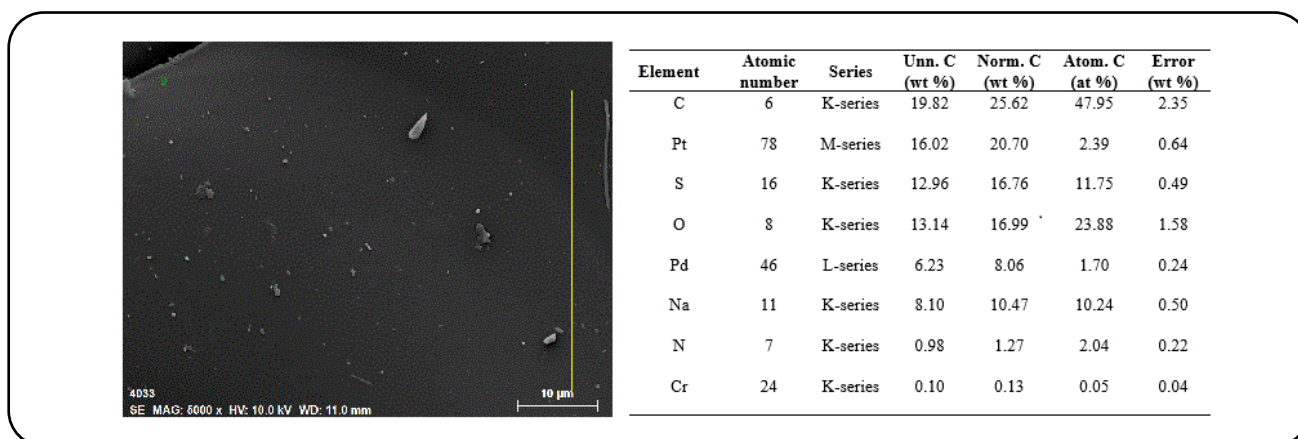| Properties	Values
Type	Strong cation exchanger
Color	yellow
pH	☐ 0.4-10
Functional groups	sulfonic acid
Ionic form	Na^+
Matrix	Styrene-divinylbenzene
Particle size	100-200 mesh
Capacity	1.9 meq/mL

Fig 3: The general adsorption mechanism of resin [30].

Fig 4: Amberlite CG-120 resin (a) SEM image, (b) EDX results for elemental composition.

Element	Atomic number	Series	Unn. C (wt %)	Norm. C (wt %)	Atom. C (at %)	Error (wt %)
C	6	K-series	19.82	25.62	47.95	2.35
Pt	78	M-series	16.02	20.70	2.39	0.64
S	16	K-series	12.96	16.76	11.75	0.49
O	8	K-series	13.14	16.99	23.88	1.58
Pd	46	L-series	6.23	8.06	1.70	0.24
Na	11	K-series	8.10	10.47	10.24	0.50
N	7	K-series	0.98	1.27	2.04	0.22
Cr	24	K-series	0.10	0.13	0.05	0.04

and Ca(II) up to 250-fold, K up to 750 fold, and Na up to 2000-fold excess electrolytes, respectively.

Method Validation

The accuracy of the method was tested by certified reference material of TMDA-70.2 Lake Ontario Water. The Co(II) value was found to be 278±18 µg/L in certified reference material which was in good agreement with the certified value of 291±21 µg/L, based on three replicate measurements at a 95% confidence level with a relative standard deviation (RSD) of 2.8% using optimum analytical parameters.

Table 2: Interference effects of some ions on the recovery of Co(II).

Ions	Tolerance level (mg/L)	R[a] (%)
Na^+	2000	95±1.0
K^+	750	100±0.5
Mg^{2+}	100	95±2.0
Ca^{2+}	250	95±2.0
Zn^{2+}	250	98±1.0
Cu^{2+}	250	100±4.0
Mn^{2+}	100	95±6.0
Al^{3+}	100	96±0.5

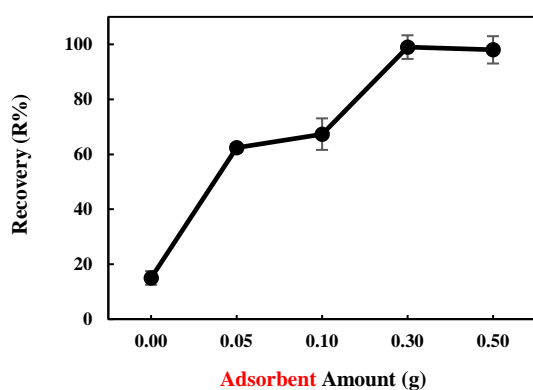[a] *Mean of three replicates ± standard deviation*

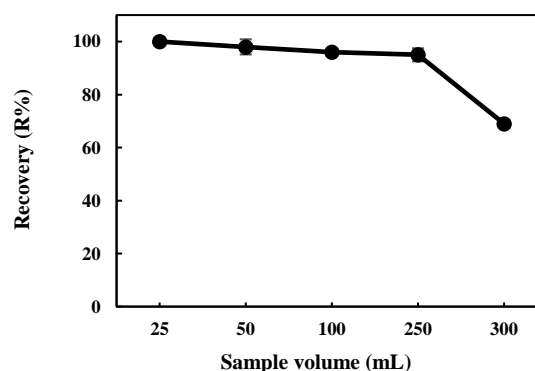*Fig. 5: The effect of adsorbent amount on the recovery of Co(II).*

Fig. 6: The effect of sample volume on the recovery of Co(II).

Analysis of Real Samples

The developed method was used for the determination of Co(II) under the optimum experimental conditions in the commercial drinking water samples supplied from local market in Burdur province and waste water supplied from Isparta province (Süleyman Demirel Organized Industrial Region) at Turkey. The method validation was also used for the determination of Co(II) in these water samples and the accuracy of the method was also tested by measuring the recovery of Co (II) spiked as different amounts in the water samples as shown in Table 3.

CONCLUSIONS

In this study, the solid phase extraction column method filled with Amberlite CG-120 resin was developed for the separation and/or preconcentration of the Co(II) prior to its FAAS detection and this method was successfully applied

for the accurate determination of it in the drinking and waste water samples including highly complex matrices. Additionally, there was no necessity of using buffer and chelating agents for the separation and preconcentration of Co(II) on the column containing Amberlite CG-120 resin. The recovery of Co(II) in these samples was found to be more than 95% and Amberlite CG-120 resin in the column was efficiently used without any loss of its adsorption properties. Using this rapid, simple, economic, accurate and precise method, enrichment factor was found to be 25-fold using 250 mL sample and 10 mL eluent volumes. The accuracy of the method was also tested by a certified reference material of TMDA-70.2 Lake Ontario Water and there was a good agreement between found and certified values at a 95% confidence level. As the proposed method was free from matrix effects, it was a promising attempt for the trace ions determination in water samples and it will have

Table 3: Determination of Co(II) in the water samples, 250 mL, N= 3.

Sample	Added Co(II) (µg/L)	Found[a], $\bar{x} \pm \frac{ts}{\sqrt{N}}$ (µg/L)	Relative error (%)
Drinking water	-	BDL[b]	-
	80	85±3	6
	160	163±6	2
Waste water	-	BDL	-
	80	81±10	2
	160	153±11	-4

[a] *95 % confidence level*
[b] *Below detection limits*

Table 4: Comparison of this method with other methods for cobalt determination

Resin	pH	LOD, µg/L	E.F.*	Samples	Measuring instrument	References
Functionalized polystyrene-divinylbenzene	9	0.8	37	Sediments	FAAS	[24]
Functionalized silica magnetite mesoporous nanoparticles	7	0.03	10.3	Natural waters	FAAS	[31]
Multiwalled carbon nanotubes	7	1.64–5.68	40	Different waters	FAAS	[32]
Functionalized silica gel	8	1.42	7.31	Water and food samples	FAAS	[33]
Amberlite CG-120	1	9.32	25	Different waters	FAAS	This study

* *Enrichment factor*

much more applied field. The analytical performance of the proposed method was compared with that of other preconcentration methods in the literature shown in Table 4.

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