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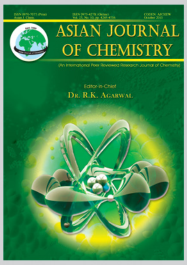

Application of a New Modified Nano Alumina as a Sorbent for Preconcentration and Determination of Cobalt ions in Food and Environmental Water Samples Prior to Flame Atomic Absorption Spectroscopy

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The first study on the high efficiency of nanometer-sized γ-alumina coated with sodium dodecyl sulfate-pyrrolidine dithiocarbamate (SDS-4-BPDC) as a new sorbent solid phase extraction has been reported. Sorbent with modified nanometer-sized alumina was used to preconcentrate and separate cobalt in food and environmental water samples. A microsample introduction system was employed for the nebulization micro-volume of diluted solution into flame atomic absorption spectroscopy. Various influencing parameters on the separation and preconcentration of trace metal, such as pH, amount of sorbent and concentration of the chelating agent, were studied. The calibration graph was linear in the range of 10-900 μg L^{-1} with detection limit of 3.1 μg L^{-1}. The relative standard deviation (RSD) for ten replicate measurements was 2.2 %. The proposed method has been applied to the determination of cobalt at trace levels in real samples such as rice, tobacco, orange, green pepper, black tea, honey, potato, spinach, mangosteen, tomato, strawberry, carrot, apple, kiwi, mushroom, cucumber, lettuce, milk, wheat sprout, tab water, river water, sea water with satisfactory results.

Key Words: New modified nano alumina, Preconcentration cobalt, Food and environmental water samples.

INTRODUCTION

Heavy metal composition of water and food samples is of interest because of their essential or toxic nature[1]. Among heavy metals, the pollution caused by cobalt is of considerable concern. Determination of cobalt assumes importance because of its widespread occurrence in sea as well as in fresh water, earth crust, meteorites, animals and plants[2]. It is a vital trace element in animal nutrition and widely distributed in the body with high concentration in liver, bone and kidney[3]. Cobalt, in the form of cobalamine, is an essential component of vitamin B_{12} required for the production of red blood cells and prevention of pernicious anaemia[4,5]. Cobalt concentration levels are very low in food and water samples and therefore sensitive and selective analytical techniques are required to carry out its detection[6,7]. Many sensitive techniques such as spectrofluorimetry, X-ray fluorescence spectrometry, neutron activation analysis[8-11], atomic absorption spectrometry (AAS), thin film sequential injection, polarography, chromatography, inductively coupled plasma mass spectrometry (ICP-MS), chemiluminescence and electrochemiluminescence[12-18] have been widely applied to the determination of cobalt. Flame atomic absorption spectrometry (FAAS) is an important instrument at this area due to its simplicity and lower cost than other instruments. However in these determinations, low concentration levels of cobalt at μg L^{-1} level and high levels of matrices are the main problems[19,20]. This limitation can be overcome by the use of a preconcentration procedure. For this purpose, various preconcentration/separation methods including coprecipitation[21], liquid-liquid extraction[22,23], flow injection extraction, solid-phase extraction (SPE)[23-25], ion exchange[26], flotation[27], cloud point extraction, dispersive liquid-liquid microextraction, membrane filtration, solvent extraction and chelating sorbents[19,20,24,25] have been used. Upto now, several kinds of solid-phase extraction sorbents such as C-18 bonded silica[28], activated oxide[29,30], silica gel, sodium dodecyl sulfate coated alumina[24], polyurethane foam[25], modified silica[27], activated carbon[31,32] and nanometer-sized materials have been used for the preconcentration and determination of cobalt. Among these sorbents, nanometer-sized materials have gained more attention due to their special properties[33]. Because nanometer-sized alumina has high surface area, high sorption capacity and high chemical activity, it could be successfully applied for the separation and preconcentration of trace metal ions in environmental samples. Recent studies on the use of surfactant-coated mineral oxide for solid-phase extraction have demonstrated these new sorbent materials to be a promising tool for the extraction/preconcentration of organic compounds in a wide polarity range[34]. For these purposes, we have developed nano-sized alumina coated with sodium dodecyl sulfate-pyrrolidine dithiocarbamate (SDS-4-BPDC), as a new and effective sorbent for the preconcentration and determination of Co by flame atomic absorption spectrometry in real samples with satisfactory results.

EXPERIMENTAL

All chemicals used were of analytical-reagent grade. The stock standard solutions containing 1000 mg L^{-1} of Co(II) were prepared by dissolving appropriate amounts of their nitrate salts in distilled water and working standard solutions were obtained by appropriate stepwise dilution of the stock standard solutions. Nano-γ-alumina (Al_2O_3-γ-powder, 40-80 nm, purity: > 99 % NanoAmor, Los Alamos, NM, USA) was activated by shaking with 4 mol L^{-1} nitric acid and washed two times with distilled water. Sodium dodecyl sulfate (Schuchardt, Germany) was used without further purification. The chelating solution was prepared by dissolving 0.082 g of 4-BPDC in 50 mL of 95 % ethanol.

A thermo M series (Model: M5) flame atomic absorption spectrometer was utilized, equipped with a 50 mm burner head, deuterium background correction and air-acetylene flame. A cobalt hollow cathode lamp (thermo scientific S51214) was used as radiation source, operated at 15 mA with a monochromator spectral bandpass of 0.1 nm for the cobalt detection, the wavelength was set at 240.7 nm resonance line. The acetylene and the air-flow rates were 0.8 and 10.0 L min^{-1}, respectively. The pH measurements were carried out by using a Metrohm pH meter (model 744) with a combined pH glass electrode calibrated against two standard buffer solutions at pH 4.0 and 7.0. A centrifuge (Kokusan Ensinkico, model H-11 N) equipped with an angle rotor (8-place, 4000 rpm, Cat.) was used to separation.

Preparation of modified nano-γ-alumina: 0.5 g of activated nano-γ-alumina was added to 10 mL solution containing 0.1 mg sodium dodecyl sulfate and 0.2 mL 4-BPDC solution in a 100 mL flask. The pH of solution was adjusted to 2 with 1 mol L^{-1} HNO_3 solutions and then the flask was shaked for 10 min[35].

A known volume of sample solution containing Co(II) in the range of 0.5-200 μg L^{-1} was prepared and added to modified nano-γ-alumina and the pH value was adjusted to 5.5 using acetic acid buffer solution. Then centrifugation at 3500 rpm for 10 min accelerated the sedimentation of the rich phase in the process of solid phase extraction. Afterwards, the metal ions retained on the sorbent, were eluted using 2 mL of 1 mol L^{-1} HNO_3. The analytes in the extracted were determined by flame atomic absorption spectrometry.

Preparation of real samples: Black tea (2.0 g), rice (2.0 g), tomato sauce (2.0 g), tobacco (2.0 g), potato (4.0 g), mangosteen (4.0 g), kiwi (4.0 g), orange (4.0 g), cucumber (4.0 g), apple (4.0 g), mushroom (4.0 g), lettuce (4.0 g), carrot (4.0 g), strawberry (4.0 g) green pepper (4.0 g), wheat sprout (2.0 g) and honey (2.0 g) samples were digested with 6 mL of concentrated HNO_3 (65 %) and 2 mL of H_2O_2 (30 %). After digestion of the samples, the volume of the digested sample was made up to 25 mL with distilled water.

A 10 mL portion of milk sample was placed in a 100 mL beaker and 10 mL of 65 % HNO_3 and 3 mL of 30 % H_2O_2 were added. The contents in the beaker were heated on a hotplate at 100 ºC for 40 min. Most of the acids were evaporated then the residue was dissolved with 10 mL of 1 mol L^{-1} HCl. The obtained clear solution was neutralized by adding NaOH and diluted in a 25 mL volumetric flask.

A 40 g spinach sample was heated in silica crucible for 3 h on a hot plate and the charred material was transferred to furnace for overnight heating at 650 ºC. The residue was cooled, treated with 10 mL concentrated nitric acid and 3 mL 30 % H_2O_2 again kept in furnace for 2 h at the same temperature so that no organic compound traces are left. The final residue was treated with 3 mL concentrated hydrochloric acid and 3 mL 70 % perchloric acid and evaporated to fumes, so that all the metals change to respective ions. The solid residue was dissolved in water, filtered and by keeping the pH at 5.5 made up to 25 mL.

RESULTS AND DISCUSSION

It is necessary to investigate the effect of all the parameters that can probably influence the extraction performance. In this methodology these parameters are the kind and amount of eluting solution and antisticking pagent, pH, ligand concentration and amount, centrifuge conditions that were investigated and optimized in order to achieve a high recovery and enrichment factor. In all optimization steps concentration of cobalt was 0.5 mg L^{-1}.

Effect of pH: pH value plays a key role in the solid-phase extraction procedure. An appropriate pH value can not only improve the adsorption efficiency, but also depress the interference of the matrix. The sorption of sodium dodecyl sulfate on nano-sized alumina is highly dependent on the pH of solution. Positively charged nano-γ-alumina surfaces effectively sorbed negatively charged sodium dodecyl sulfate at lower pH values. Therefore, retention of organic compounds on sodium dodecyl sulfate-coated nano-γ-alumina occurs. The anionic surfactant sodium dodecyl sulfate is effectively retained on positively charged nano-γ-alumina surfaces *via* formation of self-aggregates[36,37] over a wide pH range (1-6), whereas very little amount of sodium dodecyl sulfate could be retained on inert surface of nano-γ-alumina. Maximum sorption of sodium dodecyl sulfate on nano-γ-alumina was achieved at pH 1-2.9 by shaking the solution containing sodium dodecyl sulfate and nano-γ-alumina for 10 min. When solution was acidified, sodium dodecyl sulfate would form hemi-micelles on nano-γ-alumina by strong sorption. The micelles could trap 4-BPDC molecules homogeneously (Fig. 1). (The anionic surfactant, sodium dodecyl sulfate, was chosen because of its commercial availability in a high purified homogeneous form, low toxicological properties and cost)[35].

Due to retain metal ions on a solid phase materials as metal ions-chelates, the pH of the aqueous solution is an important parameter. The sorption behaviour of cobalt on the modified nano-γ-alumina in water samples was studied in the pH range of 2.0-7.0. The pH of the solution was adjusted at the required value by the addition of 1 mol L^{-1} NaOH or 1 mol L^{-1} HNO_3. According to the results, a quantitative recovery (> 95 %) was found for cobalt at the pH 5.5. Hence, pH 5.5 was chosen as the working pH (Fig. 2).

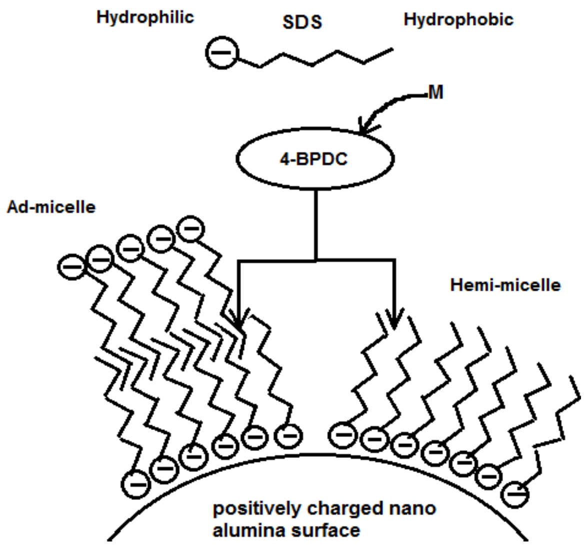

Fig. 1. A suggested binding mode of sodium dodecyl sulfate-4BPDC to nano-alumina surface, M: Co ion

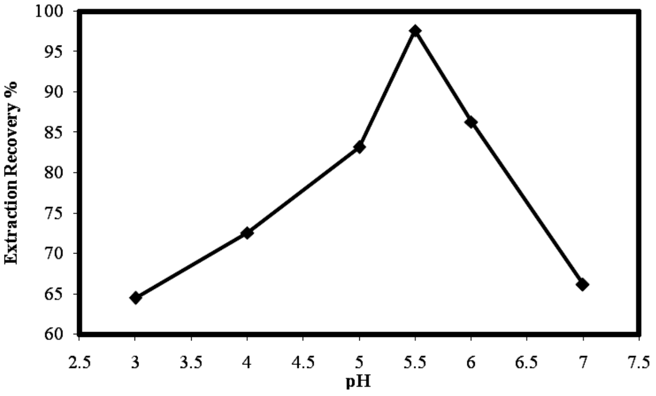

Fig. 2. Effect of pH on sorption of Co

Effect of the amount of sorbent: The influences of various amounts of sorbent (modified nano-γ-alumina) on the sorption of cobalt ions were investigated in the range of 50-500 mg. The results (Fig. 3) show that cobalt ion was completely adsorbed on the sorbent in the 400 mg of the modified nano-γ-alumina. Therefore, 400 mg was selected as the amount of sorbent necessary for all subsequent experiments.

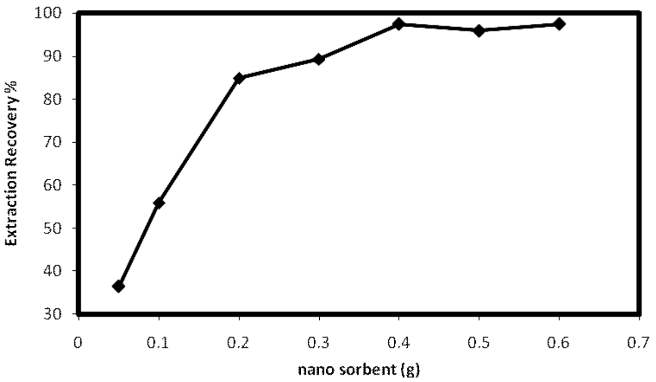

Fig. 3. Effect of the amount of modified nano-γ-alumina on the sorption of Co

Effect of eluting solution condition: In this experiment, a series of experiments were designed and performed to obtain a reasonable eluent to elute completely Co^{2+} ions after their enrichment by chelation with modified nano-γ-alumina. Various acids with various concentrations (0.08-1 mol L^{-1}) were to obtain the optimal eluent for further experiments. The results showed that HCl 0.1 mol L^{-1} accomplish the quantitative elution of target analyte, Co^{2+} ions chelated with from the 4-BPDC in solid phase extraction (Table-1).

TABLE-1
EFFECT OF TYPE AND CONCENTRATION OF
ELUENT ON THE ADSORPTION OF Co

Eluent	Concentration (mol L^{-1})	Recovery (%)
H_2SO_4	0.1	46.4
	0.5	63.5
	1.0	51.4
CH_3COOH	0.1	14.1
	0.5	29.2
	1.0	32.3
HNO_3	0.1	63.5
	0.5	67.5
	1.0	45.3
HCl	0.08	63.5
	0.1	98.8
	0.2	73.6
	0.3	72.6
	0.5	76.7
	1.0	68.5

Effect of volume of ligand: The effects of 4-BPDC volume on the recoveries of analytes were evaluated in the range of 0.05-4 mL. According to Fig. 4, extraction recovery increases up to 0.4 mL of ligand and then remains constant. Thus, 0.4 mL of ligand was chosen as optimum.

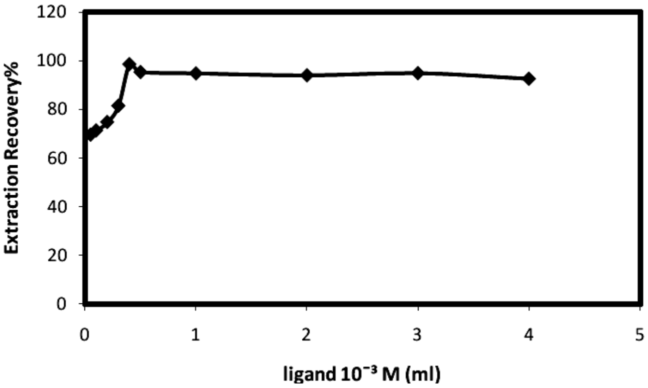

Fig. 4. Effect of volume and concentration of ligand on the sorption of Co

Effect of centrifuge conditions: The effect of centrifugation rate on the absorbance was studied in the range of 1000-4000 rpm. It was found that over 3000 rpm, solid phase completely settled, so the rate of 3500 rpm was selected as the optimum point. And the effects of centrifugation time were investigated on the settles of solid phase in the range of 5-15 min at 3500 rpm. Over 8 min, transfer of solid phase to the bottom of centrifuge tube was complete. So, the optimum centrifugation time was chosen as 10 min.

Effect of other ions: One of the main problems of the atomic absorption spectrometry for determination of the heavy metal ions is the matrix interference. In present work, the influences of the some ions, which are known as interferic ions in the flame atomic absorption spectrometric determination were investigated. Various amounts of metal ions were added to a solution containing fixed amounts of cobalt ions and the present procedure was followed. The results for this study are given in Table-2. The tolerance limit was defined as the ion concentration causing a relative error smaller than ± 5 % related to the coprecipitation and determination of the examined elements. Most of the cations and anions examined did not show interferences at the concentration of 100 times higher than that of cobalt concentration, the results are desired in view of applications to real samples including various salts at high concentration levels.

TABLE-2
INFLUENCES OF SOME FOREIGN IONS ON THE RECOVERIES OF ANALYTES

Ion	Added as	Interferent/Co(II) (weight ratio)	Recovery (%)
Na^+	Na_2SO_4	1000	95.7
K^+	K_2CO_3	1000	100.7
Mn^{2+}	$MnCl_2$	1000	97.8
NO_3^-	$NaNO_3$	1000	95.7
Fe^{3+}	$Fe(NO_3)_3$	1000	97.8
Pb^{2+}	$Pb(NO_3)_2$	1000	96.7
CO_3^{2-}	K_2CO_3	1000	99.7
SO_4^{2-}	Na_2SO_4	1000	95.7
PO_4^{3-}	Na_3PO_4	1000	102.7
Cl^-	$CaCl_2$	200	99.7
Ca^{2+}	$CaCl_2$	200	99.7
Mg^{2+}	$MgCl_2$	200	101.5
Cd^{2+}	$CdSO_4$	200	99.0
Cu^{2+}	$CuSO_4$	100	97.1
Zn^{2+}	$ZnCl_2$	100	100.7
Ni^{2+}	$NiNO_2$	100	101.7
Fe^{2+}	$FeSO_4$	40	95.4

Figures of merit: Table-3 summarizes the analytical characteristics of the optimized method, including limit of detection, reproducibility and enhancement factor. The limit of detection (LOD = 3.1 μg L^{-1}) was calculated as $3S_b/m$ (S_b: standard deviation of the blank signals, m: slope of calibration curve after preconcentration). A good correlation coefficient ($r^2 = 0.996$) was obtained and only small deviations between sequential determinations (RSD = 2.2 %) were found. The calibration curve was investigated up to 900 μg L^{-1}, which was linear. Enhancement factor (EF = 50) was obtained from the slope ratio of calibration curve after and before preconcentration. The equation of the calibration curve after the preconcentration procedure was given in eqn. (1).

$$A = 0.1098C_{(co)} + 0.0098 \ (r^2 = 0.995, r = 0.996) \quad (1)$$

Analysis of real sample: This method was applied to determine of cobalt in water and herbal samples. In order to test the applicability and reliability of the proposed method, tap water, river water, sea water, spinach, black tea, rice, tomato sauce, tobacco, orange, green pepper, potato, mangosteen, strawberry, carrot, apple, kiwi, mushroom, cucumber, lettuce, milk, wheat sprout and honey samples were analyzed. For this purpose, 10 mL of each of the samples were preconcentrated with modified nano-γ-alumina, in accordance with the proposed method. The results are shown in Tables 4 and 5. In all cases the spike recoveries confirmed the reliability of the proposed method.

TABLE-3
ANALYTICAL CHARACTERISTICS OF PROPOSED METHOD

Parameter	Analytical feature
Linear range (μg L^{-1})	10-900
Limit of detection (μg L^{-1}) (n =7)	3.1
Repeatability (RSD %) (n =10)	2.2
Enrichment factor	50
Correlation coefficient (r^2)	0.996

TABLE-4
DETERMINATION OF COBALT IN REAL AND SPIKED WATER SAMPLES

Sample	Co^{2+} spiked (μg L^{-1})	Co^{2+} detected (μg L^{-1})	Recovery (%)
Tap water[a]	-	BDL[d]	-
	50	51.2 (3.4)[e]	102.4
River water[b]	-	10.1 (4.1)	-
	50	58.7 (3.7)	97.7
Sea water[c]	-	13.2 (3.6)	-
	50	60.8 (2.9)	96.2

[a]From drinking water system of Qaemshahr, Iran; [b]Telar River; Qaemshahr, Iran; [c]Caspian sea water, Iran; [d]Below the detection limit; [e]RSD of three replicate experiments

TABLE-5
DETERMINATION OF COBALT IN HERBAL SAMPLES

Sample	Concentration of Co (×10^{-3} mg/g)	Sample	Concentration of Co (×10^{-3} mg/g)
Spinach	0.204 (4.1)[a]	Milk	BDL
Black tea	3.462 (3.9)	Wheat sprout	18.712 (4.4)
Rice	0.656 (4.7)	Orange	0.812 (3.8)
Tomato sauce	BDL[b]	Apple	BDL
Tobacco	BDL	Strawberry	BDL
Honey	BDL	Kiwi	1.572 (4.5)
Mangosteen	0.866 (2.8)	Green pepper	BDL
Potato	0.520 (3.4)	Cucumber	0.994
Mushroom	BDL	Carrot	BDL
Lettuce	0.506 (3.6)		

[a]RSD of three replicate experiments; [b]Below the detection limit

Comparison other solid-phase extraction studies: The data from the present method have been compared with those of recent reported methods on preconcentration of cobalt

TABLE-6
COMPARISON OF THE PROPOSED METHOD WITH OTHER METHODS REPORTED

Sorbents	Technique	LOD (μg L^{-1})	RSD (%)	Recovery (%)	Ref.
Modified Activated carbon	FAAS	0.80	0.85	98.3	[38]
Silica gel	FAAS	-	1.58	97	[39]
Cali resorcinarene	FAAS	2.3	1.1	97	[40]
Styrene–EGDMA	FAAS	2.0	2.52	-	[42]
Surfactant-coated alumina	FAAS	-	1.4-4.0	-	[41]
Modified nano alumina	FAAS	3.1	2.2	71.64	This work

(Table-6). Some parameters obtained are comparable to those presented by other methods. The present work has relatively low LOD and RSD when compared to other sorbent, activated carbon, silica gel, resine. Other parameter, PF (50) is relatively high enough when compared to some of the others methods. In addition, the cited methods are more complicated and use more reagents than this method, namely application of this method is simpler and takes less time.

Conclusion

These results show that the ligand loaded on the modified nano-γ-alumina is sensitive and accurate method for determination of trace amounts of cobalt ions in low concentrations. The results presented in this paper have confirmed the applicability of the separation and preconcentration of metals. The proposed solid phase extraction method is superior for having lower RSD and lower detection limits when compared to other methods (Table-6) and it is simple, rapid and low analysis cost. Therefore, this method should be successfully employed for determination of cobalt in water and food samples by flame atomic absorption spectrometry.

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