Asian Journal of Chemistry Vol. 19, No. 4 (2007), 2541-2549

Application of 1-(2-Pyridylazo)-2-naphthol for Separation and Preconcentration of Trace Amounts of Cobalt(II) in Various Samples and Its Determination by Flame Atomic Absorption Spectrometry

FATAMEH SABER MAHANI and MOHAMMAD ALI TAHER*
Department of Chemistry, Shahid Bahonar University, Kerman, Iran
E-mail: ma_taher@yahoo.com

An atomic absorption spectrometric method for the determination of trace amounts of cobalt(II) after adsorption of its 1-(2-pyridylazo)-2-naphthol (PAN) complex on microcrystalline naphthalene has been developed. This complex is adsorbed on microcrystalline naphthalene in the pH range 3.0-6.0 from a large volumes of aqueous solutions of various alloys and biological samples. After filtration, the solid mass consisting of the cobalt complex and naphthalene was dissolved with 5 mL of dimethyl formamide and the metal was determined by flame atomic absorption spectrometry. Cobalt can alternatively be quantitatively adsorbed on [1-(2-pyridylazo)-2-naphthol]naphthalene adsorbent packed in a column and determined similarly. About 0.35 µg of cobalt can be concentrated in a column from 500 mL of aqueous sample, where its concentration is as low as 0.7 ng/mL. Eight replicate determinations of 1.0 µg/mL of cobalt in final DMF solution gave a mean absorbance of 0.071 with a relative standard deviation of 1.6 %. The sensitivity for 1 % absorption was 62 ng/mL in final DMF solution. The interference of a large number of anions and cations has been studied and the optimized conditions developed were utilized for the trace determination of cobalt in various alloys and biological samples.

Key Words: Separation, Cobalt(II), 1-(2-Pyridylazo)-2-naphthol.

INTRODUCTION

Inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) may be used for the trace determination of metals in complex materials, but these instruments are highly expensive and are not free from matrix effects[1,2]. Spectrophotometry is a simple and inexpensive technique, however it is not selective and sufficiently sensitive[3]. Among the electrochemical techniques, anodic stripping voltammetry (ASV)[4-6] and differential pulse anodic stripping voltammetry (DPASV)[7] are fairly sensitive, however, they are relatively time consuming and lack selectivity and reproducibility[4-7].

The possibility of using 1-(2-pyridylazo)-2-naphthol (PAN) for the analytical purposes was investigated by Cheng and Bray[8]. This reagent reacts with many metal ions in the periodic table to form water-insoluble, coloured chelate complex and has been applied widely in the liquid extraction and spectrophotometric determination of metal ions in materials[9]. Although solvent extraction is a simple and convenient technique, but it is unsuitable if an emulsion forms in an aqueous-organic phase, solubility of the metal complex is poor or the metal complex is formed at a high temperature. These difficulties may be overcome by using molten naphthalene[10], molten paraffin[11], naphthalene adsorption[12] or benzophenone adsorption[13]. The main drawbacks of these methods are the filtration and drying operations that are required. Column methods have also been reported for the preconcentration of metals using various adsorbents such as activated carbon[14], thiol cotton[15], green tea leaves[16], chelating resins[17], cellulose[18] and polythioether[19]. Although some of them are fairly effective, their methods of preparation are lengthy and also involve rigid conditions. The desorption of the metal complex is carried out by the slow process of elution, thus making the method more time consuming.

In the present communication, a highly selective method has been developed for the preconcentration of cobalt(II) from a large volume of the aqueous phase using 1-(2-pyridylazo)-2-naphthol (PAN) and naphthalene as an adsorbent. The method is very convenient and rapid, economical (the reagent selected is easily accessible and cheap as compare to many reagents reported in the literature[20,21] especially as compare to 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol[22,23]), sensitive and selective. The adsorbent can be prepared simply by mixing the acetone solution of naphthalene and reagent in water. The adsorbed metal in the column is not eluted even after washing with water but can be dissolved easily with a small volume (< 5 mL) of the organic solvent like DMF and the metal content can be determined by atomic absorption spectrometry. A number of parameters have been evaluated and the developed method has been applied to the trace determination of cobalt in various standard alloys and biological samples. It may also be employed for the environmental samples.

EXPERIMENTAL

A Zeiss Atom absorption spectrometer FMD 3 (Germany) was used. All absorption measurements were performed under the following operating conditions: wavelength: 240.7 nm; slit setting: 0.1 nm; current: 25 mA; acetylene flow setting: 10 (pressure: 0.9 kp.cm^{-2}); air flow setting: 16 (pressure: 1.2 kp.cm^{-2}). A Beckman pH meter was employed for pH measurements. A funnel-tipped glass tube (60 × 6 mm) was used as a column for preconcentration. It was plugged with polypropylene fibers and then filled with the adsorbent to height of 1.0-1.2 cm after slightly pressing with a flat glass rod. All glassware and column were washed with mixture of concentrated sulfuric acid and concentrated nitric acid (1+1) before use. All reagents were of analytical reagent grade. A standard cobalt solution was prepared from cobalt(II) chloride in distilled water and standardized by known methods[24]. Buffer solution of pH 4.5 was prepared by mixing of 0.5 M acetic acid and 0.5 M sodium acetate solutions in appropriate ratio. A solution of 1-(2-pyridylazo)-2-naphthol (0.1 %) was prepared in ethanol. A solution of naphthalene (20 %) in acetone was used. Solution of alkali metal salts (1 %) and various metal salts (0.1 %) were used to study the interference of anions and cations, respectively. Double distilled water was used whenever required.

Preparation of loaded PAN-naphthalene adsorbent

A mixture consisting of 1 g of PAN, 20 g of naphthalene, 10 mL of water and 100 mL of acetone was stirred on the stirrer hot plate arrangement at *ca*. 40ºC for a few minutes to obtain a clear solution of the reagent and naphthalene. Then it was mixed with 1000-1500 mL of distilled water at room temperature. The coprecipitated mixture was further stirred for 3 h and allowed to stand for 12 h at room temperature. The supernatant solution was drained off with a siphon and the mixture was washed twice with double distilled water. The final adsorbent is a slurry of PAN-naphthalene in water and stored in a bottle.

General procedure for the column method

An aliquot of cobalt solution containing 0.35-13.0 µg of cobalt was taken in a 25 mL beaker. The pH of this solution was adjusted to 4.5 with the addition of 2 mL of buffer solution and diluted to about 20 mL with distilled water. The column loaded with the PAN-naphthalene adsorbent was conditioned to pH 4.5 with 2-3 mL of buffer and then the metal solution was passed through the column at a flow rate of 1 mL min^{-1}. The packing was washed with a small volume of water and then aspirated strongly for a few minutes, pushing down the naphthalene material with a flat glass rod to eliminate the excess of water attached to the naphthalene. The solid mass, consisting of the metal complex along with naphthalene, was dissolved out the column with 5 mL of dimethylformamide (DMF). The solution was aspirated into an air-acetylene flame and the absorbance measured at 240.7 nm against a reagent blank. The absorbances for standard amounts of cobalt were measured and a calibration curve was constructed against a reagent blank prepared in a similar manner.

General procedure for microcrystalline naphthalene

An aliquot of cobalt solution (containing 0.35-13.0 µg) was placed in a 100 mL of an Erlenmeyer flask with tightly fitting stopper. Then 1 mL of

0.1 % of the reagent (PAN) was added to it and the mixture was diluted to 30-40 mL with water. The pH was adjusted to 4.5 with 2 mL of the buffer. The solution was mixed well and allowed to stand for few seconds. Then, 2 mL of a 20 % solution of naphthalene in acetone was added to it with continuous shaking. The solid mass so formed consisting of naphthalene and metal complex was separated by filtration on a Whatman filter paper (No. 1041). The residue was dried in the folds of a filter paper and transferred to the Erlenmeyer flask. The solid mass consisting of the metal complex along with naphthalene was dissolved with 5 mL of dimethylformamide (DMF). The solution was aspirated into an air-acetylene flame and the absorbance measured at 240.7 nm against a reagent blank solution prepared in the same way. A calibration graph was prepared by taking various known amounts of cobalt under the conditions given above.

RESULTS AND DISCUSSION

Reaction conditions

The reaction conditions were investigated with 5 µg of cobalt. Adsorption were carried out at different pH, keeping other variables constant. It was found that the cobalt complex was quantitatively adsorbed on naphthalene in the pH range 3.0-6.0. Addition of 0.5-8 mL of buffer, did not have any effect on the adsorption. Therefore, 2.0 mL of the buffer was used in all the subsequent experiments. The reagent concentration was also varied. It was found that adsorption was quantitative for 0.2-4.0 mL of 0.1 % reagent. Consequently, 1.0 mL of reagent solution was used in subsequent studies. Various amounts of naphthalene was added to the sample solution keeping other variables constant, it was observed that the peak height remained constant with the addition of 1.0-4.5 mL of naphthalene solution. Therefore, 2 mL of 20 % naphthalene solution was used in subsequent studies. The effect of shaking time on the adsorption indicated that the peak height remained constant over the range of 0.5-7.0 min. Therefore, 1 min of shaking time was recommended in the present work.

While in the case of column method, the flow rate was 0.2 to 8 mL min^{-1}. It was found that a flow rate of 0.2-5.0 mL min^{-1} did not affect adsorption. A flow rate of 1 mL min^{-1} was recommended in all experiments.

The volume of the aqueous phase was varied in the range of 10-700 mL under the optimum conditions, keeping other variables constant. It was observed that the signal height was almost constant up to 300 mL (preconcentration factor of 60). However, for convenience, all the experiments were carried out with 20-40 mL of the aqueous phase.

Whereas, in the case of column method, peak height was almost constant up to an aqueous phase volume of 500 mL. Therefore, a preconcentration factor 100 can achieved by the column.

Choice of solvent

A number of solvent were tried to dissolve the PAN-cobalt-naphthalene mixture. Since the solid mass is dissolved in a small volume (3-5 mL) of solvent, it is essential to select a solvent in which the chelate is highly soluble. The solid material is insoluble in ordinary organic solvents such as toluene, 1,2-dichloroethane, *n*-hexane, nitrobenzene, *iso*-amyl alcohol, *n*-amyl alcohol, ethyl acetate, methyl isobutyl ketone, chloroform and dioxane but soluble in dimethyl sulfoxide, dimethyl formamide (DMF) and propylene carbonate. DMF was preferred because of the high solubility and stability. It was found that 2-3 mL of this solvent was sufficient to dissolve the mixture, thus enhancing the sensitivity of the method further. Since only a small volume (3-5 mL) of the solvent is required to dissolve the solid mass, it was essential to study the effect of the surplus water attached to the adsorbent. It was found that the surplus water caused the absorbance to decrease by 12-15 % and led to an error in the determination. Thus it was necessary to eliminate the water attached to naphthalene completely by aspirating it.

Calibration and sensitivity

Considering that it is possible to retain 0.15 µg of cobalt from 500 mL of solution passing through the column, the dissolution with 5.0 mL DMF gives a detection limit of 0.3 ng/mL for cobalt at the minimum instrumental settings. The linearity was maintained in the concentration range of 0.7 ng/mL to 0.5 µg/mL cobalt in aqueous solution or 0.07 to 2.6 µg/mL cobalt in final DMF solution with a correlation factor of 0.9996. Eight replicate determinations of 5 µg of cobalt in final 5 mL DMF solution gave a mean absorbance of 0.071 with a relative standard deviation of 1.6 %. The sensitivity for 1 % absorption was 62 ng/mL in final DMF solution.

Retention capacity of the adsorbent

The retention capacity of the adsorbent was determined by a batch method. The experiment was performed by taking 500 µg of cobalt, 2 mL of buffer solution (pH 4.5) and 40 mL of water in a beaker. This solution was transferred into a separating funnel and then a suitable amount of the PAN-naphthalene adsorbent was added. The separating funnel was shaken vigorously on a mechanical shaker for 5 min. The solid mass was separated by filtration and cobalt was determined from the filtrate by AAS. The solid mass on the filter-paper was dried in an oven, kept in a desiccator and then weighed to determine the mass of the adsorbent. The maximum amount of cobalt retained with 6.5 mg g^{-1} of PAN in the adsorbent.

Effect of diverse ions

Various salts and metal ions were added individually to a solution containing 5 µg of cobalt and the general procedure was applied. The tolerance limit was set as the diverse ion required to cause ± 3 % error in the determination of cobalt. The results obtained are given in Table-1. Among the anions examined, large amounts of chloride, bromide, nitrate, acetate, carbonate and sulphate could be tolerated. Citrate, oxalate, orthophosphate, tartrate and EDTA interfered. Except EDTA, a relatively low amount of these anions could be tolerated. Obviously the stability constants of Co-EDTA complex must be higher than Co-PAN complex. Of the metal ions examined, did not interfere up to mg levels. Thus the proposed method is selective and can be used to determination of cobalt in standard alloys and biological samples without any prior separation.

TABLE-1
EFFECT OF DIVERSE SALTS AND METAL IONS

Salt or ion	Tolerance limit	Salt or ion	Tolerance limit
$CH_3COONa.3H_2O$, KNO_3	1 g	Pb(II)	70 mg
K_2SO_4	300 mg	Cd(II)	60 mg
KI, NaF	250 mg	Sb(III)	50 mg
Thiourea	150 mg	Ag(I)	20 mg
NH_4Cl, $Na_3PO_4.12H_2O$,	120 mg	Cu(II), Fe(III)	15 mg
K_2CO_3	120 mg	Mn(II), Ti(IV)	13 mg
$Na_2S_2O_3$	100 mg	Cr(VI), Cr(III), Ni(II)	10 mg
Sodium potassium tartrate	20 mg	Se(VI), Ga(III), Al(III)	9.5 mg
KSCN	15 mg	U(VI)	7.0 mg
Sodium oxalate	12 mg	Mo(VI)	6.5 mg
Trisodium citrate	10 mg	Pd(II), Te(IV)	5.9 mg
Dimethyl glyoxime	9 mg	Os(VIII)	4.5 mg
Na_2EDTA	70 μg	Bi(III), Hg(II)	3.6 mg
Mg(II)	200 mg	Rh(III), V(V)	3.5 mg
Ca(II)	120 mg	Ru(III)	3.0 mg

Analysis of cobalt in standard alloys and steel samples

The proposed method was applied to the determination of cobalt in Nippo Keikinzoku Kogyo (NKK) CRM No. 916 and No. 920 Aluminum Alloy and Japanese Standards of iron and Steel (JSS) CRM 651-7 and 653-7 Stainless Steel. A sample of the standard aluminum alloy or steel (0.1 g) was completely dissolved in 6-14 mL of hydrochloric acid (1+1) by heating on a water-bath and then 1 mL of 30 % (v/v) hydrogen peroxide was added to it. The excess of peroxide was decomposed by heating the sample on the water-bath. The solution was cooled, filtered if needed and diluted to 100 mL with distilled water in a standard flask. An aliquot (1-2 mL) of this sample was taken in a 20 mL beaker and the general procedure was applied. The results obtained are given in Table-2. These results are in agreement with the certified values.

TABLE-2
ANALYSIS OF COBALT IN STANDARD ALLOYS

Sample	Composition (%)	Concentration (%)	
		Certified value	Found*
JSS 651-7 Stainless Steel	C, 0.047; Si, 0.072; P, 0.028; Cr, 18.60; S, 0.0063; Mo, 0.84; Al, 0.002; N, 0.0312; Cu, 0.082; Mn, 1.72; Ni, 9.20	0.22	0.213 ± 0.008[a]
JSS 653-7 Stainless Steel	C, 0.068; Si, 0.63; Cr, 22.53; Cu, 0.030; Mn, 1.72; Ni, 13.91; N, 0.0276	0.35	0.34 ±0.01[b]
NKK No. 916 Aluminum Alloy	Si, 0.41; Fe, 0.54; Mg, 0.10; Cr, 0.05; Zn, 0.30; Ti, 0.10; Sn, 0.05; Pb, 0.04; Sb, 0.01; B, 0.0006; Zr, 0.05; Bi, 0.03; Cu, 0.27; Mn, 0.11; Ni, 0.06; V, 0.02	0.03	0.029 ± 0.001[a]
NKK No. 920 Aluminum Alloy	Si, 0.78; Fe, 0.72; Mg, 0.46; Cr, 0.27; Zn, 0.80; Ti, 0.15; Sn, 0.20; Pb, 0.10; Sb, 0.10; Bi, 0.06; Ga, 0.05; Ca, 0.03; Cu, 0.71; Mn, 0.20; Ni, 0.29; V, 0.15	0.10	0.097 ± 0.004[b]

*Average of five determinations, ± standard deviation, [a]Column method was applied, [b]Microcrystalline naphthalene method was applied.

Analysis of cobalt in biological samples

The accuracy and applicability of the proposed method has been applied to the determination of cobalt in National Institute for Environmental Studies (NIES) No.1 Pepperbush; NIES, No.3 Chlorella; NIES, No.7 Tea Leaves. A 0.1 g sample was taken in a beaker and dissolved in concentrational nitric acid (*ca.* 5 mL) with heating. The solution was cooled, diluted and filtered. The filtrate was made to 100 mL with water in a calibrated flask. NIES, No.8 Vehicle Exhaust Particulates (1 g) was dissolved in 18 mL of concentrated nitric acid, 18 mL of concentrated perchloric acid and 2 mL of concentrated hydrofluoric acid in a 100 mL teflon beaker, evaporated to a small volume, filtered through a filter paper and made up to 100 mL with distilled water. An aliquot (10-50 mL) of the sample solution was taken individually and cobalt was determined by the general procedure. The results are given in Table-3 which are in good agreement with the certified values.

TABLE-3
ANALYSIS OF COBALT IN BIOLOGICAL SAMPLES

Sample	Composition	Concentration (µg/g)	
		Certified value	Found[*+]
NIES, No.1 Pepperbush	K, 1.51 ± 0.06; Mn, 0.203±0.107; Mg, 0.408±0.020; Ca, 1.38±0.07% Cd, 6.7±0.5; Ni, 8.7±0.6; Fe, 205±17; Cu, 12±1; Pb, 5.5±0.8; Zn, 340±20; Rb, 75±4; Ba, 165±10; Na, 106±13; Sr, 36±4; As, 2.3±0.3; P,(1100); Cr,(1.3); Cs, (1.2); Tl, (0.13); Hg, (0.056) µg/g	23 ± 3	24 ± 1[b]
NIES, No.3 Chlorella	K,1.24±0.06; Ca, 0.49±0.03; Fe, 0.185±0.010; Mg, 0.33±0.02; P,(1.7) Zn, 20.5±1.0; Sr, 40±3; Cu, 3.5±0.3; Mn, 69±5; Cd,(0.026); Pb,(0.60); Sc, (0.013) µg/g	0.87 ± 0.05	0.85 ± 0.03[a]
NIES, No.7 Tea Leaves	Pb, 0.80; Cd, 0.030; Sb, 0.014; Zn, 33; Cr, 0.15; Al, 775; Mg, 1530; Ba, 5.7; K, 18600; Sc, 0.011; Na, 15.5; Sr, 3.7; Ca, 3200; Cs, 0.22l; Cu, 7.0; Mn, 7.00; Ni, 6.5 µg/g	0.12	0.122 ± 0.003[a]
NIES, NO. 8 Vehicle Exhaust Particulates	K, 0.115±0.008; Ca, 0.53±0.02; Mg, 0.101±0.005; Al, 0.33±0.02; Zn, 0.104±0.005; Na, 0.92±0.008 Sr, 89±3; Cu, 67±3; Ni, 18.5±1.5; Cd, 1.1±0.1; Pb, 219±9; As, 2.6±0.2; Cr, 25.5±1.5; V, 17±2; Sb, 6.0±0.4; Cs, (0.24); Rb, (4.6); Sc, (0.055); La, (1.2); Br, (56); Ag, (0.2); Se, (1.3); Mo, (6.4); Ce, (3.1); Th, (0.35); Sm, (0.20); Eu, (0.05); Lu, (0.02) µg/g	3.3 ± 0.3	3.4 ± 0.1[b]

*Average of five determinations, ± standard deviation, [+]Standard addition method was applied, [a]Column method was applied, [b]Microcrystalline naphthalene method was applied, NIES: National Institute of Environmental Studies reference materials, NIES, No. 1, No. 3 & No. 8 (Values in parentheses were approximate and not certified).

Conclusion

An efficient adsorbent generated simply by mixing the solutions of PAN and naphthalene has been developed and tried for the preconcentration of cobalt from a large volume of the aqueous solution of standard reference materials using AAS. Since PAN reacts with many metal ions, therefore, similar procedure may also be developed for other metal ions too. It is not possible to develop selective methods for metal ions using this adsorbent in spectrophotometry since many metal-PAN complexes absorb at close wavelengths 550-590 nm. However, with the use of AAS this problem can be easily solved.

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(*Received*: 10 December 2005; *Accepted*: 27 November 2006) AJC-5284