

Flame atomic absorption spectrometric determination of trace amounts of cobalt in standard alloys and biological samples after preconcentration of its 1,10-phenanthroline complex on tetraphenylborate – microcrystalline naphthalene adsorbent

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A rapid, simple and sensitive method has been developed for determination of trace amount of cobalt using flame atomic absorption spectrometry. Cobalt is quantitatively retained as 1,10-phenanthroline-tetraphenylborate ion-associate complex on microcrystalline naphthalene in the pH range 2.6-9.5 from a large volume of its aqueous solutions of various standard alloys and biological samples. After filtration, the solid mass consisting of the cobalt complex and naphthalene is dissolved in 5 mL of dimethylformamide (DMF) and the metal is determined using flame atomic absorption spectrometry by measuring the absorbance at 240.7 nm. Cobalt-1,10-phenanthroline complex can alternatively be quantitatively retained on ammonium tetraphenylborate-naphthalene adsorbent packed in a column at a flow rate of 2 mL/min under the same conditions and determined similarly. In this case, 1.0 µg of cobalt is concentrated in a column from 400 mL of its aqueous sample, where its concentration is as low as 2.5 ppb. Eight replicate determinations of 4.0 ppm cobalt gives a mean absorbance of 0.120 with a relative standard deviation of 1.8%. The sensitivity for 1% absorption is 147 ppb. The conditions have been optimized and utilized for trace determination of cobalt in various standard samples.

Sodium tetraphenylborate (TPB) and its derivatives have been used in the estimation of alkali and other univalent metal ions¹⁻³. It has also been used as a counter ion in the extraction and adsorption of some metal complexes on microcrystalline naphthalene⁴. A literature survey reveals that metal ions may be preconcentrated on various adsorbents such as thiol cotton⁵, silanized glass beads⁶, silica gel⁷, Amberlite XAD-4 resin⁸, cellulose⁹, green tea leaves¹⁰ and polythioether foams¹¹. Some of these adsorbents may be fairly effective for preconcentration of metal ions, but their methods of preparation are lengthy and involve rigid control of experimental conditions. The desorption of the metal is also carried out by the slow process of elution (the metal complex is probably held by the interior surfaces of the adsorbent and thus the adsorbed complex is not eluted easily), hence the procedure is time consuming. Solvent extraction is a simple and convenient technique for separating and concentrating metal ions, but it can not be applied directly to metal ions which form stable complexes with the chelating agents only at elevated temperature. This difficulty may be overcome by

using naphthalene as the extractant¹² for thermally stable metal chelates¹³. Solid-liquid separation after adsorption of metal chelates on microcrystalline naphthalene is more rapid and convenient and can be applied to many types of metal complexes¹⁴⁻¹⁷. The preconcentration of metals as their cationic complexes is also possible by passing their aqueous solution over naphthalene-NH₄-TPB adsorbent taken in a column. The microcrystalline naphthalene method is rapid but the column method gives a better preconcentration factor¹⁸⁻²⁰.

In the present paper, a highly selective and sensitive preconcentration method has been developed, using 1,10-phenanthroline as the complexing agent, TPB⁻ as the counter ion and microcrystalline naphthalene as adsorbent. The method is very convenient and rapid, economical (the reagent selected is easily accessible and cheap as compared to many reagents reported in the literature²¹⁻²³ especially as compared to 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol²⁴), sensitive and selective. The metal complex along with the adsorbent can be dissolved easily in a few millilitre of

DMF and determined by flame atomic absorption spectrometry. The interference of a number of metal ions and anions on the determination of cobalt has been studied in detail and the developed method employed for its estimation in various complex materials like standard alloys and biological samples.

Materials and Methods

A Shimadzu AA 670 flame atomic absorption spectrometer was used with the following conditions: wavelength: 240.7 nm, lamp current: 6.0 mA, slit width: 0.2 nm, burner height: 6.0 mm, acetylene flow: 2.2 lmin⁻¹, air flow: 8.0 lmin⁻¹. 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 a 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 nitric acid (1+1) before use.

A standard cobalt solution was prepared from cobalt(II) chloride in distilled water and standardized by known methods²⁵. A solution of 1, 10-phenanthroline (0.2%) was prepared in distilled water in the presence of a few drops of acetic acid. Buffer solutions of pH 3-6, 6-8 and 8-11 were prepared by mixing appropriate ratios of acetic acid (0.5 M)-sodium acetate(0.5 M), sodium dihydrogen phosphate (0.1 M)-dipotassium hydrogen phosphate (0.1 M) and ammonia solution (0.5 M)-ammonium acetate (0.5 M) solutions, respectively. A solution of sodium tetraphenylborate (1%, TPB) was prepared in distilled water. A solution of naphthalene (20%) was prepared in acetone. Solutions of alkali metal salts (1%) and various metal salts (0.1%) were used for studying the interference of anions and cations, respectively.

To prepare NH₄ TPB adsorbent a solution of naphthalene was prepared by dissolving 20 g of naphthalene in 40 mL of acetone on a hot-plate stirrer at 30-35°C. This solution was mixed with 1500 mL of distilled water containing 25 mL of 1 mol/L ammonium acetate and 75 mL of 1 mol/L ammonia solution (~pH 9.5), with continuous stirring at room temperature. Then, to this solution, 500 mL of an aqueous solution containing 1.7 g of TPB was added. The solution was stirred for about 2 h and then allowed to stand for another 2 h. The supernatant solution was decanted off and the remaining solid mass was washed twice with distilled water. The

adsorbent in the form of a slurry was stored in a bottle for subsequent use.

General procedure for the column method

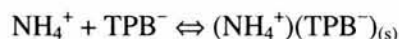
An aliquot of the solution (up to 400 mL) containing 1.0-35.0 µg of cobalt was taken in a beaker and 2.0 mL of 1,10-phenanthroline solution (0.2%) and 2.0 mL of acetate buffer of pH ~4.5 were added to it. The column loaded with the adsorbent NH₄-TPB-naphthalene was conditioned to pH ~4.5 by passing 2-5 mL of the acetate buffer solution at a flow rate of 2 mL min⁻¹. The cobalt sample solution prepared above was then passed at a flow rate of 2 mL min⁻¹. The packing in the column was washed with a few milliliters of distilled water and then aspirated strongly for 2-3 min, pushing down the solid mass in the column with a glass rod in order to eliminate the excess water attached to the adsorbent. The metal complex was dissolved out of the column along with naphthalene with 5 mL of DMF. The solution was aspirated into an air-acetylene flame and the absorbance was measured at 240.7 nm against a reagent blank.

General procedure for microcrystalline naphthalene

An aliquot of cobalt solution (up to 200 mL containing 1.0-35.0 µg) was placed in an Erlenmeyer flask with a tightly fitting stopper. Then a 2.0 mL of 1,10-phenanthroline solution (0.2%) was added to it. The pH was adjusted to ~4.5 with 2 mL of the buffer, and then 2 mL of TPB (1%) solution was added to it. The solution was mixed well and allowed to stand for a 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 DMF. The solution was aspirated into an air-acetylene flame and the absorbance was 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

The TPB⁻ forms a weakly bonded ion-pair with NH₄⁺ in aqueous solution and coprecipitates with microcrystalline naphthalene as follows:



From the experimental observations, the NH_4 -TPB ion-pair, produced from TPB^- and ammonium acetate in aqueous solution, is found to be unstable when supported on naphthalene and partly desorbed from the surface of the naphthalene in the column on the passage of buffer of $\text{pH} \sim 4.5$. However, the NH_4 -TPB ion-pair prepared in acetate buffer of $\text{pH} \sim 9.5$ is highly stable and TPB^- is not desorbed even on washing with water or the buffer of $\text{pH} \sim 4.5$ later on. The adsorbent shows excellent absorption characteristics for various cationic metal complexes, such as $\text{Fe}(1,10\text{-Phen})_3^{2+}$. In this work, TPB^- has been selected as the counter-ion because of its purity and moderate price.

The optimum conditions have been established using 20 μg of cobalt. The adsorption of cobalt on this adsorbent is found to be maximum in the pH range 2.6-9.5. In subsequent studies, the pH was maintained at ~ 4.5 . Addition of 0.5-5 mL of the buffer did not affect the retention of cobalt and hence 2 mL buffer is recommended. Cobalt was quantitatively adsorbed on the adsorbent over the range 1.0-3.0 mL of 1,10-phenanthroline solution (0.2%). Therefore, a 2.0 mL volume of the reagent is recommended in the present study.

Various volume of 20% solution of naphthalene in acetone were added to the sample solutions keeping other variables constant. It was observed that the signal height remained constant with the addition of 1.0-4.0 mL of naphthalene solution. Therefore, 2.0 mL of its solution was used in the subsequent study. The effect of shaking time on the adsorption indicates that the signal height remained constant over a range 0.5-5.0 min. Therefore, 1.0 min of shaking time was maintained in the present work.

In the case of the column method, the flow rate was varied from 0.2 to 8 mL/min. It was found that a flow rate of 0.2-7.0 mL min^{-1} did not affect adsorption. A flow rate of 2 mL/min was recommended in all experiments, however in the case of a large volume of the sample, a flow rate of 7 mL/min may be used.

The volume of the aqueous phase was varied in the range of 10-700 mL under the optimum conditions, keeping the other variables constant. It was observed that the signal height was almost constant up to 200 mL (preconcentration factor of 40). However, for convenience, all the experiments were carried out with 40 mL of the aqueous phase, whereas, in the case

of column method, signal height was almost constant up to an aqueous phase volume of 400 mL. Therefore, a preconcentration factor of 80 can be achieved by the column which is two times than the microcrystalline method.

A number of solvents were tried, to dissolve the metal complex along with naphthalene. 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, stable and is sensitive for atomic absorption spectrometric measurements. The solid material is insoluble in ordinary organic solvents such as toluene, 1,2-dichloroethane, *n*-hexane, nitrobenzene, isoamyl alcohol, *n*-amyl alcohol, ethyl acetate, methyl isobutyl ketone, chloroform and dioxane, but is soluble in dimethyl sulfoxide, DMF, and propylene carbonate. DMF was preferred because of the high solubility of the metal complex and naphthalene. It was found that 2-3 mL of this solvent was sufficient to dissolve the entire mixture, thus further enhancing the sensitivity of the method.

The retention capacity of adsorbent was determined by a batch method. The experiment was performed by adding 500 μg of cobalt, 2 mL of the buffer ($\text{pH} \sim 4.5$) and a suitable amount of reagent 1,10-phenanthroline to 40 mL of water in a beaker. This solution was transferred into a mixture and then a suitable amount of the adsorbent naphthalene- NH_4 -TPB was added to it. The separatory funnel was vigorously shaken on a mechanical shaker for 5 min. The solid mass was separated by filtration and cobalt in the filtrate was determined 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 was 1.4 mg/g of the adsorbent.

Preliminary experiments indicates that 0.4 μg of cobalt can be preconcentrated from 400 mL of the aqueous solution on this adsorbent in a column. It can be dissolved with 5.0 mL DMF and thus gives a detection limit of 1 ppb for cobalt at the minimum instrumental settings. The linearity was maintained in the concentration range 2.5 ppb to 3.5 ppm cobalt in aqueous solution or 0.20 to 7.0 ppm cobalt in the final DMF solution with a correlation factor of 0.9997. Eight replicate determinations of 20 μg of cobalt in 5 mL DMF solution gave a mean absorbance of 0.120 with a relative standard deviation of 1.8%. The sensitivity for 1% absorption was 147 ppb.

Table 1—Tolerance limits for the determination of 5 µg of cobalt

Salt or ion	Tolerance limit
CH ₃ COONa.3H ₂ O, KNO ₃	1 g
K ₂ SO ₄ , KI	350 mg
NH ₄ Cl, Na ₃ PO ₄ .12H ₂ O, K ₂ CO ₃ , NaF	250 mg
Sodium potassium tartrate	90 mg
Thiourea, KSCN, NaClO ₄	60 mg
Sodium oxalate, Na ₂ S ₂ O ₃	20 mg
Trisodium citrate	15 mg
Mg(II)	150 mg
Ca(II)	95 mg
Cd(II), Sb(II), Pb(II), Mn(II)	50 mg
Ti(IV),	25 mg
Zn(II), Ag(I), Al(III)	15 mg
Cr(VI), Cr(III)	10 mg
Se(VI), Ga(III)	9.0 mg
Mo(VI), U(VI)	8.5 mg
Pd(II), Te(IV)	7.0 mg
Os(VIII), Bi(III)	6.5 mg
Rh (III), V(V)	6.0 mg
Ru(III), Hg(II)	4.5 mg
Ni(II), Cu(II)	1.0 mg

Effect of diverse ions

Various salts and metal ions were added individually to a solution containing 20 µg of cobalt and the general procedure was applied. The tolerance limit was set as the concentration of the diverse ion required to cause $\pm 3\%$ error in the determination of cobalt. The results obtained are given in Table 1. Among the salts examined, most could be tolerated up to gram or milligram levels except EDTA. Citrate or tartrate enhanced the tolerance limit of coexisting metal ions being acting as masking agent for them. Thus the proposed method is relatively selective and can be used for the determination of cobalt in various alloys and biological samples without any prior separation.

Analysis of cobalt in standard alloys and steel samples

The proposed method was applied to the determination of cobalt in Nippo Keikinzoku Kogyo (NNK) 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 0.1 g sample of the standard aluminum alloy or steel 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

Table 2—Analysis of cobalt in standard alloys

Sample	Certified value (%)	Determined by present method* (%)
JSS 651-7 Stainless Steel	0.22 $\pm$ 0.008	0.214 $\pm$ 0.006 ^a
JSS 653-7 Stainless Steel	0.35 $\pm$ 0.01	0.343 $\pm$ 0.009 ^b
NKK No. 916 Aluminum alloy	0.03 $\pm$ 0.004	0.029 $\pm$ 0.002 ^a
NKK No. 920 Aluminum alloy	0.10 $\pm$ 0.007	0.104 $\pm$ 0.005 ^b

*Average of five determinations, $\pm$ standard deviation

^a Column method was applied.

^b Microcrystalline naphthalene method was applied.

Table 3—Analysis of cobalt in biological samples

Sample	Certified value (µg/g)	Determined by present method* (µg/g)
NIES, No.1 Pepperbush	23 $\pm$ 3	22 $\pm$ 1 ^b
NIES, No.3 Chlorella	0.87 $\pm$ 0.05	0.84 $\pm$ 0.03 ^{a+}
NIES, No.7 Tea leaves	0.12 $\pm$ 0.008	0.115 $\pm$ 0.006 ^{a+}
NIES, No. 8 Vehicle exhaust particulates	3.3 $\pm$ 0.3	3. 2 $\pm$ 0.2 ^b

*Average of five determinations, $\pm$ standard deviation

^aStandard addition method was applied.

^bColumn method was applied.

^bMicrocrystalline 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)

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 of this sample was taken in a beaker and the general procedure was applied. The results obtained are given in Table 2. These results are in agreement with the certified values.

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 conc. nitric acid ($\approx$ 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.

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