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Column Preconcentration of Cobalt Using 4-(5-Bromo-2-pyridylazo)-1,3-diaminobenzene and Ammonium Tetraphenyl- borate Supported on Naphthalene and Its Analysis Using Atomic Absorption Spectrometry†

TOHRU NAGAHIRO*, KATSUYA UESUGI and MASATADA SATAKE‡
Faculty of Engineering
Himeji Institute of Technoloy, Himeji 671-22, Japan

A method has been established for the determination of trace amount of cobalt employing column preconcentration of cobalt with 4-(5-bromo-2-pyridylazo)-1,3-diaminobenzene(5-Br-PADAB) and ammonium tetraphenylborate supported on microcrystalline naphthalene as an adsorbent for cobalt/5-Br-PADAB complex. The optimum pH range for the formation of cobalt/5-Br-PADAB complex and its adsorption on to the adsorbent packed into a column was 3.5–6.0. The column content was dissolved with N,N-dimethyl formamide and cobalt was determined using flame atomic absorption spectrometry. The calibration graph was linear up to 18 μg of cobalt in 5 ml of final solution. Seven replicate analyses for 12 μ g of cobalt gave a mean absorbance of 0.110 with a relative standard deviation of 0.83%. The method has been applied for cobalt analysis in alloys, pepperbush and pond sediment.

INTRODUCTION

The methods of solid-liquid separation after liquid-liquid extraction using naphthalene as an extractant[1–7] and solid-liquid separation after the adsorption of metal complexes on to microcrystalline naphthalene[8–14] were developed for the determination of trace amounts of metals. These methods are especially useful for the metal complexes that have low solubility in organic solvents, but are more complicated than the usual liquid-liquid extraction method. In order to overcome this drawback, the method of preconcentration of metal ion using a column loaded with an adsorbent has been developed for the determination of trace amounts of metals. The ion-pair materials such as protonated 1,10-phenanthroline tetraphenylborate[15], tetradecyldimethylbenzylammonium(TDBA)/thiocyanate[16], TDBA/perchlorate[17], TDBA/1,2-dihydroxybenzene-3,5-disulfonate[18] supported on micro-

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‡Faculty of Engineering, Fukui University, Fukui 910, Japan

crystalline naphthalene have been used as the adsorbents for metal ions or metal complexes. This method provides the basis for a simple and rapid technique for the preconcentration of metal ions from an aqueous phase. The proposed method in this communication has been established for the determination of trace amount of cobalt employing column preconcentration of cobalt with 4-(5-bromo-2-pyridylazo)-1,3-diaminobenzene(5-Br-PADAB) and ammonium tetraphenylborate supported on microcrystalline naphthalene and applied toward cobalt analysis in alloys, pepperbush and pond sediment.

EXPERIMENTAL

All absorbance measurements were made with a Perkin-Elmer Model 403 atomic absorption spectrophotometer. A hollow-cathode lamp for cobalt was obtained from Hamamatsu Photonics Ltd. Measurements of pH were carried out with a Toa-Dempa HM-6A pH meter. A funnel-tipped glass tube (60×6 mm i.d.) was used as a column.

All reagents were of analytical-reagent grade and deionised, distilled water was used throughout.

Standard cobalt(II) solution: Prepared by diluting an aliquot of a standard stock solution (1000 ppm, Wako Chemicals) with water.

5-Br-PADAB solution, 0.5%: Prepared in ethanol.

Buffer solution, pH 4.8: Prepared by mixing 1 M acetic acid and 1 M ammonium acetate.

Adsorbent: A 10 g amount of naphthalene was dissolved in acetone and diluted to 30 ml. The naphthalene solution was then transferred into 1500 ml of an aqueous solution containing 100 ml of a buffer solution (pH 9.5) prepared by mixing 1 M ammonia water and 1 M ammonium acetate in a fast stream with continuous stirring. A 100 ml of an aqueous solution containing 1.7 gm. of sodium teraphenylborate was added to this suspension in the same manner. This suspension was stirred constantly for 2 hrs. and then allowed to stand for an hrs. The supernatant liquid was drained off by decantation and the naphthalene mixture was washed two or three times with water. The slurry naphthalene mixture was stored in a bottle.

General procedure

A 1 ml aliquot of 0.5% 5-Br-PADAB and 1 ml of buffer solution (pH4 .8) are added to about 20 ml of sample solution containing up to 18 μg of cobalt in a 50 ml beaker and the pH is adjusted to 4.8 with 1 M sodium hydroxide solution. A 2 ml aliquot of buffer solution (pH 4.8) is passed through the column loaded with adsorbent (1 cm in height) at a flow-rate of 2 ml min^{-1}. The sample solution is then added and the column is washed with distilled water. After the column was aspirated to exclude water, the coloured adsorbent is dissolved with N,N-dimethylformamide and diluted to 5 ml. The solution is then aspirated into

air-acetylene flame to be subjected to a measurement at 241 nm with a cobalt hollow-cathode lamp.

RESULTS AND DISCUSSION

Effect of pH

The effect of pH on the formation of cobalt/5-Br-PADAB complex (Co, 12 μg) and its adsorption on the adsorbent was studied by the general procedure. The optimum pH range was 3.5–6.0. Subsequent studies were conducted at pH 4.8.

Effect of 5-Br-PADAB Concentration

Various amounts of 0.5% 5-Br-PADAB solution were added to the solutions containing 12.0 μg of cobalt(II) and the general procedure was followed. Cobalt was quantitatively determined in the range of 0.3–2.0 ml of 0.5% 5-Br-PADAB solution. Consequently, 1 ml of 0.5% 5-Br-PADAB solution was added in subsequent studies.

Effect of flow-rate and volume of aqueous phase

The effect of flow-rate on the adsorption of cobalt/5-Br-PADAB complex (Co, 12 μg) on to the adsorbent was studied by the general procedure. The flow-rate was varied from 0.5 to 10.0 ml min^{-1}. The flow-rate did not affect the adsorption in this range. Subsequent studies were carried out at a flow-rate of 2 ml min^{-1}. The volume of aqueous phase containing 12 μg of cobalt was varied from 10 to 1000 ml and the adsorption remained maximum and constant up to 500 ml. Subsequent studies were carried out at about 20 ml for convenience.

Calibration graph, precision and sensitivity

A calibration graph for cobalt was constructed by the general procedure. It was linear up to 18 μg of cobalt in 5 ml of the final solution. Seven replicate analyses for 12 μg cobalt gave a mean absorbance 0.110 with a relative standard deviation of 0.83%. The sensitivity for 1% absorption was 0.096 μg ml^{-1}.

Effect of foreign ions

The sample solutions containing 12 μg of cobalt(II) and various amounts of foreign ions were prepared and the determination of cobalt was carried out using the general procedure. The tolerance limits of foreign ions (error < 3%) are given in Table 1. The method is fairly selective and may be applied for cobalt analysis in various samples.

Application of the Method to Standard Reference Samples

The proposed method has been applied to the determination of cobalt in standard reference samples.

TABLE 1
EFFECT OF FOREIGN SALTS AND IONS

Salts or ions	Tolerance limit
Thiourea	500 mg[a]
Glycoletherdiamine-N,N,N′,N′-tetraacetic acid	40 mg
$Na_2C_2O_4$	4 mg
KCN	2 mg[a]
Na_2SO_4, KSCN	2 mg
Sodium tartrate, NaCl, NH_4Cl, NaI, $NaClO_4$, $CH_3COONa{\cdot}3H_2O$, KNO_3, KH_2PO_4	1 mg
Mg(II), Al(III), Ca(II), V(V), Cr(VI), Mn(II), Zn(II), Mo(VI), Ag(I), Cd(II), W(VI), Pt(IV), Hg(II), Pb(II), Bi(III)	1 mg[a]
Ni(II)[b], Cu(II)[c]	1 mg
Pd(II)[d]	300 μg
Fe(III)[e]	100 μg

Co(II) taken, 12 μg
[a]Maximum value tested.
[b]A 4 mg amount of sodium citrate was added.
[c]A 500 mg amount of thiourea was added.
[d]A 300 mg amount of thiourea was added.
[e]A 100 mg amount of ascorbic acid was added.

Determination of Cobalt in Standard Alloys.

A 0.1 gm. amount of aluminium alloy or high-speed steel was accurately weighed in a beaker and dissolved in 6 or 14 ml of hydrochloric acid (1 + 1) by heating on a water-bath, after which 1 ml of 30% hydrogen peroxide was added. After the excess of hydrogen peroxide was decomposed by heating, the solution was cooled, filtered, and diluted to 100 ml for NKK No. 920 or 1000 ml for JSS 607-6 with distilled water. A 10 ml aliquot of the sample solution for NKK No. 920 or 2 ml of the sample solution for JSS 607-6 was taken in a beaker and to this were added 1 ml of 10% ammonium citrate and 80 mg of thiourea for NKK No. 920 or 1 ml of 10% ammonium citrate. 400 Mg of thiourea and 10 mg of glycoletherdiamine-N,N,N′,N′--tetraacetic acid (GEDTA) for JSS 607-6. From this point, the general procedure was applied.

Determination of cobalt in pepperbush and pond sediment

Analytical procedure for pepperbush: A 3 gm. amount of pepperbush was accurately weighed and transferred into a Kjeldahl flask. This sample was dissolved in the mixture of 35 ml of nitric acid and 1 ml of perchloric acid by heating. The solution was then cooled, filtered and diluted to 50 ml with distilled

water. A 7 ml aliquot of the sample solution was taken in a beaker and to this were added 1 ml of 10% ammonium citrate, 400 mg of thiourea and 10 mg of GEDTA. From this point, the general procedure was applied.

TABLE 2
ANALYSIS OF STANDARD REFERENCE SAMPLES FOR COBALT

Samples	Composition, %	Cobalt, %	
		Certified value	Found[a]
NKK[b] No. 920 Aluminium Alloy	Si : 0.78; Fe : 0.72; Cu : 0.71; Mn : 0.20; Mg : 0.46; Cr : 0.27; Ni : 0.29; Zn : 0.80; Ti : 0.15; Sn 0.20; Pb : 0.10; V : 0.15; Bi : 0.06; Ga : 0.05; Sb : 0.01; Ca : 0.03	0.10	0.092 ± 0.003
JSS[c] 607-6 High-Speed Steel	C : 0.75; Si : 0.32; Mn : 0.30; P : 0.012; S : 0.006; Ni : 0.058; Cr : 4.14; Mo : 0.30; Cu : 0.028; W : 16.96; V : 0.86; N : 0.0220	4.72	4.30 ± 0.13
NIES[d] No. 1 Pepperbush	K : 1.51 ± 0.06; Ca : 1.38 ± 0.07; Mg : 0.408 ± 0.020; Mn : 0.203 ± 0.017; P : (0.11)[e]; Fe : 205 ± 17 ppm; Zn : 340 ± 20 ppm; Ba : 165 ± 10 ppm; Na : 106 ± 13 ppm; Rb : 75 ± 4 ppm; Sr : 36 ± 4 ppm; Cu : 12 ± 1 ppm; Ni : 8.7 ± 0.6 ppm; Cd : 6.7 ± 0.5 ppm; Pb : 5.5 ± 0.8 ppm; As : 2.3 ± 0.3 ppm; Cr : (1.3 ppm)[e];Cs : (1.2 ppm)[e]; Tl : (0.13 ppm)[e] ; Hg : (0.056 ppm)[e]	2.3 ± 3ppm	20.9 ± 1.0 ppm
NIES[d] No. 2 Pond Sediment	K : 0.68 ± 0.06; Ca : 0.81 ± 0.06; Al : 10.6 ± 0.5; Fe : 6.53 ± 0.35; Na : 0.57 ± 0.04; P : (0.14)[e]; Si : (21)[e]; Ti : (0.64)[e]; Mn : (770 ppm)[e]; Zn : 343 ± 17 ppm; Rb : (42 ppm)[e]; Sr : (110 ppm)[e]; Cu : 210 ± 12 ppm; Ni : 40 ± 3 ppm; Cd : 0.82 ± 0.06 ppm; Pb : 105 ± 6 ppm; As : 12 ± 2 ppm; Cr : 75 ± 5 ppm; Hg : (1.3 ppm)[e]; V : (250 ppm)[e] : Sc : (28 ppm)[e]; La : (17 ppm)[e]; Br : (17 ppm)[e]; Sb : (2.0 ppm)[e]	27 ± 3 ppm	23.1 ± 1.2 ppm

[a]Average of four determinations.
[b]Nippon Keikinzoku Kogyo
[c]Japanese Standards of Iron and Steel
[d]National Institute for Environmental Studies
[e]The values in parentheses are not certified (reference values).

Analytical procedure for pond sediment: A 3 gm amount of pond sediment was accurately weighed, dissolved in 15 ml of aqua regia, filtered and diluted to 100 ml. A 10 ml aliquot of the sample solution was taken in a beaker and to this were added 1 ml of 10% ammonium citrate and 10 mg of GEDTA. From this point, the general procedure was applied.

The data for cobalt analysis in standard reference samples are given in Table 2

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