EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF COBALT(II) WITH p-METHYLISONITROSOACETOPHENONE

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ABSTRACT

A method has been developed for extractive separation and spectrophotometric determination of cobalt (II) employing p-methylisonitrosoacetophenone (HIMAP). The method is based on the formation, at pH 6.8 to 7.8, of a Co–HIMAP complex, which can be quantitatively extracted into chloroform. The chloroform extract shows absorption maximum at 380 nm. At this wavelength Beer's law is obeyed over the range 0.1–4 μg of cobalt per ml and molar absorptivity is 23,077 l mol^{-1} cm^{-1}. The average of 10 determinations of 5 μg of cobalt in 10 ml solution was 4.98 μg and the standard deviation 0.175 μg. The range defined by 95% confidence limits was 4.855 μg to 5.105 μg. The composition of the extracted species is found to be 1:3 (Co:HIMAP) by Job's continuous variation and mole ratio method. Interference by various ions has been studied. The proposed method has been applied to the determination of cobalt in high-speed steel and cast iron.

INTRODUCTION

SEVERAL oximes have been used widely for the spectrophotometric determination of metal ions[1,2]. A literature survey shows that the analytical applications of p-methylisonitrosoacetophenone (HIMAP) have not been studied. In the present communication, HIMAP has been found to be a sensitive and selective reagent for the extractive separation and spectrophotometric determination of cobalt. The method has been applied to determination of cobalt in high-speed steel and cast iron.

EXPERIMENTAL

Apparatus

The absorbance measurements were made on a Carl Zeiss VSU 2P spectrophotometer using 1 cm silica cells and on a Bausch and Lomb Spectronic 20 using 1 cm glass cells. For measurement of pH, an ELICO LI-120 model pH meter was used.

Reagents

All the chemicals used were of A. R. grade. All the solutions were prepared in double-distilled water. The cobalt stock solution was prepared by dissolving the requisite amount of cobalt acetate in double-distilled water containing dilute acetic acid and was standardized gravimetrically[3]. HIMAP was synthesized by the procedure recommended by Müller and Pechmann[4]. A 2% solution of reagent in ethanol (1:1) was used for extraction purposes.

RECOMMENDED PROCEDURES

Extraction

To an aliquot of cobalt acetate (1 ml) containing 1 mg of cobalt, 1 ml of 2 M NH_4Cl and 2 ml of 2% alcoholic solution of HIMAP were added and the pH of the solution was adjusted to the desired value with dilute solutions of NH_4OH and/or HNO_3, keeping total volume to 10 ml. The solution was equilibrated for 2 min with 10 ml of chloroform. The phases were allowed to separate and cobalt in each phase was estimated by the nitroso-R-salt method[3]. The pH of the equilibrated aqueous phase was measured. The extraction coefficient was calculated in the usual way. The extraction was carried out with different solvents to identify the most satisfactory solvent.

Spectrophotometric determination

To solutions containing 1–40 μg of cobalt, 1 ml of 2 M NH_4Cl and 1 ml of 1% alcoholic solution of

HIMAP were added. The pH was adjusted to 7.2 with dilute solutions of NH_4OH and/or HNO_3, keeping total volume to 10 ml. The solution was equilibrated for 2 min with 10 ml of chloroform and the phases were allowed to separate. The chloroform extract was collected in a 10 ml measuring flask and made up to the mark with chloroform, when required. The absorbance of the chloroform extract at 380 nm was measured using a reagent blank. The amount of cobalt was determined from a calibration curve prepared by the same procedure.

Determination of cobalt in high-speed steel and cast iron

Samples (0.1–1 g) were dissolved by boiling with aqua regia (10 ml). The solution was evaporated to dryness and the residue was dissolved in 6 N HCl (100 ml). An aliquot of the above solution was equilibrated with an equal volume of di-isopropyl ether to remove Fe(III). The separated aqueous phase was evaporated to dryness and the residue was dissolved in 5 ml of distilled water and treated with 20 mg of ammonium acetate to mask Cr(III). Finally the solution was diluted to 10 ml with water. To an aliquot of this solution (1 ml), 1 ml of 2 M NH_4Cl and 1 ml of 1% alcoholic solution of HIMAP were added. The pH of the solution was adjusted to 7.2 with dilute solutions of NH_4OH and/or HNO_3, keeping total volume to 10 ml. The solution was equilibrated for 2 min with 10 ml of chloroform and the two phases were allowed to separate. The separated chloroform phase was shaken for 2 min with 10 ml of 1 N HCl to remove nickel. The absorbance of the chloroform extract at 380 nm was measured using a reagent blank and the amount of cobalt present was determined from a calibration curve as described earlier.

RESULTS AND DISCUSSION

Extraction

Results of extraction studies (table 1) show that cobalt can be quantitatively extracted by HIMAP into chloroform from an aqueous solution of pH 6.8 to 7.8.

From values of extraction coefficient of cobalt with different solvents, the following order of decreasing extractability was obtained: Chloroform > benzene > toluene > isobutyl methyl ketone > ethyl

Table 1 *Extraction coefficient of cobalt with HIMAP into chloroform as a function of pH*

pH	Extraction coefficient	Percentage extraction
1	0.02	1.96
2	0.11	9.91
3	0.136	11.97
4	0.167	14.31
5	0.60	37.50
6	2.44	70.50
6.5	49.00	98.00
6.7	124.06	99.20
6.8	199.00	99.50
7.0	199.00	99.50
7.5	199.00	99.50
7.8	199.00	99.50
8.0	99.00	99.00
8.5	39.00	97.50
9.0	23.41	95.90
10.0	1.77	63.90
11.0	0.047	4.49

acetate > nitromethane > nitrobenzene > benzyl alcohol > carbon tetrachloride > isoamyl alcohol > isobutanol. This shows that chloroform is the most satisfactory solvent.

A 50-fold molar excess of reagent is adequate for complete extraction of cobalt. Addition of excess reagent had no adverse effect.

Beer's law, molar absorptivity and precision

The chloroform extract of Co–HIMAP complex shows absorption maximum at 380 nm. At this wavelength Beer's law is obeyed over the cobalt concentration range 0.1–4 μg/ml and molar absorptivity is 23,077 l mol^{-1} cm^{-1} calculated on the basis of total cobalt taken. The average of 10 determinations of 5 μg of cobalt in 10 ml solution was 4.98 μg and the standard deviation 0.175 μg. The range defined by 95% confidence limits was 4.855 μg to 5.105 μg.

Effect of other ions

The following ions (in mg/10 ml) do not interfere in the spectrophotometric determination of cobalt: 10 mg of each of Ca(II), Mg(II), Li(I), Mo(VI), Ba(II), W(VI), Tl(I), Se(IV), Ir(IV), Bi(III), As(III), Sb(III), Hg(II), Pt(IV); 5 mg of Pb(II); 2 mg of V(V); 0.5 mg of Rh(III); 0.01 mg of each of Fe(II), Fe(III) and Ni(II); 20 mg of each of chloride, bromide, iodide, fluoride, chlorate, bromate, iodate, sulphite, sulphate, thiosulphate,

nitrate, nitrite, acetate and thiocyanate; 10 mg of phosphate and tartrate; 5 mg of pyrophosphate. Ions such as Cu(II), Mn(II), Zn(II), U(VI), Zr(IV), Th(IV), Be(II), Ce(IV), Cd(II), Ag(I), Cr(III), Pd(II), Ru(III), cyanide, citrate, oxalate and EDTA hinder the extraction of cobalt into chloroform. However, the interference by these ions can be removed by using appropriate masking agents (table 2). Interference due to cyanide and EDTA can be removed by boiling the mixture with HNO_3 before the extraction.

Composition

The composition of extracted species is found to be 1:3 (Co:HIMAP) by Job's continuous variation and mole ratio method.

Table 2 *Masking agents required to suppress interference by other ions*

Interfering ion(s)	Masking agent
Citrate and oxalate	Sodium molybdate
Mn(II), Zn(II), U(VI), Th(IV), Zr(IV), Ce(IV) and Be(II)	Sodium fluoride
Cd(II) and Ag(I)	Potassium iodide
Cr(III)	Ammonium acetate
Cu(II)	Sodium thiosulphate
Pd(II) and Ru(III)	Thiourea

Table 3 *Determination of cobalt in high speed steel and cast iron*

| Sample | Cobalt(II), found (%) | |
	Present* method	Nitroso-R-salt* method
High-speed steel	46.036	46.123
Cast iron	0.0224	0.025

*Average of three determinations.

Determination of cobalt in high-speed steel and cast iron

The proposed method have been used for estimation of cobalt in high-speed steel and cast iron. Results obtained are comparable with those of the nitroso-R-salt method[3] (table 3).

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2. Hargis, L. G. and Howell, J. A., *Anal. Chem.*, 1978, **50**, 243R; 1980, **52**, 306R; 1982, **54**, 171R; 1984, **56**, 225R.
3. Vogel, A. I., *Text book of quantitative inorganic analysis*, Longman Green and Co. Ltd., London, 1961.
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