Solid-liquid Separation after Liquid-liquid Extraction: Spectrophotometric Determination of Cobalt by Extraction of its 2-Methoxyethyl Xanthate in Molten Naphthalene

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A selective spectrophotometric method has been developed for the determination of cobalt after extraction of its 2-methoxyethyl xanthate complex into molten naphthalene. Cobalt reacts with this xanthate in the ratio of 1 : 2 (metal : ligand ratio) in a pH range of 3.5—9.2 and over an acid range of 2.5—7.0 M. It absorbs strongly at 355 nm. Beer's law is obeyed over the concentration range of 2.5—46.0 µg of cobalt in 10 ml of the final solution. The molar absorptivity and sensitivity in terms of Sandell's definition are calculated to be 1.287×10^4 1 mol^{-1} cm^{-1} and 0.0046 µg/cm^2 respectively. Ten replicate determinations of sample solution containing 25 µg of cobalt gives a mean absorbance of 0.546 with a standard deviation of ±0.0037 and a relative standard deviation of ±0.67%. Interference by various ions has been studied and the conditions developed for the determination of cobalt in complex materials such as alloys.

INTRODUCTION

Several methods have been developed for the determination of cobalt using xanthates as a complex forming reagent. For instance, solvent extraction of cobalt ethyl xanthate in hydrochloric acid[1] and sulphuric acid[2] media has been used for the determination of cobalt. Other methods, such as column chromatography[3] and xanthateethylacetate extraction[4] in the presence of salting out agents have also been used for its determination.

In the present communication, a method has been developed for the determination of cobalt in various synthetic samples and alloys after extraction of its 2-methoxyethyl xanthate into molten naphthalene. Since it has been observed that the higher homologue xanthates are relatively more stable than their lower ones, potassium-2-methoxyethyl xanthate was employed. The various advantages of this technique, »solid-liquid separation after liquid-liquid extraction«, e. g. the equilibrium in the two phases is attained quickly, a small amount of the organic substance (2 g) is needed for the complete extraction etc. have already been stated in our previous communications.[5,6] Interference by diverse ions has been studied in detail and conditions have

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been developed for the determination of cobalt in complex materials such as alloys.

<div align="center">EXPERIMENTAL</div>

Reagents

A solution of cobalt chloride was prepared from an analytical grade sample in distilled water and standardized.[7] Potassium-2-methoxyethyl xanthate was prepared by adding a slurry of potassium hydroxide to 2-methoxyethanol at a temperature below 10 °C, and then carbon disulphide was added dropwise after the mixture had been kept in ice-salt mixture. It was purified and recrystallized[8] and a 0.2% solution of the reagent was prepared in distilled water. Naphthalene, benzene, diverse cations and anion salts, perchloric acid (70%) and liquid ammonia solutions used were of analiytical grade.

Equipment

An Elico pH meter, Sp-500 and SP-700 spectrophotometers (Pye Unicam), Atomic absorption spectrophotometer (Pye Unicam) were used for pH adjustment, absorbance measurement and comparison of the results respectively.

General Procedure for Extraction

An aliquot of cobalt solution was placed in a beaker and to this was added 2 ml of 0.2% potassium-2-methoxyethyl xanthate. The acid concentration or pH (Figure 2) was adjusted with perchloric acid and ammonia solutions in a total volume of 20 ml with distilled water. This solution was then transferred to a 100 ml round bottomed flask and warmed to about 60 °C in a water-bath. Two grams of naphthalene was added and the flask was stoppered. Heating was continued untill the naphthalene melted and formed a separate liquid layer. The flask was taken out of the water-bath and shaken vigorously untill the naphthalene separated out as a solid mass. The process of melting and stirring was repeated twice and then the flask was allowed to stand. The naphthalene was separated from the aqueous phase by filtration, dried in the folds of filter papers, dissolved in benzene and the volume was made up to 10 ml in a standard flask. This solution was then dried by adding 2 g of anhydrous sodium sulphate. A portion of this solution was placed in a 1 cm cell and the absorbance at wavelength of 355 nm was measured against a reagent blank. A calibration curve was prepared under similar conditions.

<div align="center">RESULTS AND DISCUSSION</div>

Absorption Spectra

The absorption spectra of potassium 2-methoxyethyl xanthate and its cobalt complex in naphthalene benzene solutions were recorded against water and reagent blank respectively (Figure 1). Cobalt-2-methoxyethyl xanthate shows maximum absorption at 355 nm, the absorption of the reagent being negligible at this wavelength. All absorbance measurements were made at 355 nm for subsequent studies.

Effect of Acidity

Extraction of the chelate was carried out at various pH values up to 11 as well as in acid concentrations over a range of 10—0.1 M with perchloric acid and ammonia solutions. Other conditions were kept constant. The absorbance remained constant over the pH range of 3.5—9.2 or in the acid range of 2.5—7.0 M (Figure 2). These ranges were based on experimental observations only.
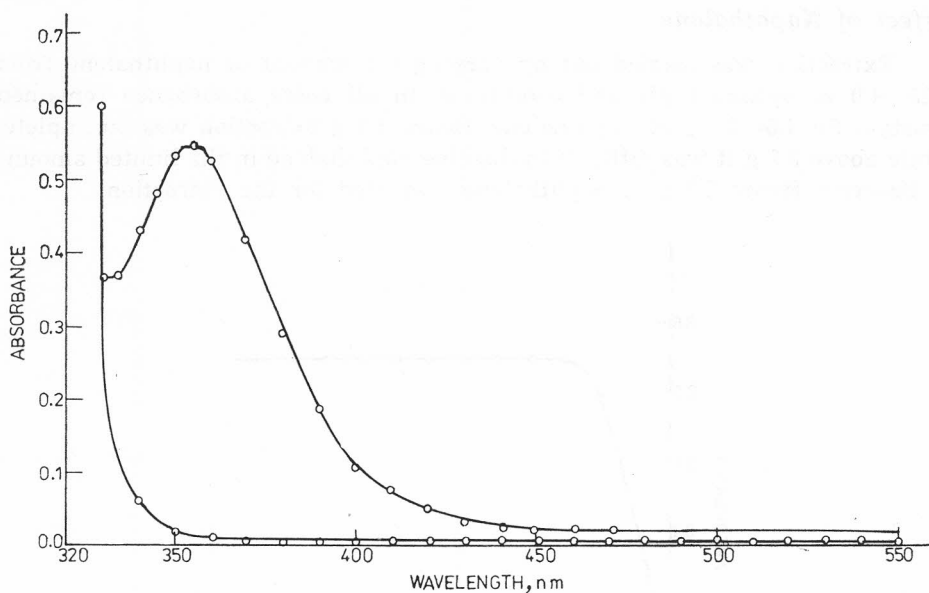
Figure 1. Absorption Spectra of Potassium-2-methoxyethyl xanthate and its cobalt xanthate in naphthalene-benzene solution Reagent blank: 2 ml (0.2%), naphthalene: 2 g HCLO$_4$: 4 M, reference: Water; Co: 25 μg, rest of the conditions were the same as above, reference: reagent blank.
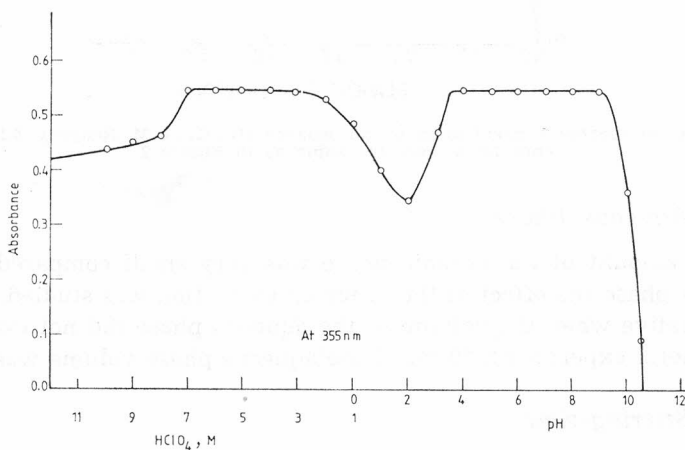

Figure 2. Effect of pH on absorbance Co: 25 μg, wavelength; 355 nm, reagent; 2 ml (0.2%), naphthalene: 2 g, total volume: 10 ml with benzene, reference: reagent blank.

Effect of Reagent

As shown in Figure 3, addition of more than 1 ml of 0.1% potassium-2-methoxyethyl xanthate solution was required to obtain maximal and reproducible absorbance for 25 μg of cobalt. Smaller amounts gave incomplete complex formation. Hence 2 ml of 0.2% solution of the reagent was preferred for the quantitative extraction of cobalt.

Effect of Naphthalene

Extraction was carried out by varying the amount of naphthalene from 0.25—4.0 at optimum pH and conditions. In all cases absorbance remained constant for 1.5—3.5 g of naphthalene. Below 1.5 g extraction was incomplete, while above 3.5 g it was difficult to dissolve naphthalene in the limited amount of benzene. Hence 2.0 g of naphthalene was used for the extraction.
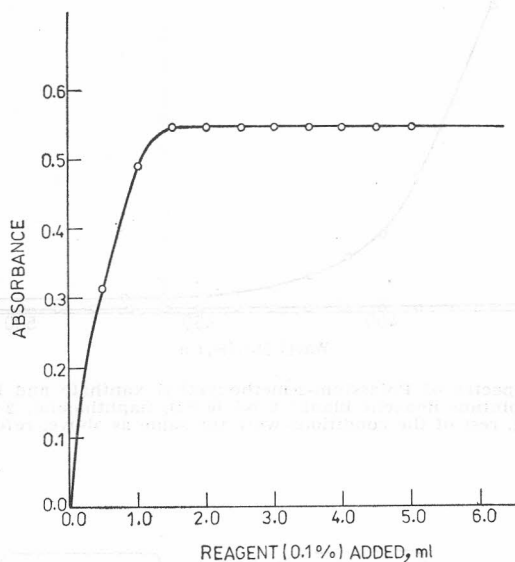

Figure 3. Effect of reagent concentration on absorbance HCLO$_4$: 4 M, Reagent: 0.1⁰/o rest of the conditions were the same as in Figure 2.

Effect of Aqueous Phase

As the amount of the organic phase was very small compared to that of the aqueous phase the effect of the latter on extraction was studied. Extraction was quantitative when the volume of the aqueous phase did not exceed 40 ml. For the general experiment, 20 ml of the aqueous phase volume was preferred.

Effect of Stirring-time

The effect of stirring time on the absorbance was examined. It was observed that the extraction of the chelate into molten naphthalene was very fast and no change in the degree of extraction occurred when the stirring time was varied from 1—30 min.

Effect of Electrolytes

Various electrolytes such as sodium chloride, sodium nitrate and sodium acetate (0.01—0.1 M) caused no improvement in the absorbance indicating the absence of salting effect.

Choice of Solvent

Tests were made with various organic solvents in order to dissolve the mixture of the chelate and naphthalene. The chelate was soluble in organic solvents such as benzene, toluene, xylene, chlorobenzene o-dichlorobenzene, dichloroethane, chloroform, acetone, dimethylformamide, and carbon tetrachloride at room temperature. However, solvents such as acetonitrile and dimethylsulphoxide are not suitable for dissolving the naphthalene chelate. Benzene was selected for dissolving the complex because the absorbance was maximum in this solvent.

Stability of the Colour Complex

The absorbance of the benzene extract of the complex was recorded at different intervals of time. It was constant for 24 hrs.

Composition of the Complex

The composition of cobalt-2-methoxyethyl xanthate was established by Job's method of continuous variation and the mole ratio method. A sharp peak at 0.33 mole fraction and a clean break at 1 : 2 mole ratio confirmed the formation of $Co(C_4H_7O_2S_2)_2$ under these conditions.

Further the composition of the complex was ascertained by the logarithmic method.[9] The required values for $\log (MR_n)/(M^{n+})$ and $\log (HR)$ for this method were calculated and a curve plotted as shown (Figure 4). A straight
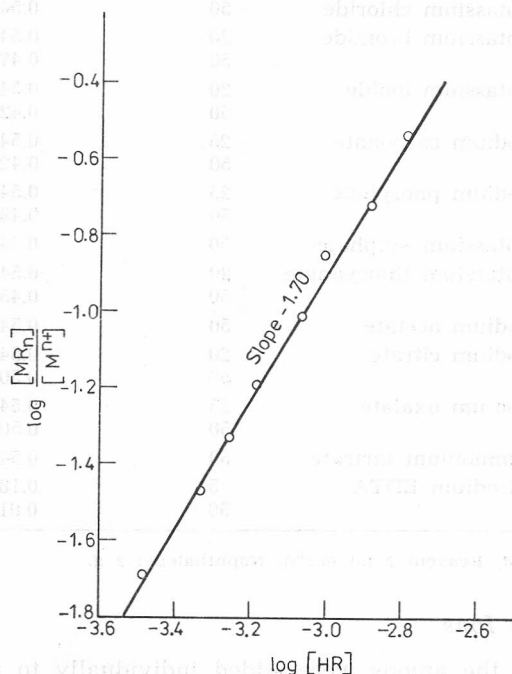

Figure 4. Logarithmic method of formula determinations. Initial concentration of cobalt: 0.85×10^{-3} M, potassium-2-methoxyethyl xanthate: 0.85×10^{-3} M, $HClO_4$: 4 M, rest of the conditions were the same as in Figure 2.

line of slope equal to 1.70 was obtained which confirmed the formation of the
above complex under the stated conditions.

Beer's law and sensitivity

Under the optimum conditions described above, a calibration curve was
constructed at 355 nm. It was linear over the concentration range 2.5—46.0
µg of cobalt in 10 ml of the final solution. The molar absorptivity and sensi-
tivity in terms of Sandell's definition were calculated to be 1.287×10^4 lmol^{-1}
cm^{-1} and 0.0046 µg/cm^2 at 355 nm. Ten replicate determinations of the sample
solution containing 25 µg of cobalt gave a mean absorbance of 0.546 with a
standard deviation of ± 0.0037 and a relative standard deviation of $\pm 0.67^0/0$.
The efficiency of the method was checked by determination of cobalt in some
alloys (Table III). A 1 to 5 fold excess of of Ni, Cr, Fe, Cd, Cu, As, V, Mo,
Mn, Pb, Zn, Sn, Bi and W showed an error of about $\pm 0.90^0/0$ for an average
of seven determinations.

TABLE I

Effect of Diverse Anions

Salt added	Amount added (mg)	Absorbance at 355 nm
—	—	0.546
Sodium fluoride	25	0.545
	50	0.510
Potassium chloride	50	0.545
Potassium bromide	20	0.545
	50	0.470
Potassium iodide	20	0.545
	50	0.425
Sodium carbonate	25	0.545
	50	0.425
Sodium phosphate	25	0.543
	50	0.485
Potassium sulphate	50	0.545
Potassium thiocyanate	20	0.543
	50	0.450
Sodium acetate	50	0.547
Sodium citrate	20	0.545
	50	0.500
Sodium oxalate	25	0.543
	50	0.500
Ammonium tartrate	50	0.544
Disodium EDTA	5	0.185
	50	0.015

Co: 25 µg, HCLO$_4$: 4 M, Reagent 2 ml (0,2$^0/0$), Naphthalene: 2 g.

Effect of Diverse Ions

50 mg salt of the anions were added individually to aliquot containing
25 µg of cobalt and the determination was carried out by the general procedure.
Among the anions examined (Table I) only EDTA interfered. Determination is

not possible even at very low concentration of EDTA. Among the cations examined (Table II) Pd(II), Ir(III), Pt(II), Fe(III) and Cu(II) interfered, but their relatively low amounts could be tolerated and thus the method can safely be applied for the determination of cobalt in complex materials.

<div align="center">TABLE II</div>

<div align="center">*Effect of Diverse Cations*</div>

Metal salt added	Metal added (μg)	Absorbance at 355 nm
—	—	0.546
Aluminium nitrate	300	0.550
Ammonium molybdate	100	0.560
Ammonium metavanadate	100	0.550
Antimony(III) chloride	150	0.542
Bismuth nitrate	100	0.548
Cadmium chloride	100	0.541
Copper(II) chloride	100	0.490
	50	0.544
Chromium nitrate	100	0.545
Indium sulphate	100	0.546
Iridium(III) chloride	100	0.562
	50	0.550
Iron(III) chloride	100	0.480
	60	0.535
Lead(II) nitrate	100	0.551
Manganese(II) acetate	150	0.547
Mercury(II) chloride	100	0.545
Nickel chloride	100	0.550
Palladium chloride	100	0.600
	30	0.550
Platinum(II) chloride	100	0.553
	60	0.548
Rhodium(III) chloride	100	0.550
Ruthenium(III) chloride	100	0.552
Sodium arsenite	200	0.542
Sodium tungstate	200	0.550
Stannous chloride	150	0.545
Thorium(IV) nitrate	150	0.545
Uranyl acetate	200	0.548
Zinc sulphate	100	0.542
Zirconyl chloride	200	0.545

Conditions same as Table I.

Determination of Cobalt in Alloys

A 0.1 g sample of the alloy was placed in a beaker and 10—15 ml of concentrated hydrochloric acid and a few drops of concentrated nitric acid were added. The mixture was heated on a hot-plate untill it dissolved completely and the solution was reduced to about 5 ml. This solution was cooled to room temperature and 10 ml of concentrated hydrochloric acid were added. It was diluted to about 100 ml with distilled water, filtered and made up to a final volume of exactly 500 ml in a standard flask. An aliquot was taken and 2 ml of the reagent solution and 1 ml of 2% NaF solutions were added. The medium was adjusted to 4 M of perchloric acid by the addition of concen-

trated perchloric acid and the determination was carried out by the general procedure. The results of this determination are given in Table III.

<div align="center">TABLE III</div>

Determination of Cobalt in Alloys

Name of the alloy	Certified composition (%)	Amount of cobalt		Amount of cobalt found by this method (μg)	Awerage (μg)	Error (%)
		Taken (μg)	Found by AAS (μg)			
Eligiloy M-1712	Co: 40.0, Cr: 20.0, Ni: 15.0, Mn: 2.0, Mo: 7.0, Fe: 15.0, Be: 0.05, C: 0.15.	30.00	30.20	29.90 30.10 30.20 30.40 30.50 30.30 30.40	30.25	+0.83
High Speed Steel	Co: 9.25, Mn: 0.4, Si: 0.35, S: 0.05, P: 0.05, Cr: 4.15, Mo: 5.5, W: 6—18.5, Rest Fe*	24.00	24.15	24.20 24.00 23.90 24.30 24.40 24.30 24.50	24.23	+0.95
JSS, 607-6 High Speed Steel SKH-3	Co: 4.72, V: 0.86, W: 16.96, Mo: 0.30, Cr: 4.14, Ni: 0.058, Cu: 0.028, S: 0.006, P: 0.012, Mn: 0.30, Si: 0.32, C: 0.75 Rest Fe*	18.90	19.04	19.00 19.40 19.10 18.80 19.00 19.20 19.10	19.08	+0.97
JSS, 655-4 Stainless Steel SUS 347	Co: 0.28, Nb: 0.60, Ta: 0.03, W: 0.024, Mo: 0.051, Cr: 18.54, Ni: 11.48, Cu: 0.088 S: 0.006, P: 0.033, Mn: 1.58, Si: 0.60, C: 0.055, Rest Fe*	10.40	10.45	10.60 10.30 10.50 10.70 10.30 10.50 10.70	10.51	1.04

Conditions same as Table I.

* Iron was masked by the addition of sodium fluoride solution during extraction.

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SAŽETAK

Spektrofotometrijsko određivanje kobalt-2-metoksietil-ksantata nakon njegove ekstrakcije u rastaljenom naftalenu i separacije čvrste i tekuće faze

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Razrađena je selektivna spektrofotometrijska metoda za određivanje kobalta nakon njegove ekstrakcije u obliku kobalt-2-metoksietil-ksantata u rastaljenom naftalenu. Kobalt reagira s ovim ksantatom u molnom odnosu 1 : 2 (metal : ligand) u području pH od 3,5 do 9,2 odnosno u području koncentracije kiseline ($HClO_4$) od 2,5 do 7,0 mol dm^{-3}. Kod valne duljine od 355 nm apsorpcija kompleksa slijedi Beer-ov zakon u području sadržaja kobalta od 2,5 do 46,0 µg u 10 ml mjerene otopine.

Molarni apsorpcijski koeficijent i osjetljivost izraženi prema prema Sandell-ovoj definiciji iznosi 1,287 · 10^4 mol^{-1} cm^{-1} i 0,0046 µg cm^{-2}. Deset ponovljenih mjerenja uzoraka koji su sadržavali 25 µg kobalta dalo je srednji faktor apsorpcije od 0,546, srednju devijaciju od ±0,0037 i relativnu standardnu devijaciju od ±0,67⁰/o. Ispitan je utjecaj različitih iona i razrađena metoda za određivanje kobalta u kompleksnom materijalu-legurama.