

Liquid-Liquid Extraction and Separation of Cobalt(II) from Sodium Acetate media using Cyanex 272

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Available online at: www.isca.in

(Received 29th November 2011, revised 15th December 2011, accepted 20th December 2011)

Abstract

A simple liquid-liquid extraction method has been developed for the quantitative extraction of cobalt(II) from an aqueous solution of 0.5 M sodium acetate using cyanex 272 [bis (2,4,4-trimethyl phenyl) phosphinic acid] in toluene as extractant. Cobalt(II) was quantitatively back extracted from the organic phase using 3.0 M nitric acid. The effects of various parameters affecting the extraction equilibrium of cobalt(II) such as sodium acetate concentration, cyanex 272 concentration, equilibration time, effect of various diluents, diverse ions and stripping agents have been studied. The separation of cobalt(II) from various binary as well as multicomponent mixtures has been achieved depending on the difference in the extraction and stripping behavior towards these metals. The method was extended for the separation and determination of cobalt(II) from real samples. The reliability of method is assured by comparison of the results with those obtained using AAS.

Keywords: solvent extraction, cobalt(II), cyanex 272, sodium acetate, nitric acid,

Introduction

Cobalt and nickel are among the most important nonferrous metals. Cobalt is not found as a native metal but is mainly obtained as a by product of nickel and copper mining activities. The main ores of cobalt are cobaltite, glucodot, smaltite etc. Cobalt(II) forms the coordination complexes which are exhibiting considerable activities towards pathogenic bacteria^{1,2}. The extraction and separation of cobalt is of great relevance and interest with the increasing demand for this metal and its compounds. There are several methods exists for the separation of cobalt from copper and nickel. They depend on the concentration of cobalt and the exact composition of used ore. Solvent extraction appears to meet the requirements for the performance and economics to replace the conventional separation methods. For the extractive separation of cobalt, copper and nickel from aqueous solutions either oxime or organophosphorous based extractants are often employed^{3,4}. The various organophosphorous extractants have been preferred for separation of cobalt because of better selectivity. The separation ability of organophosphorous extractants for cobalt and nickel follows the order phosphinic acid > phosphonic acid > phosphoric acid⁵. Recovery cobalt in presence of Mg from sulphate solution using cyanex 272 and cyanex 301 has been reported⁶. Cobalt has been separated by supported liquid membrane and solvent extraction using cyanex 272^{7,8}. Extraction of cobalt(II) from sulphate solution has been carried out using cyanex 301 and cyanex 302⁹⁻¹¹. Sodium salts of several organophosphorous extractants have been used for the separation of cobalt¹²⁻¹⁴. Synergistic effect

of cyanex 272 and cyanex 302 on separation of cobalt and nickel by D₂EHPA has been studied¹⁵. Flow sheets for recovery of cadmium, nickel and cobalt from synthetic sulphate solutions using D₂EHPA, cyanex 272 and cyanex 923 have been developed^{16,17}. Extraction of cadmium, nickel and cobalt from spent Ni-Cd batteries using cyanex 272 has been studied^{18,19}. Separation of rare earth elements, cobalt and nickel from spent nickel – metal hydride batteries using cyanex 272 has been reported^{20,21}. Cyanex 272 has been successfully employed for the separation of cobalt and nickel from sulphate solution²²⁻²⁴.

But no attempts have been made for the separation of the cobalt (II) from associated elements from sodium acetate media using cyanex 272. This paper reports the results from the studies on the extraction of cobalt from sodium acetate media using cyanex 272 diluted in toluene. The advantages of this method over the reported methods are, that the sodium acetate is not hazardous, the concentration of cyanex 272 required for quantitative extraction is low and a clean cut separation of Co(II) from other associated metal ions has been achieved.

Material and Methods

Instrumentation: An atomic absorption spectrometer (Perkin-Elmer), a digital flame photometer (PI, Model no. 041, India) and a Ziess spectrophotometer (Spekol-10, Germany) were used for the determination of concentration of metal ions in the aqueous phase. A digital pH meter (Model LI-120, ELICO, India) with a combined electrode and a wrist action mechanical flask shaker were used.

Reagents: The commercial cyanex 272, i.e. bis (2,4,4-trimethyl phenyl) phosphinic acid supplied by Cytec Canada Inc., was used as such in the study without any further purification. Standard stock solution of cobalt(II) was prepared by dissolving 2.116 g of cobaltous chloride hexahydrate (AnalaR grade, Merck) in 100 mL of doubly distilled deionised water and standardized gravimetrically by a known method²⁵. A solution containing 50 µg/mL of cobalt(II) was prepared by appropriate dilution of the standard stock solution. Sodium acetate and toluene of analytical grade from Merck were used.

General Procedure: An aliquot of cobalt(II) solution (1mL of 100 µg/mL) was mixed with sodium acetate to make its concentration of 0.5 M in a total volume of 10 mL of the solution. The solution was then transferred to a separating funnel; 10 mL of 0.05 M cyanex 272 in toluene was added and it was equilibrated for 10 minute on a wrist action flask shaker. The two phases were allowed to settle and separate. After separating two phases cobalt(II) was back extracted from the organic phase by shaking with 10 mL of 3.0 M nitric acid and was estimated either by AAS or spectrophotometrically with PAR at 520 nm²⁶. The concentration of Co(II) was calculated from the calibration curve. All experiments were carried out at room temperature.

Results and Discussion

Extraction of cobalt(II) as a function of sodium acetate concentration with cyanex 272: The optimum concentration for the quantitative extraction of cobalt was ascertained by extracting cobalt with 0.05 M cyanex 272 in toluene as the diluent. Figure 1 shows the effect of varying concentrations of sodium acetate on extraction of Co(II). The sodium acetate concentration was varied from 0.01 to 1.0 M. The results show that extraction efficiency of cobalt was increased constantly with increase in sodium acetate concentration and was quantitative (100 %) from 0.4 M sodium acetate. For further studies of cobalt(II) extraction 0.5 M sodium acetate was used.

Extraction as function of Cyanex 272 concentration: In order to optimize the conditions for extraction of Co(II), cyanex 272 with varying concentration (0.001 to 0.1 M) were employed. It was found that 0.04 M cyanex 272 was sufficient for quantitative extraction of 100 µg of Co(II) from 0.5 M sodium acetate. However, in the recommended procedure 0.005 M Cyanex 272 in toluene was used to ensure the complete extraction of metal ion. Figure 2 shows the effect of varying concentrations of cyanex 272 on extraction of Co(II).

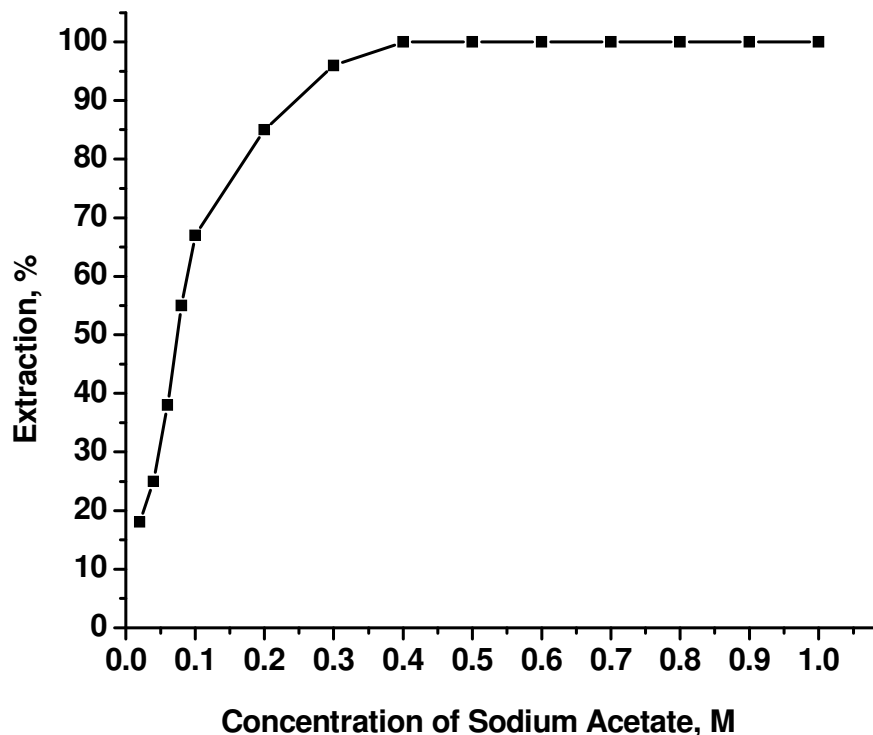


Figure-1
Effect of sodium acetate concentration on extraction of Co(II)

Period of equilibration: The extraction time of Co(II) was carried out with varying periods from 1 to 15 minutes of shaking. The extraction was completed within 5 minutes of shaking, which was employed throughout the investigation. However, prolonged shaking has no adverse effect on the extraction.

Choice of stripping agents: Co(II) complexed in the organic phase was back extracted from the organic phase with

various mineral acids such as nitric acid, sulphuric acid, hydrochloric acid, perchloric acid, acetic acid and hydrobromic acid. Effect of various stripping agents on extraction of Co(II) is shown in figure 3. The stripping of Co(II) was found to be quantitative with 3.0 to 8.0 M nitric acid, 7.0 to 8.0 M perchloric acid and 1.0 to 8.0 M sulphuric acid. The stripping was found to be incomplete with acetic acid, hydrobromic acid and hydrochloric acid. In the proposed method 3.0 M nitric acid was used as a strippant.

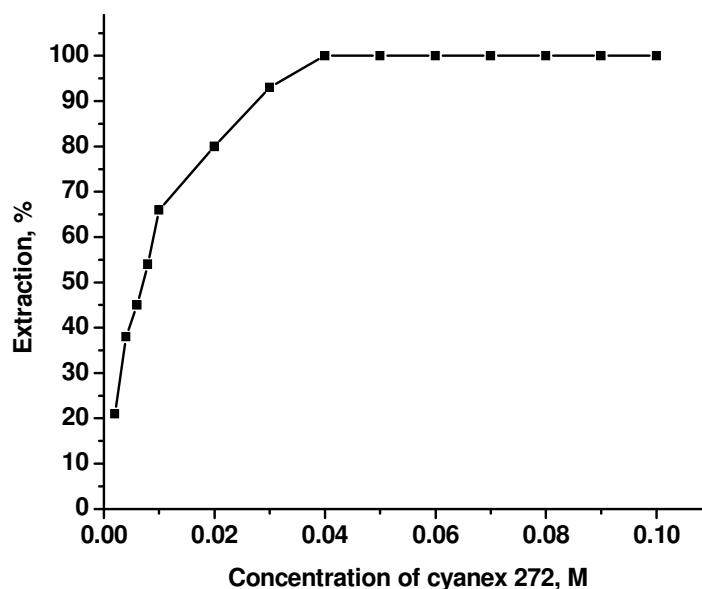


Figure-2
 Effect of Cyanex 272 concentration on extraction of Co(II)

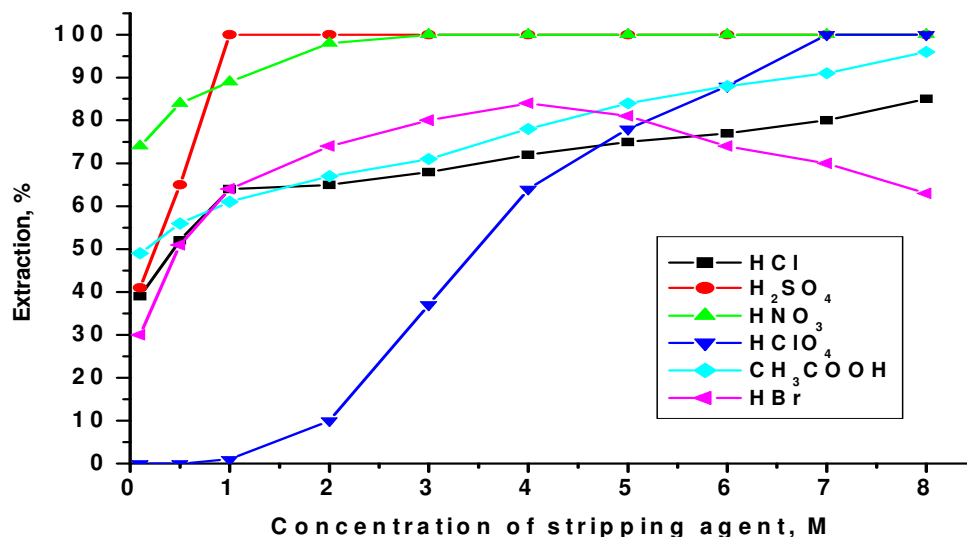


Figure-3
 Effect of Various stripping agents

Influence of various diluents: A number of solvents namely toluene, carbon tetrachloride, xylene, chloroform, tetrachloroethane, 1,2 dichloroethane and nitrobenzene were employed to discern the effect of varying nature of the organic diluents on the extraction of Co(II). The results obtained are summarized in table 1. As apparent from the data the percent extraction of Co(II) was quantitative with toluene only and it was incomplete with xylene (90 %), chloroform (39 %), tetrachloroethane (61 %), 1, 2, dichloroethane (49 %), nitrobenzene (95 %) and carbon tetrachloride (60 %). However, a definite correlation between percent extraction and dielectric constant could not be established.

Table-1

Influence of various diluents on extraction of Co(II)

Diluents	Dielectric constant	Extraction %
Carbon tetrachloride	2.24	60
Xylene	2.30	90
Toluene	2.38	100
Chloroform	4.80	39
Tetrachloroethane	8.20	61
1,2 Dichloroethane	9.08	49
Nitrobenzene	34.80	95

Effect of varying concentration of cobalt(II): Figure 4 shows the effect of concentration of Co(II) on percentage of extraction. Co(II) was extracted with 10 mL of 0.05 M cyanex 272 from 0.5 M sodium acetate using toluene as a diluent. The concentration of Co(II) was varied from 100 to 1600 µg/10 mL. It was found that 10 mL of 0.05M cyanex 272 was adequate to extract Co(II) quantitatively up to 700 µg per 10 mL of sample solution.

Effect of diverse ions: Different amounts of diverse ions were added to 100 µg of cobalt(II) and mixture was extracted according to procedure. The tolerance limit of an ion was taken as maximum amount causing an error not greater than ±2% in the extraction of cobalt(II). Amongst the transition metals cadmium(II), copper(II), zinc(II) and manganese(II) were co-extracted along with cobalt(II). Other d-block cations were not extracted and showed high tolerance limit. Most of the s-block, p-block and f-block cations, anions of organic and inorganic acids showed very high tolerance limit except EDTA which has 0.2 mg tolerance limit. Effect of various foreign ions on extraction of cobalt(II) is summarized in table 2.

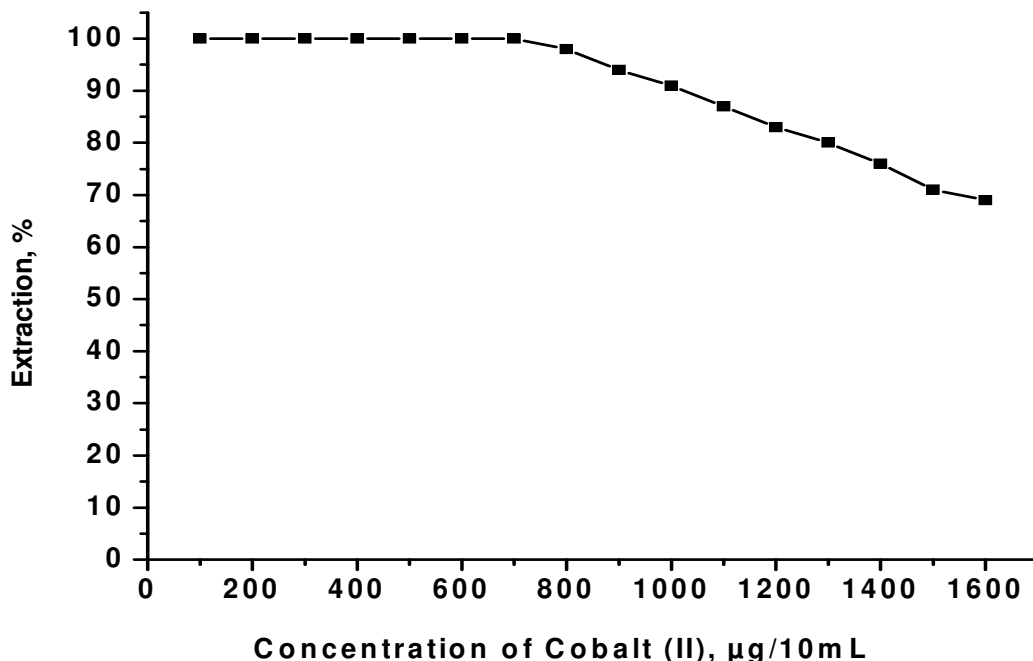


Figure-4

Effect of metal ion concentration on extraction of Co(II)

Table-2
Separation of Co(II) from binary mixtures

Ion	Added as	Tol. Limit (mg)	Ion	Added as	Tol. Limit (mg)
Li ⁺	LiCl	2	Tl ³⁺	Tl(NO ₃) ₃ .3H ₂ O	10
Mg ²⁺	MgCl ₂ .6H ₂ O	3	Sb ³⁺	SbCl ₃	10
K ⁺	KCl	2	Y ³⁺	Y(NO ₃) ₃	15
Rb ⁺	RbCl	10	Ce ³⁺	CeCl ₃ .6H ₂ O	2
Cs ⁺	CsCl	15	Zr ⁴⁺	Zr(NO ₃) ₄ .4H ₂ O	10
Cr ⁶⁺	K ₂ Cr ₂ O ₇	1	V ⁴⁺	VO ₂ .4H ₂ O	5
Be ²⁺	BeSO ₄ .4H ₂ O	15	Th ⁴⁺	Th(NO ₃) ₄ .6H ₂ O	5
Ca ²⁺	CaCl ₂	10	Mo ⁶⁺	(NH ₄) ₆ Mo ₇ O ₂₄ .4H ₂ O	3
Sr ²⁺	Sr(NO ₃) ₂	10	W ⁶⁺	Na ₂ WO ₄ .4H ₂ O	5
Ba ²⁺	Ba(NO ₃) ₂	10	U ⁶⁺	UO ₂ (NO ₃) ₂ .6H ₂ O	5
Cu ²⁺	CuCl ₂ .2H ₂ O	Coextract	Cl ⁻	HCl	15
Ni ²⁺	NiCl ₂ .6H ₂ O	5	Br ⁻	HBr	15
Mn ²⁺	MnCl ₂ .4H ₂ O	Coextract	Oxalate	Oxalic acid	15
Zn ²⁺	ZnCl ₂	Coextract	ClO ₄ ⁻	HClO ₄	10
La ³⁺	LaCl ₃	5	SCN ⁻	NH ₄ SCN	10
Cd ²⁺	CdCl ₂	Coextract	SO ₄ ²⁻	H ₂ SO ₄	15
Sn ²⁺	SnCl ₂	5	BO ₃ ³⁻	H ₃ BO ₃	10
Fe ³⁺	FeCl ₃ .6H ₂ O	2	Tartrate	Tartaric acid	15
Al ³⁺	Al ₂ (SO ₄) ₃ .16H ₂ O	10	EDTA	EDTA	0.2
Hg ²⁺	HgCl ₂	1	Ascorbate	Ascorbic acid	12
Cr ³⁺	Cr(NO ₃) ₃ .9H ₂ O	2	PO ₄ ³⁻	H ₃ PO ₄	15

Separation of cobalt(II) from ternary mixtures:

Separation of Co(II) from ternary mixtures containing commonly associated metal ions, e.g. Fe(III), Ni(II), Pb(II), V(IV) and Cu(II) was carried out by taking advantage of the differences in the extraction conditions of metal ions as shown in table 3. Ternary mixtures of Cu(II), Co(II), Fe(III); Pb(II), Co(II), Fe(III); Cu(II), Co(II), Ni(II); Pb(II), Co(II), Ni(II); Cu(II), Co(II), V(IV); Pb(II), Co(II), V(IV) were resolved by the recommended procedure of cobalt(II). Under the optimum extraction conditions of Co(II), Pb(II)/Cu(II) was quantitatively extracted into the organic phase along with cobalt(II). From the organic phase first Pb(II)/Cu(II)

was stripped with 0.7 M perchloric acid, under this condition cobalt(II) was remains in organic phase. Finally cobalt(II) was stripped out with 3.0 M nitric acid. The metal contents in respective stripping phases were determined using respective spectrophotometric procedures.

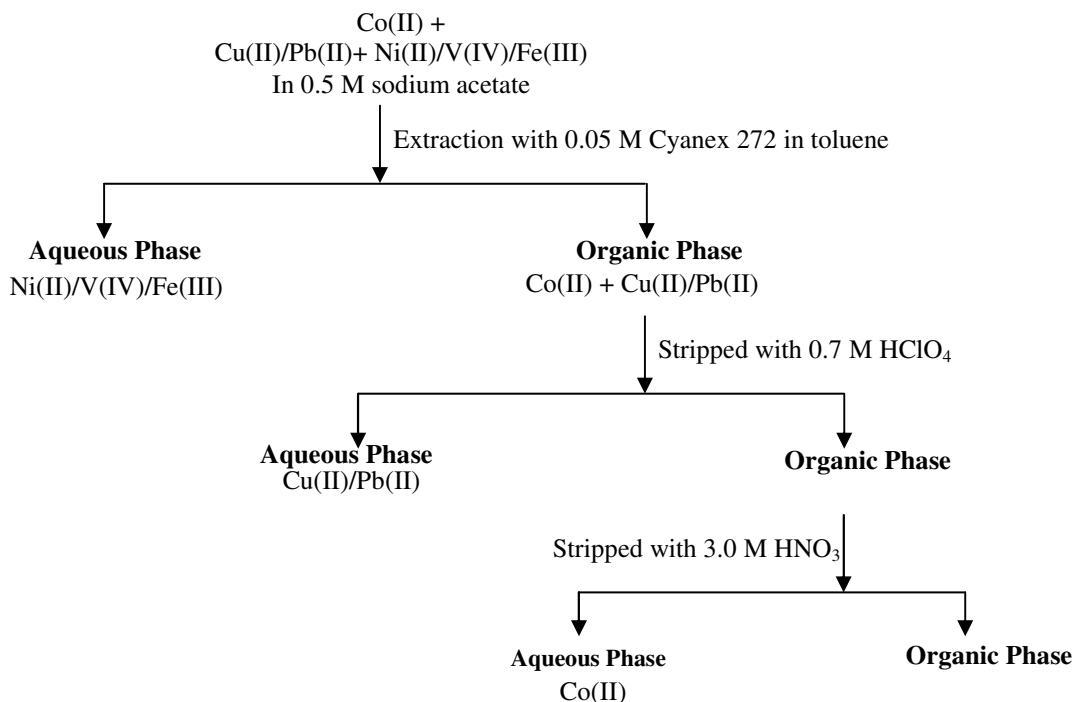
Ni(II), V(IV) and Fe(III) were remained unextracted in the aqueous phase, which were determined by appropriate spectrophotometric methods. Schematic representation for sequential separation of Co(II) from other associated metal ion is as shown in scheme 1.

Table-3
Separation of Co(II) from multicomponent mixtures

Mixture	Taken µg	Found* µg	Recovery* %	Standard Deviation	Extractant	Strippant
1. Cu(II)	25	24.3	97.2	0.13	A	0.7 M HClO ₄
Co(II)	50	49.2	98.4	0.07	A	3.0 M HNO ₃
Fe(III)	25	24.5	98.0	0.09	Aq. Phase	--
2. Pb(II)	25	24.9	99.6	0.09	A	0.7 M HClO ₄
Co(II)	50	49.8	99.6	0.06	A	3.0 M HNO ₃
Fe(III)	25	24.2	96.8	0.12	Aq. Phase	--
3. Cu(II)	25	24.3	97.2	0.11	A	0.7 M HClO ₄
Co(II)	50	49.7	99.4	0.09	A	3.0 M HNO ₃
Ni(II)	25	24.9	99.6	0.08	Aq. Phase	--
4. Pb(II)	25	24.9	99.6	0.11	A	0.7 M HClO ₄
Co(II)	50	49.6	99.2	0.05	A	3.0 M HNO ₃
Ni(II)	25	24.8	99.2	0.09	Aq. Phase	--
5. Cu(II)	25	24.3	97.2	0.07	A	0.7 M HClO ₄
Co(II)	50	49.2	98.4	0.11	A	3.0 M HNO ₃
V(IV)	25	24.5	98.0	0.06	Aq. Phase	--
6. Pb(II)	25	24.3	97.2	0.04	A	0.7 M HClO ₄
Co(II)	50	49.5	99.0	0.05	A	3.0 M HNO ₃
V(IV)	25	24.4	97.6	0.1	Aq. Phase	--

A- 0.5 M sodium acetate, 0.05 M Cyanex 272 in toluene

* average of triplicate analysis



Scheme-1
Sequential separation of Co(II) from multicomponent mixtures

Separation and determination of cobalt(II) from aquatic plants:

The aquatic plant sample was washed to remove periphyton, dust and sediment particles. The plant sample was dried for 8 to 10 days and heated in oven at 110°C. The dried sample was grounded using mortar till finely dry powder was formed. The dried sample was weighed accurately and dissolved in nitric acid and perchloric acid mixture (3:1). The resulting mixture was evaporated to dryness and extracted with distilled deionised water. The solution was heated to boiling and filtered using Whatmann filter paper No. 1. The sample solutions of plant samples were analyzed as per the proposed method and cobalt(II) content was determined. The results obtained with proposed method shows good agreement with those obtained by AAS as shown in table 4.

Table-4
Determination of cobalt(II) from aquatic plants

Aquatic plant	Amount of Co(II) found* µg/10g		Standard Deviation
	AAS method	Proposed method	
Eicchornia crassipes	250.4	249.0	0.08
Hydrilla	360.6	359.5	0.05
Salvinia	410.8	409.4	0.11

* average of triplicate analysis

Separation and determination of cobalt(II) from composite material samples:

The proposed method was employed for the analysis of cobalt(III) in composite materials. Accurately weighed sample was treated with 10 mL aqua-regia and heated to moist dryness; the procedure was repeated for three times. Then the solution was filtered through Whatmann filter paper No.1 and diluted to 100 mL with distilled deionised water. An aliquot sample solution was analyzed as per the general procedure and cobalt content was determined. The results were in good agreement with result obtained from AAS as shown in table 5.

Table - 5
Determination of cobalt(II) from composite materials

Composite material	Amount of Co(II) found* mg/gm		Standard Deviation
	AAS method	Proposed method	
ZnCoFe ₂ O ₄	34.12	34.01	0.10
ZnCoCeFeO ₄	27.08	26.95	0.05
ZnCoLaFeO ₄	24.44	24.11	0.09

* average of triplicate analysis

Determination of cobalt(II) from alloys: The proposed method was applied for the determination of cobalt(II) in different alloys. Known weight of alloy was heated up to 700 °C for 2 hours to remove organic matter. The sample was treated with 15 mL nitric acid and perchloric acid mixture (3:1) and heated to moist dryness, the procedure is repeated

for three times. Then the solution was filtered through Whatmann filter paper No.1 and diluted to 100 mL with distilled deionised water. An aliquot sample solution was analyzed as per the general procedure and cobalt content was determined. The results were in good agreement with those obtained by atomic absorption spectroscopy as shown in table 6.

Table-6
Determination of cobalt(II) from alloys

Alloy	Amount of Co(II) found* mg/gm		Standard Deviation
	AAS method	Proposed method	
Nickel based alloy (387 BCS)	101.40	101.13	0.08
Vitallium	498.45	497.61	0.12

Conclusions

The present investigations have resulted in offering a convenient liquid-liquid extraction method for separation of cobalt(II). Cobalt(II) can be extracted by cyanex 272 dissolved in toluene from sodium acetate medium. The obtained results show that cyanex 272 is a potential extractant for the extraction of cobalt(II) from sodium acetate medium. This method has number of advantages over existing methods such as easy phase separation, less equilibration time and single extraction is sufficient for quantitative extraction of cobalt. Cyanex 272 extracts cobalt(II) very rapidly, equilibrium was reached within 5 minutes. Extractive separation method proposed is simple and provides a reliable means for the selective and sequential separation of cobalt(II) when present in various matrices with other metal ions. Important application of proposed method is separation of Co(II) from Co(II), Cu(II) and Ni(II) mixture, which is useful for analysis of number of alloys. The method is also useful for the extraction of cobalt(II) from real samples such as aquatic plants and composite materials. The method is simple, selective and has good reproducibility (approximately ±2%).

Acknowledgment

The authors are thankful to UGC-SAP and DST-FIST, Department of Chemistry, Shivaji University, Kolhapur.

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