



**Research Paper** 

**Medical Science** 

# **Extractive Separation of Iron and Cobalt Using** Tributylphosphine Oxide as an Extractant

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ABSTRACT

Extraction studies of Iron and Cobalt are undertaken from salicylate media using Tributylphosphine oxide (TBPO) as extractant. Optimum extraction conditions are evaluated and compared critically, for both ions. The nature of extracted species is ascertained with logD-logC plots. Extraction mechanism is discussed for both the systems, which is found to proceed through formation of solvated species. The method permits mutual separation of Iron (III) and Cobalt (II) and from associated elements.

Method also facilitates separation of iron (III) from alloys and pharmaceutical samples.

# **KEYWORDS : Tributylphosphine oxide, Extraction, Iron, Cobalt**

# **INTRODUCTION:**

Iron is an important element from industrial point of view. It is used for the preparation of hard alloys, which are used in various industrial processes. Besides this, iron is invariably present in various pharmaceutical preparations. Cobalt is also important metal from industrial point of view. Both iron and cobalt often occur together. In view of this, separation and purification of iron and cobalt from each other is greatly desired.

Various solvent extraction methods have been used for the extraction of Iron. The neutral extractants such as Tri-n-butyl phosphate [1,2,3], Bis (2-ehtylhexyl) phosphate [4,5], Thiothenoyltrofluoroacetone [6], 18-crown-6 [7], methyl isobutyl ketone [8] and Tri-n-octylphosphine oxide [9] are used for the extraction of Iron from halide, thiocyanate and perchlorate media.

In our laboratory Triphenylphosphine oxide (TPPO) has been extensively used for the extraction studies of Iron and cobalt from halide and salicylate media [10]. However, the existing methods suffer from limitations such as longer extraction period [1,6], strict controlling of temperature [6], multiple extraction [10], critical pH range [2,8,10], large interferences [6,8]. Tributylphosphine oxide (TBPO) has also been used as a potent extractant in this laboratory for extraction of uranium and thorium [11], scandium, yttrium and lanthanum [12], titanium and zirconium, Tellurium [13] bismuth, copper and lead [14].

In the present study we propose study of solvent extraction behavior of trivalent iron and divalent cobalt from salicylate media with Tributylphosphine oxide (TBPO) as an extractant. The method is also free from above mentioned drawbacks and facilitates separation and determination of Iron and cobalt from associated elements, synthetic mixtures, alloys and pharmaceuticals. The method is highly selective and reproducible.

# **EXPERIMENTAL:**

#### Apparatus:

Absorbance and pH measurements are carried out on Spectronic 20 D (Milton Roy and Co.) and Control Dynamics Digital pH meter with combined glass electrode respectively.

# **Reagents:**

The stock solution of Iron (III) is prepared by dissolving 1.809 g of Ferric nitrate (AR grade) in distilled water containing 2cm<sup>3</sup> of concentrated nitric acid and diluted to 250cm<sup>3</sup>, similarly stock solution of cobalt (II) prepared by dissolving 1.192 g of Cobalt sulfate (AR grade) in distilled water containing 2cm<sup>3</sup> of concentrated sulfuric acid and diluted to 250 cm<sup>3</sup> The solutions are standardized by known methods [15] and diluted further as required.

Tributylphosphine oxide (TBPO) (Aldrich) is used for the extraction studies.

10% aqueous solution of thiocyanate is used for the spectrophotometric determination of Iron [16].

All other chemicals used are of Analytical Reagent grade.

# General extraction procedure:

Microgram amounts of iron and cobalt are extracted from 25 cm<sup>3</sup> aliquot of solution adjusted to appropriate pH and sodium salicylate concentrartion. The optimum extraction conditions are reported in table 1. The extracted iron and cobalt are back extracted from the organic phase with 0.5 mo dm<sup>-3</sup> sulfuric acid and 0.1 mol dm<sup>-3</sup> nitric acid respectively. The stripped iron and cobalt are determined spectrophotometrically using thiocyanate method [16] and Nitroso-R-salt [16] respectively.

# **RESULTS AND DISCUSSION:**

The extraction of iron and cobalt is studied at various pH values (1.5 to 7.0) (fig. 1), sodium salicylate concentrations (6.25 x 10<sup>-3</sup> to 5 x 10<sup>-2</sup> mol dm<sup>-3</sup>) with TBPO dissolved in toluene as extractant. It is found that iron (III) gets guantitatively extracted from 1.5 x 10<sup>-2</sup> to 3x 10<sup>-2</sup> mol dm<sup>-3</sup> sodium salicylate at pH 2.8 – 3.1 with 5 cm<sup>3</sup> of 2.1x10<sup>-1</sup> TBPO dissolved in toluene. Similarly cobalt gets quantitatively extracted from 8.75 x 10<sup>-2</sup> mol dm<sup>-3</sup> sodium salicylate at pH 3.0 – 3.7 with 5 cm<sup>3</sup> of 2.29x10<sup>-2</sup> mol dm<sup>-3</sup> TBPO dissolved in toluene.

Variation in the shaking period from 5 sec to 120 sec indicates that a shaking period of 45 sec. is adequate for quantitative extraction of both iron and cobalt from the salicylate solutions. However, prolonged shaking has no adverse effect on the extraction in both cases.

Various diluents like toluene, xylene, benzene and carbon tetrachloride are tried for their suitability as diluents. It is observed that the extraction is quantitative for iron with toluene and xylene. While for cobalt extraction is guantitative under the given conditions with toluene, xylene and carbon tetrachloride. Toluene is used as diluent for both the cases as it gives better and quick phase separation.

Several stripping agents like nitric acid, hydrochloric acid, sulphuric acid, ammonium hydroxide and sodium hydroxide are used for the back extraction of iron and cobalt. It is found that 0.05-1.5 mol dm<sup>-3</sup> of sulfuric acid back extract iron and 0.02-2 mol dm<sup>-3</sup> sulfuric acid for cobalt, 0.1-0.5 mol dm<sup>-3</sup> of hydrochloric acid for both iron and cobalt, while 0.05-0.2 mol dm<sup>-3</sup> nitric acid back extract cobalt quantitatively from the organic phase.

# Nature of extracted species:

The composition of the extracted species is ascertained using log-log plots. The plot of log of distribution ratio verses log of sodium salicylate concentration (at fixed pH, and TBPO concentrations) gives slope of 3.08 and 2.09 for iron and cobalt respectively. This indicates a molar ration of 1:3 of the iron with respect to salicylate and molar ration of 1:2 of cobalt with respect to salicylate. Similarly the plot of log of distribution ratio verses log of extractant concentration (at fixed pH and salicylate concentration) gives straight lines with slopes 2.14 and 1.96 for iron and cobalt systems respectively. The slopes predict the number of extractant molecules coordinated with the metal ion. Thus, the probable extracted species for iron system is Fe(Hsal), TBPO and that for cobalt system is Co(Hsal), 2TBPO, where Hsal- stands for the salicylate ion. In both cases metal salicylate is solvated by the extractants and transferred into the organic phase.

#### Effect of diverse ions:

Varying amounts of foreign ions are added to the fixed amount of iron and cobalt to study their interference in general extraction and subsequent determination of bismuth. The tolerance limit is set at the amount of the foreign ion causing  $\pm 2\%$  error in the recovery of the bismuth. The results are reported in Table 2.

#### APPLICATIONS

Binary separation of iron (III) from copper (II), lead (II), cobalt (II), antimony (III), tellurium (IV), vanadium (V) and chromium (VI):

Iron is commonly associated with lead, copper, chromium and vanadium in industrially important alloys. Under the optimum extraction conditions of iron, the metal ions Sb, Te, V and Cr do not show any extraction either into TBPO phase. Which facilitates their separation from the binary mixtures. Iron from the organic phase is back extracted with 0.2 mol dm<sup>3</sup> sulfuric acid and determined as described in the general extraction procedure. Unextracted antimony (III), tellurium (IV), vanadium (V) and chromium (VI) are determined in the aqueous phase spectrophotometrically with iodide [17], stannous chloride [17], 4(2-pyridylazo resorcinol) PAR method [17] and diphenyl carbaazide (DPC) [18] methods, respectively.

Copper (II), lead (II) get completely extracted along with iron, however, both are selectively back extracted from the organic phase using 0.2 mol dm<sup>3</sup> nitric acid and determined spectrophotometrically with 4(2-pyridylazo resorcinol) PAR [17] method. Cobalt also gets partially extracted (40%) along with iron. The mutual separation of iron and cobalt is achieved by selectively stripping cobalt from the organic phase with 0.2 mol dm<sup>3</sup> nitric acid, mixed with unextracted cobalt and determined spectrophotometrically at 500 nm with Nitroso-R-salt(Sodium-1-nitroso 2-hydroxynapthalene-3-6disulphonate)

#### Analysis of alloys:

The proposed methods are applied to the various commercial alloy samples such as tin based white metal (BCS-178/2), leaded gunmetal (BCS-183/4) alloy. The detail procedure is given below.

Weigh 500 mg of each of tin based white metal and leaded gunmetal alloy, dissolve it in 3-5 cm<sup>3</sup> of concentrated nitric acid and evaporate to dryness. The residue is taken up with water and precipitate of metastannic acid is filtered off. The precipitate is first washed with hot dilute nitric acid and then with hot water. To the filtrate add 2.5 mg cobalt solution and dilute to 25 cm<sup>3</sup>. A 10 cm<sup>3</sup> of aliquot of this solution is taken up for the extraction and determination of the iron and cobalt by the proposed method. The results are reported in Table 4.

#### Analysis of pharmaceutical sample:

Iron is found in pharmaceutical products like Theragran-M (Sarabhai chemicals Ltd, India), Vimgran (Sarabhai chemicals Ltd, India), and Fersolate (Glaxo India Ltd). Five tablets of each formulation are taken and dissolved in minimum quantity of perchloric acid, the solution is evaporated to dryness and residue is dissolved in concentrated hydrochloric acid. Finally solution is filtered and taken up in water. Each solution is diluted to 25 cm<sup>3</sup> with distilled water and 1 cm<sup>3</sup> aliquot of each for the extraction and determination of the Iron by the proposed method. The results are reported in Table 4.

#### **CONCLUSIONS:**

The results ascertain the fact that Tributylphosphine oxide is potent extractant for extraction of metals. It can be applied as a novel extractant for various metal extraction studies from varied systems. The proposed methods for iron and cobalt have several distinct advantages over those discussed in the introduction.

- 1. The methods are simple, rapid and precise.
- 2. It needs no pre-equilibration or use of salting out agents.
- 3. Extraction occurs in single step.
- 4. The methods are highly reproducible and the total analysis time is only about 20 minutes.
- The methods are highly selective; they provide the separation and quantitative determination of iron and cobalt from commonly associated elements, multicomponent mixtures, alloys

and pharmaceutical samples.

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# Table 1: Optimum Extraction conditions for Fe (III) ad Co (II).

Metal ion (50- 250) µg	Aqueous phase, [Salicylate] mol dm <sup>-3</sup>	pН	Organic phase, 5cm <sup>3</sup> TBPO in toluene, mol dm <sup>-3</sup>	Extrac- tion period, sec.	Stripping solution	Estimation procedure
Fe (III)	1.5 x 10 <sup>-2</sup> to 3x 10 <sup>-2</sup>	2.8- 3.1	2.1x10 <sup>-1</sup>	45	0.5 mol dm <sup>-3</sup> H <sub>2</sub> SO₄ (2x5cm <sup>3</sup> )	Spectrophoto- metrically by Thiocyanate [18]
Co (II)	8.75 x 10 <sup>-2</sup>	3.0- 3.7	2.29x10 <sup>-2</sup>	45	0.1 mol dm <sup>-3</sup> HNO <sub>3</sub> (2x5cm <sup>3</sup> )	Spectrophoto- metrically by Nitroso-R-salt [16]

### Table 2: Diverse ion effect

Aqueous Phase :	2X10 <sup>-2</sup> mol dm <sup>-3</sup> sodium salicylate at pH 2.8 – 3.1 for Iron (III) system				
	8.75X10 <sup>-2</sup> mol dm <sup>-3</sup> sodium salicylate at pH 3.0 – 3.7 for Co (II) system				

Foreign ions	Tolerance limit, μg			
	Fe(III)	Co(II)		
Cu(II)	2500	200		
Pb(II)	2000	5000		
Mn(II)	2000	2000		
Ba(II)	4000	2500		
Zn(II)	2000	2000		
Cd(II)	2000	3000		
Mg(II)	2000	2000		
Sb(III)	1000	2500		
AI(III)	500	3000		
La(III)	200	500		
Fe(III)	2000	200		
Y(III)	1500	1000		
EDTA	*none	none		
Th(IV)	2000	1000		
Zr(IV)	none	1000		
Hf(IV)	none	1000		
Ti(IV)	none	None		
Ce(IV)	200	500		
Te(IV)	200	200		
V(V)	2000	1000		
U(VI)	1000	1500		
Cr(VI)	2500	500		
Mo(VI)	1500	500		
SO <sub>4</sub> <sup>2-</sup>	3000	1000		
Cl <sup>-</sup>	1000	1000		
NO3 <sup>-</sup>	2000	1000		
SCN	2500	500		

\*Not tolerated

Table 3: Separation of Fe(III) and Co(II) from binary and multicomponent mixtures.

Composition of the mixture, µg	Recovery,*%	Relative error, *%	Estimation procedure for the added ion
Fe, 100;	99.5	0.5	PAR[17]
Cu, 50	99.2	0.8	
Fe, 100;	99.7	0.3	PAR[17]
Pb, 50	99.1	0.9	
Fe, 100;	99.1	0.9	Nitroso-R-Salt[16]
Co, 100	99.6	0.4	
Fe, 100;	99.2	0.8	lodide[17]
Sb, 200	99.3	0.7	
Fe, 100;	99.3	0.7	SnCl <sub>2</sub> [17]
Te, 200	99.3	0.7	
Fe, 200;	99.4	0.6	PAR[17]
V, 50	99.6	0.4	
Fe, 200;	99.7	0.3	DPC[18]
Cr, 50	99.6	0.4	
Fe, 100; Pb, 100 Cu, 100; Ni, 200 Co,50	99.2	0.8	
Fe, 100; Sb, 100 Te, 100; U, 100 Cr,100	99.1	0.9	

Sample	Composition (%)	Fe(III) added or Cer- tified value, mg	Co(II) added or Cer- tified value, mg	Recov- ery of Fe(I- II),mg	Recov- ery of Co(II),mg	C.V.,%*	¢
Vimgran (Sarabhai chemicals)	Calcium carbonate USP 250mg; iron(II) sulfate IP,34mg; Potassium iodide IP, 0.3mg; Copper sulfate IP, 4.0mg; man- ganese sulfate 6.6mg	12.51 <sup>b</sup>	-	12.44	-	0.88	
Fersolate (Glaxo)	Dried iron(II) sulfate IP, 195mg; copper sulfate, IP,2.6mg; manganese sulfate IP, 2.6mg	71.72 <sup>b</sup>	-	71.23	-	1.21	

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amount per 100 mg of alloy

mg per tablet

\*Average of triplicate analysis

**BCS-** British Chemical Standard

\* Average of triplicate analysis

### Table 4: Estimation of Fe (III) and Co(II) in alloys and pharmaceutical samples

Sample	Composition (%)	Fe(III) added or Cer- tified value, mg	Co(II) added or Cer- tified value, mg	Recov- ery of Fe(I- II),mg	Recov- ery of Co(II),mg	C.V.,%*	
						Fe	Со
Tin base white metal (BCS 178/2)	Sn,82.2; Cu,4.58; Ni,0.17; Bi,0.11; Fe,0.024; Sb,9.45; Pb,3.18; Cd,0.14; Zn,0.040 + 2.5 mg Co(II)	0.024ª	2.5	0.022	2.48	0.85	0.51
Leaded gunmetal (BCS- 183/4)	Cu,84.06; Sn,7.27; Pb,3.15; Ni,1.0; P0.09; Fe,0.056; Sb,0.23; As,0.13; S,0.11; + 2.5mg Co(II)	0.056ª	2.5	0.055	2.49	0.33	0.23
Thera- gran-M (Sarabhai chemicals)	Potassium iodide IP, 0.2mg; dried iron (II) sulfate IP, 41mg; copper sulfate IP, 8mg	15.08 <sup>b</sup>	-	15.02	-	0.56	



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