

Extractive determination of cobalt (II) using tri-iso-octylamine

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A selective and quantitative extraction method for the determination of cobalt(II) using tri-iso-octylamine (TIOA), a high molecular weight tertiary amine, into cyclohexane from aqueous hydrochloric acid medium has been developed. The effects of concentration of HCl, extractant, metal ions, role of various diluents and diverse ions on the extraction of cobalt have been studied. The method has been successfully applied to the estimation of cobalt in several ores and pharmaceutical drug samples.

Cobalt is an important trace element in animal nutrition. Cobalt deficiency is exhibited by retarded growth rate, loss of appetite and irritation of the gastrointestinal tract, nausea, diarrhoea etc. Determination of cobalt in several complex matrices is, therefore, of considerable interest. In an extensive work of Sato¹, extraction of U(VI) and Co(II) from HCl media with 0.1 M tri-octylamine in benzene, effect of LiCl and temperature has been described. Sato also applied series of alkylamines to study the effect of alkyl chain, solvent etc. since then, Co(II) extraction procedure and its number of variation have been reported by many workers^{3,11}, which include the study of the effect of nature of amine, alkyl chain length and its substitution, and presence of various anions like SCN⁻, CN⁻, NO₃⁻, organic acid etc. Cetyl pyridinium chloride¹² was used to determine cobalt in soil by spectrophotometry, showing practically no interference. In another work¹³ extraction equilibria of Co(II) and Ni(II)-thiocyanates with Aliquot 336 in ethyl acetate was studied. The result encouraged the application of Co(II) extraction with high molecular weight tertiary amine into a non-polar solvent for its determination in unknown samples.

Experimental

The absorbance measurements were carried out on a Shimadzu atomic absorption spectrophotometer (Model AAS 646). A stock solution of cobalt(II) was prepared by dissolving 1 gm. CoSO₄ in deionised water and it was standardised by EDTA titration, A

working stock solution of strength 50 µg/ml. of cobalt(II) was prepared by appropriate dilution. All other reagents used were of A.R. Grade. An aliquot of 2.5 ml of Co(II) solution (125 µg) was mixed with 7.5 ml of HCl 6 M. The solution was transferred to a separating funnel and shaken with 10 ml of 0.05 M TIOA in cyclohexane for three mins. The layers were allowed to settle for five mins. After the layers separation, the organic extract was stripped with 10 ml water and absorbance was measured by AAS - 646 using proper instrumental parameters.

Preparation of pharmaceutical drug samples

The samples were treated with conc. HNO₃ on a hot plate at a low temperature to avoid violent flashing. The residue was cooled and HNO₃ was added to it again. The temperature of the hot plate was raised to 400°C. The mass was leached with HNO₃ (1:1) and evaporated to dryness. Finally, the residue was dissolved in water and the volume was made up to 50 ml. in a volumetric flask.

Results and discussion

The effect of various solvents on the extraction of cobalt-chloride complex was studied in 6 M HCl. Co(II) 125 µg was complexed with 6 M HCl. The amine concentration was kept 0.05 M. The results show that the extraction was maximum in cyclohexane. The order was cyclohexane > carbon tetrachloride > toluene > xylene > diethyl ether > amyl alcohol > chloroform > 1,2-dichloro ethane. The effect of [HCl] concentration on the extraction of cobalt-chloride complex was studied in different molar concentration of hydrochloric acid varying from 3.6 to 10 M. The results show that the extraction was maximum in 6 M HCl. The metal ion could be completely stripped from the organic phase by de-ionised water. The contact time was varied from 1 to 10 min. It was observed that the extraction was quantitative within 5 min.

The effect of amine concentration ranging from 0.01 M to 0.1 M in cyclohexane on the extraction of 125 µg Co(II) in 6 M HCl was studied. It was found that the extent of extraction increased with increasing amine concentration and that extraction was maximum at 0.06 M TIOA concentration after which there was no further increase in Co(II) extraction.

A set of solutions containing different amounts of cobalt(II) were examined by the recommended procedure. 0.06 *M* TIOA in cyclohexane was found to be quantitative for metal ion concentration up to 150 μg above which the extraction was found to be incomplete.

Effect of diverse ions

Extraction of cobalt(II) was studied in presence of several foreign cations and anions. A tolerance limit was set for the recovery of cobalt within $\pm 2\%$. The concentrations of interferences are given in Table 1. Fe(III) and Cr(III) were found to cause interferences and therefore, were removed before extraction.

High molecular weight amine extraction procedure for cobalt was applied for the determination of cobalt in some ores and drug samples. Ores were brought into solution by usual procedure¹⁵. Attack of drug-samples have been described before.

Table 1—Effect of diverse ions

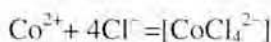
Diverse ions	Amount added (mg)	Recovery %
Na (I)	10,000	100
K (I)		100
Al (III)	5,000	100
V (IV)		102
Cu (II)		97
Zn (II)		100
Pb (II)		99.8
Ti (IV)		98.2
Mo (VI)	2,000	101
SO ₄ ²⁻		100
SiO ₃ ²⁻		100
PO ₄ ³⁻		99.57
Mn (II)	500	98
Ni (II)		99.5
Fe (III)		96.20*
Cr (III)		95.50*

*In presence of F⁻

Aliquot portion of the sample solution, pretreated with hydrochloric acid was extracted using TIOA. Triplicate extractions were carried out to ensure complete extraction. Organic phase was stripped with deionised water and metal content was determined by AAS taking usual precaution and computed from a standard curve. The results are compared with the values obtained by direct AAS. (Tables 2 and 3)

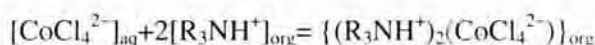
Nature of extracted species

The nature of extracted species was ascertained by plotting of $\log k_D$ against $\log [\text{Cl}^-]$. A straightline with slope ~ 4 was obtained which indicates anionic complex formation according to the following equation.



$$k_1 = \frac{[\text{CoCl}_4^{2-}]}{[\text{Co}^{2+}][\text{Cl}^-]^4} \quad \dots (1)$$

The fact that the extracted species contain bi-negative complex was confirmed by the slope of the straightline obtained by plotting $\log k_D$ against $\log [\text{TIOA}]$. The slope was ~ 2 indicating the extraction reaction to be,



$$\begin{aligned} \text{Therefore, } k_1 &= \frac{[(\text{R}_3\text{NH}^+)_2(\text{CoCl}_4^{2-})]_{\text{org}}}{[\text{CoCl}_4^{2-}]_{\text{aq}}[\text{R}_3\text{NH}^+]_{\text{org}}^2} \\ &= \frac{[(\text{R}_3\text{NH}^+)_2(\text{CoCl}_4^{2-})]_{\text{org}}}{k_1[\text{Co}^{2+}][\text{Cl}^-]^4[\text{R}_3\text{NH}^+]_{\text{org}}^2} \end{aligned}$$

[From Eq. (1)]

$$\therefore k^1 = k \cdot k_1 = \frac{[(\text{R}_3\text{NH}^+)_2(\text{CoCl}_4^{2-})]_{\text{org}}}{[\text{Co}^{2+}]_{\text{aq}}[\text{Cl}^-]_{\text{aq}}^4[\text{R}_3\text{NH}^+]_{\text{org}}^2}$$

Table 2—Determination of cobalt in ore samples

Sample	Trader code	Wt. taken(g)	Amount of cobalt present (Direct AAS) (μg)	Amount of Cobalt* found (Present Method) (μg)
Ni ore	GSI/74/59557/98	0.1	200	200 $\pm$ 1.54
Ni ore	GSI/74/5957/64	0.1	150	147 $\pm$ 2.23
Tata - Steel	66/4	0.1	5.73	5.70 $\pm$ 0.30

*Average of three determinations

Table 3—Determination of cobalt in pharmaceutical drugs

Sample	Amount of cobalt direct AAS (μg)/Tab.	Amount of cobalt* Present method (μg)/Tab.
Becozyme (M/s Roche)	0.17	0.17 $\pm$ 0.016
Neurobion (M/s Merek)	0.24	0.26 $\pm$ 0.012
Cobadex Forte (M/s Glaxo India)	0.24	0.23 $\pm$ 0.02

* Average of three determinations.

$$\text{or, } k^1 = \frac{k_D}{[\text{Cl}^-]_{\text{aq}}^4 [\text{R}_3\text{NH}^+]_{\text{org}}^2}$$

$$\therefore k_D = \frac{[(\text{R}_3\text{NH}^+)_2 \text{CoCl}_4^{2-}]_{\text{org}}}{[\text{Co}^{2+}]_{\text{aq}}}$$

$$\therefore k_D = k^1 [\text{Cl}^-]_{\text{aq}}^4 [\text{R}_3\text{NH}^+]_{\text{org}}^2$$

Taking log of both sides

$$\log k_D = \log k^1 + 4 \log [\text{Cl}^-] + 2 \log [\text{R}_3\text{NH}^+] \quad \dots (2)$$

From Eq. (2), it is found that the plot of $\log k_D$ against $\log [\text{Cl}^-]$ is linear with a slope=4 and the plot of $\log k_D$ against $\log [\text{R}_3\text{NH}^+]$ is also linear with a slope=2, confirming the reality of the extraction.

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