

## EXTRACTION, SEPARATION AND DETERMINATION OF COPPER (II) AND IRON (III) BY HIGH MOLECULAR WEIGHT AMINES

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The work describes the development of analytical methods for the extraction, separation and trace determination of Cu (II) in the presence of macro-amount of Fe (III) and the application of these methods to the analyses of geological samples i.e. the ores of Cu such as malachite, azurite and pyrite of Waziristan Agency. An investigation of the complexes formed between Cu (II) and Fe (III) in the presence of hydrochloric acid and thiocyanate were carried out and extractability of Cu(II)-SCN complex by two types of long chain high molecular weight amines (HMWA) Alamine 336 and Tribenzylamine were examined. The extraction of the thiocyanate complex by high molecular weight amines indicate that the species are anionic in nature. The results achieved were successful and gave better results than the existing methods.

**Key word:** Extraction, Copper, Highmolecular weight amines.

### Introduction

High molecular weight amines (HMWA) particularly the highly branched alkyl amines, have been used for the separation of several pairs of metals as anions [1] and for the extraction of metals such as uranium and plutonium [2,3]. In several cases the elucidation of the structure of anionic species have also been studied [4,5]. The most popular and cheapest method of extraction and separation of metals is as the thiocyanate complex from hydrochloric acid into an organic phase containing the amine. In analytical chemistry large number of reagents have been used for the detection and determination of metal ions. Copper was determined accurately with benzyl reagent [6]. Spectrophotometric determination of copper with ammonium hydroxide was also proposed by various investigators [7,8]. They used primary, secondary and tertiary amines for the extraction of copper complex. The extraction of copper complexes with benzoate into chloroform as well as its spectrophotometric determination have also been examined [9]. Bock [10] made an extensive study of the extractability of many metal thiocyanates into an immiscible natural organic solvent and it has shown that a sizeable number of metal thiocyanates are extractable into organic solvents. More recently advantage has been taken of the use of thiocyanate complexing as a method of chemical separation [11]. Separation of Cu from other metals containing Ni, Zn, Fe etc., at its cuprous thiocyanate complex have been extracted with chloroform pyridine [12], cupferron [13] and sodium dithiocarbamate [14] was also used for quantitative extraction and separation of copper from Fe, Ni but extraction is possible in chloroform and butanol. In addition to thiocyanate, so other complexing reagents used for spectro-

photometric determination and separation of Cu (II) & Fe (III) are time consuming and the applications to the analysis of ores and minerals are rarely discussed [15-18]. Little literature is available on developing a valid and sensitive spectrophotometric methods, separation as well as determination of Cu (II) and Fe (III).

Looking at the pattern of previous research, the present work was undertaken with specific view to investigate sensitive and rapid analytical procedure for the separation and estimation of Cu(II) and Fe (III) and further applied for the estimation of trace amount of copper in ores and minerals. The procedure is based on the extraction as well as separation of copper as its thiocyanate complex into tribenzylamine an alamine 336.

### Experimental

**Apparatus.** Erma Spectrophotometer Model LS-7 was used.

**Reagents.** (i) *Standard copper solution.* One gram copper metal (analar) was dissolved in a minimum volume of 1:1 HNO<sub>3</sub> and diluted to one liter with distilled water. Further solutions were made from these stock solutions to 20 µg/ml. (ii) *Iron solution (1000 mg/ml).* 0.1 gm Iron wire (analar) was dissolved in a few ml of hydrochloric acid (to acidify) and diluted with distilled water to 100 ml. The stock solution was further diluted with distilled water 20 µg/ml. (iii) *Potassium Thiocyanate solution.* A 70% (7.2M) solution was prepared from analar grade potassium thiocyanate by dissolving the required amount in distilled water with shaking and then diluting to required concentration. The solution is stable for a long time.



**Tribenzylamine.** The solution (0.2M) was prepared by dissolving the crystals in chloroform.

**Alamine-336.** The solution (5% v/v) was prepared by mixing the amine in thiophene free benzene.

All other chemicals used were of analar grade.

**Formation of Cu (II)-SCN complex and extraction by amines.** Investigations were carried out for the formation of complex between Cu (II) and thiocyanate ions by transferring a suitable amount of Cu (II) and Fe(III) to a 100 ml separatory funnel followed by the addition of thiocyanate solution in the acidic medium, the extractability of the coloured species was investigated by shaking the aqueous phase with 5 ml of tribenzylamine for 2 mins. The phases were allowed to separate as no trace of copper was ever found in the aqueous phase whereas Fe(III) SCN complex formed remained in the aqueous phase.

The organic phase was collected in a dried flask after passing it through a small filter paper (5 cm) to remove suspended water droplets. The absorption spectrum after extraction and separation was shown graphically in Fig. 1.

**Effect of acid concentration.** The effect of different molar concentrations of hydrochloric acid on the extraction of copper as its thiocyanate complex and its separation from iron

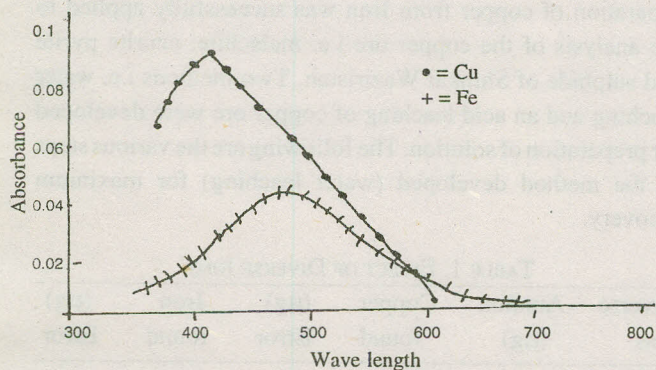


Fig. 1. Absorption spectrum of Cu(II) & Fe(III) after extraction into tribenzylamine.

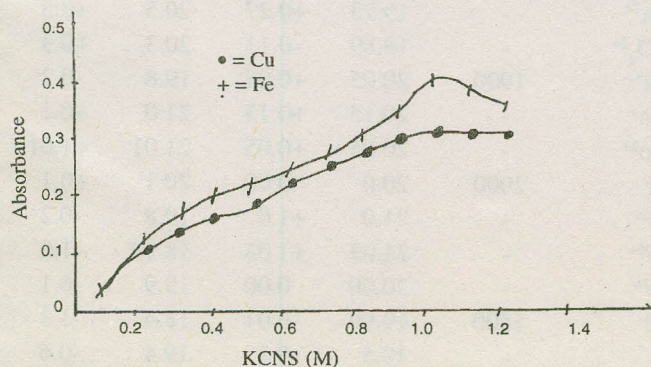


Fig. 3. Effect of thiocyanate on the extraction & separation of Cu(II) & Fe(III).

was studied in the range of 0.1 MHCl, to find the suitable concentration of efficient extraction and constancy in absorbance. It was found that 1.3 MHCl was the most suitable for efficient extraction. The effect is shown graphically in Fig. 2.

**Effect of thiocyanate concentration.** The effect of potassium thiocyanate range 0.1-3.0 M was studied and 1.0-1.3 M thiocyanate solution was found to be most suitable concentration for maximum colour intensity and quantitative extraction and separation of copper and iron. The results shown in the Fig. 3.

**Effect of time.** Having studied the effect of HCl and KCNS concentration, efforts were also made to undertake studies to choose the optimum time for shaking the two phases. The effect of time in the range of 10-120 sec. was studied and 1 min. (60 sec.) was found suitable for maximum extraction. Results are given in Fig. 4.

**Effect of amine concentration.** Tribenzylamine and alamine-336 were used as the extractant and their extraction efficiency was studied in the range 0.02 to 0.3M. and 0.2 M chloroform solution of tribenzylamine gave better results in subsequent extraction of the system.

A benzene solution of the alamine 336 when used as extractant, a very clear solution was obtained. This was in

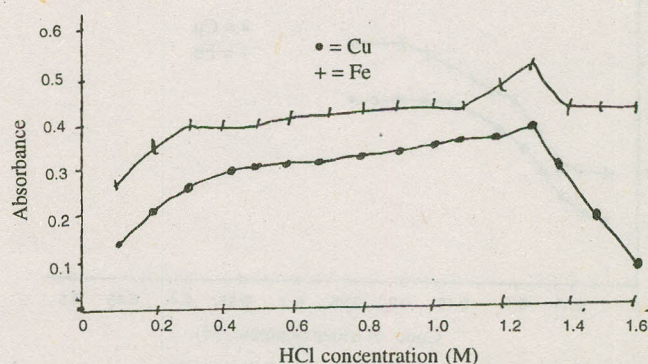


Fig. 2. Effect of HCl concentration on extraction & separation of Cu(II) & Fe(III).

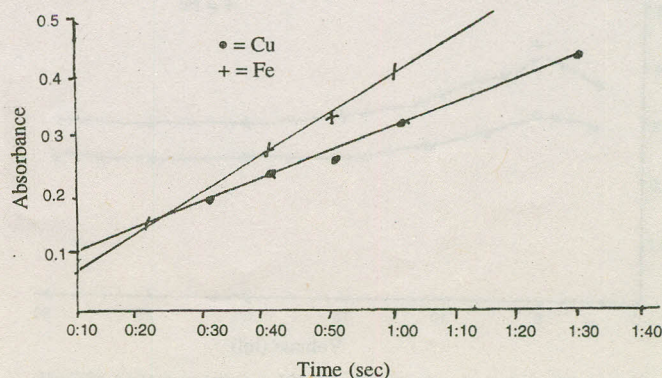


Fig. 4. Effect of time on the extraction & separation of Cu(II) & Fe(III).



confirmation with our earlier work in extraction of metal anionic complex species [14]. Results are given in Fig.5.

**Effect of dilution/phase volume ratio.** Keeping the acid concentration 1.3M, organic amine 0.2M phase and thiocyanate concentration 1M constant, the effect of phase volume ratio  $V_{org}/V_{aq}$  was studied by varying the volume of the aqueous phase. It was observed that the ratio 1:1 is the most suitable ratio for quantitative and excellent extraction and separation of Cu (II)-SCN complex. Results are represented in Fig 6.

**Effect of the diverse ions.** Efforts were also made to the effect of interfering radicals which probably have diverse effects on the efficient extraction. The effect of thiocyanate in hydrochloric acid on number of elements was examined. Mn (II) interferes in the extraction due to its reddish Mn (II)-SCN complex formation. The effect of anions i. e.  $SO_4^{2-}$ ,  $Cl^-$ ,  $CO_3^{3-}$ ,  $PO_4^{3-}$  did not interfere seriously. Comparative results are given in Table 1.

**Calibration, stability, sensitivity.** Solution of known copper and iron contents were extracted and determined by the foregoing procedure and absorbance was measured at 420 nm and 400nm in the concentration range of 0.5-0.6 ppm. Beer's

law was closely obeyed. The molar absorption coefficient was formed to be  $1.013 \times 10^4$  l. mole<sup>-1</sup> cm<sup>-1</sup> for copper and  $0.9 \times 10^4$  l. mole<sup>-1</sup> cm<sup>-1</sup> for iron. The yellowish brown coloured complex of Cu (II)-SCN extracted into organic phase and separated from red blood colour complex of Fe (III)-SCN was allowed to stand for 6-7 hrs, the change observed in optical density.

The stability of the organic extract was found to be dependent on HCl, thiocyanate and the rate of extraction after the addition of the reagents.

**Analysis of synthetic mixture.** Investigations were carried out to analyse synthetic mixtures of copper and iron. The results were reproducible through the mixture contained variable amounts of copper and iron. The results are shown in Table 2.

**Analysis of unknown mixture.** As a final check on the method for the spectrophotometric determination, separation of Cu(II) and Fe(III), various unknown were also analysed. The results in Table 3 indicated that the maximum extraction in the determination did not exceed 3%.

## Results and Discussion

**Application to the analysis of copper ore of Waziristan area.** The method developed for the determination and separation of copper from Iron was successfully applied to the analysis of the copper ore i.e. malachite, azurite pyrite and sulphide of Shinkai Waziristan. Two methods i.e. water leaching and an acid leaching of copper ore were developed for preparation of solution. The following are the various steps of the method developed (water leaching) for maximum recovery.

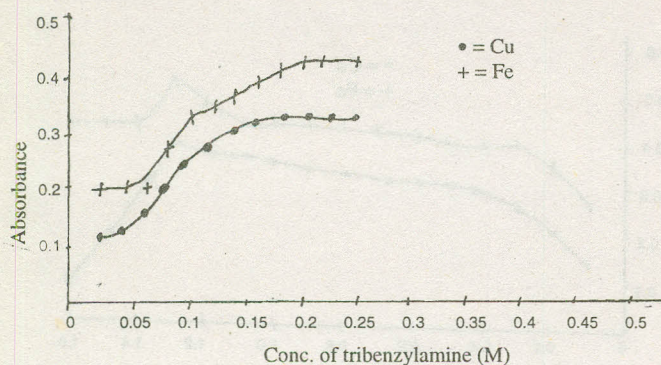


Fig. 5. Effect of amine concentration on overall extraction.

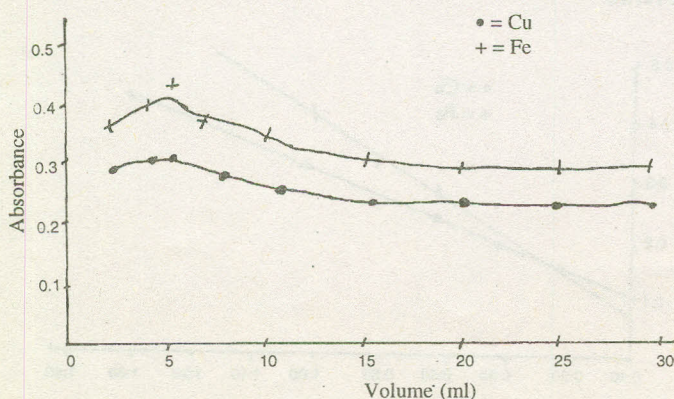


Fig. 6. Effect of phase volume ratio ( $V_{org}/V_{aq}$ ) on the extraction of Cu(II) & Fe(III).

TABLE 1. EFFECT OF DIVERSE IONS.

Diverse Ions	Amount ( $\mu$ g)	Copper found ( $\mu$ g)	( $\mu$ g) Error	Iron found ( $\mu$ g)	( $\mu$ g) Error
Mg <sup>2+</sup>	500	19.0	-0.1	19.0	-0.4
Ca <sup>2+</sup>	-	20.1	+0.1	20.0	0.0
Mn <sup>2+</sup>	-	22.8	+2.2	24.01	4.01
Ba <sup>2+</sup>	-	19.73	+0.27	20.5	+0.5
PO <sub>4</sub> <sup>2+</sup>	-	19.89	-0.11	20.3	+0.3
Al <sup>3+</sup>	1000	20.05	+0.05	19.8	-0.2
Na <sup>+</sup>	-	20.15	+0.15	21.0	+0.1
Co <sup>2+</sup>	-	20.05	+0.05	21.01	+1.01
Ti	2000	20.0	0.00	20.1	+0.1
V <sup>5+</sup>	-	21.0	+1.0	19.8	-0.2
W <sup>6+</sup>	-	21.03	+1.03	18.99	-1.0
U <sup>3+</sup>	-	20.00	0.00	19.9	-0.1
Cl <sup>-</sup>	1500	19.99	-0.01	18.4	-1.3
I <sup>-</sup>	-	19.5	-0.5	19.4	-0.6
SO <sub>4</sub> <sup>2-</sup>	-	19.8	-0.2	19.4	-0.6



1. Fused 0.5 gm of well agitated sample into platinum crucible with fusion mixture ( $\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$ ) in the ratio of 1:1 in a muffle furnace at 800-850°C.

2. The fused mass was leached out for 1-2 hrs with distilled water at 60°C using an electric water bath.

3. The soluble part was filtered and diluted to 250 ml with distilled water followed by adding as much hydrochloric acid so that the final acid concentration was 1.3M HCl.

4. Transferred 3 ml aliquot and 2 ml of 1M potassium thiocyanate solution to 100 ml separating funnel, mixed & diluted to 10 ml with distilled water.

5. 5 ml tribenzyl amine solution in chloroform was added and shaken the two phases for 1 min.

6. Allowed the phases to separate and after the equilibrium was attained, the organic phase was separated into a dried flask after passing it through a whatmen filter paper to remove the suspended water droplets. The investigated method was compared with already established methods [19,20] i. e. atomic absorption spectrophotometric method and pyridine thiocyanate method. The results were reproducible shown in Table 4.

### Conclusion

The anionic complexes of copper and iron formed with thiocyanate in presence of hydrochloric acid were studied. Various parameters which effect the extraction and separation of Cu (II)-SCN and Fe (III)-SCN such as the change in organic diluent, type of amines, acid concentration, time etc., have been studied. The complex of Cu (II)-SCN is readily extracted into tribenzylamine in chloroform whereas the complex of Fe (III)-SCN remained in the aqueous phase because the extraction of Fe (III) [21,22] by HMWA depends markedly on amine structure whereas Fe (III) extraction is weak to negligible with the all amines tested. Advantage of this method for the extractions and separation of Cu (II) and Fe (III) by liquid-liquid extraction system is that it is rapid and sharp and utilize readily available equipment and cheaper. Aliphatic amines of comparable efficiency may be commercially available.

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TABLE 2. ANALYSIS OF SYNTHETIC MIXTURE.

S.No.	Copper (µgs)			Iron (µgs)		
	Added	Found	Error	Added	Found	Error
1.	3	3.0	0.00	4	3.99	0.01
2.	6	6.3	+0.3	8	7.89	0.11
3.	9	9.1	+0.1	12	12.0	0.00
4.	12	12.0	0.00	16	16.00	0.00
5.	15	14.8	-0.2	20	20.10	+0.10
6.	18	17.9	-0.1	24	24.15	+0.15
7.	21	21.05	-0.05	28	28.00	0.00
8.	24	24.0	0.00	32	32.97	-0.03
9.	27	26.8	-0.2	36	36.03	+0.03
10.	30	30.0	0.00	40	40.0	0.00
11.	33	33.0	0.00	44	43.8	-0.2
12.	36	35.7	-0.3	48	48.2	+0.2
13.	39	39.12	0.12	52	52.0	0.00
14.	41	41.00	0.00	56	56.0	0.00

TABLE 3. ANALYSIS OF UNKNOWN MIXTURE.

S.No.	Cu(µgs)		Iron(µgs)		Error	
	Added	Found	Added	Found	Cu(11)	Fe(111)
1.	8	12	7.93	12.0	-0.07	0.00
2.	12	20	12.00	20.1	0.00	+0.1
3.	16	28	15.99	28.02	-0.01	+0.02
4.	20	30	20.01	30.00	+0.01	0.00
5.	27	40	27.2	40.1	+0.2	+0.1
6.	32	45	32.07	44.99	+0.07	-0.01
7.	43	50	43.00	49.99	0.00	-0.01

TABLE 4. COMPARATIVE ANALYSIS REPORT OF COPPER (ORES OF SHINKAI WAZIRISTAN AGENCY USING THIOCYANATE AND OTHER STANDARD METHODS [21,22].

Sample No.	Atomic absorption Spectro- photometric method	Pyridine thiocy- anate method	Present method
1.	0.25	0.26	0.25
2.	0.22	0.21	0.23



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The atomic absorption spectra of copper and iron formed with thiocyanate in presence of hydrochloric acid were studied. Various parameters which affect the extraction and separation of Cu(II) and Fe(III) such as the change in organic solvent type, thiocyanate concentration, time etc. have been studied. The complex of Cu(II)-SCN is readily extracted into benzene whereas in chloroform whereas the complex of Fe(III)-SCN remained in the aqueous phase because the extraction of Fe(III) depends mainly on the structure whereas Fe(III) extraction is weak to negligible with the all organic solvent. Advantage of this method for the extraction and separation of Cu(II) and Fe(III) by liquid-liquid extraction system is that it is simple and highly reproducible. Available equipment and reagents. A typical analysis of copper-iron efficiency may be summarized as follows:

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Table 2. Analysis of Synthetic Mixtures

Sample No.	Copper (µg)		Iron (µg)	
	Added	Found	Added	Found
1	7.0	7.0	4.0	3.99
2	8.0	8.0	5.0	4.99
3	9.0	9.0	6.0	5.99
4	10.0	10.0	7.0	6.99
5	11.0	11.0	8.0	7.99
6	12.0	12.0	9.0	8.99
7	13.0	13.0	10.0	9.99
8	14.0	14.0	11.0	10.99
9	15.0	15.0	12.0	11.99
10	16.0	16.0	13.0	12.99
11	17.0	17.0	14.0	13.99
12	18.0	18.0	15.0	14.99
13	19.0	19.0	16.0	15.99
14	20.0	20.0	17.0	16.99
15	21.0	21.0	18.0	17.99
16	22.0	22.0	19.0	18.99
17	23.0	23.0	20.0	19.99
18	24.0	24.0	21.0	20.99
19	25.0	25.0	22.0	21.99
20	26.0	26.0	23.0	22.99
21	27.0	27.0	24.0	23.99
22	28.0	28.0	25.0	24.99
23	29.0	29.0	26.0	25.99
24	30.0	30.0	27.0	26.99

Table 3. Analysis of Unknown Mixtures

Sample No.	Copper (µg)		Iron (µg)	
	Added	Found	Added	Found
1	7.0	7.0	4.0	3.99
2	8.0	8.0	5.0	4.99
3	9.0	9.0	6.0	5.99
4	10.0	10.0	7.0	6.99
5	11.0	11.0	8.0	7.99
6	12.0	12.0	9.0	8.99
7	13.0	13.0	10.0	9.99
8	14.0	14.0	11.0	10.99
9	15.0	15.0	12.0	11.99
10	16.0	16.0	13.0	12.99
11	17.0	17.0	14.0	13.99
12	18.0	18.0	15.0	14.99
13	19.0	19.0	16.0	15.99
14	20.0	20.0	17.0	16.99
15	21.0	21.0	18.0	17.99
16	22.0	22.0	19.0	18.99
17	23.0	23.0	20.0	19.99
18	24.0	24.0	21.0	20.99
19	25.0	25.0	22.0	21.99
20	26.0	26.0	23.0	22.99
21	27.0	27.0	24.0	23.99
22	28.0	28.0	25.0	24.99
23	29.0	29.0	26.0	25.99
24	30.0	30.0	27.0	26.99