



## Solvent extraction of Cu(I) from waste etch chloride solution using tri-butyl phosphate (TBP) diluted in 1-octanol

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### ABSTRACT

Cuprous ion has wide applications in various industries due to its properties to form stable coordination compound of high solubility with different ligands. Compared to extensive R&D work on solvent extraction of cupric ion, the limited work is reported on cuprous ion extraction using organic extractant. Therefore, in the present work, solvent extraction studies have been carried out for the extraction of cuprous ion Cu(I) from chloride solution using extractant tri-butyl phosphate (TBP) diluted in 1-octanol, for application to recover Cu(I) from the etch waste of printed circuit boards (PCBs). Initially, the studies were carried out for the selection of suitable diluent to be used for Cu(I) extraction from chloride solution. The organic 1-octanol was found effective diluent for TBP. The behavior and reaction mechanism of TBP diluted in 1-octanol was also studied for the extraction of Cu(I) from chloride solution. Various process parameters viz. contact time, concentration of chloride ion, hydrochloric acid and extractant, temperature, etc., were also studied. The extractant TBP diluted in 1-octanol was found suitable for the extraction of Cu(I) from the waste chloride solution (containing both Cu(I) and Cu(II)) generated from the plant of PCBs manufacturing. The extraction isotherm plot indicates the requirement of two stages for the complete extraction of Cu(I). The studies revealed the formation of complex  $[\text{CuCl}_2 \cdot \text{H}^+ \cdot \text{TBP}]$  in the organic phase. The extraction and stripping studies showed the suitability of the TBP diluted in 1-octanol for the recovery of cuprous ion from the waste chloride etch solution of PCBs.

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### 1. Introduction

In electronics industries, copper is extensively used as engineering material for the fabrication of micro-electronic components, micro-engineered structures and precision parts. Copper etching is considerably important process for getting smooth surface, particularly in the fabrication of printed circuit boards (PCBs). Due to high etching capacity and easy regeneration properties, the cupric chloride is an acceptable etchant in these industries. In PCBs manufacturing industries, solution composed of cupric chloride and hydrochloric acid is used as an etchant to oxidize and dissolve metallic copper, which results in the generation of a large amount of waste solution containing cupric and cuprous ions. The concentrations of etch solution depends on the etching medium and the material to be leached. Etch waste effluent generally contains high copper contents (40–60 g/L Cu) in comparison to the etch wash liquor (2–10 g/L Cu). In addition to etching, the waste solutions containing copper are also being generated through pickling and

electroplating processes. The acidic effluents thus generated are normally treated with lime to neutralize, but it consumes acid and produces sludge of mixed metal hydroxides.

Cementation or electrolytic recovery of copper from etch waste is not advisable in respect to purity of copper recovered [1]. Therefore, the separation of copper by solvent extraction is attractive. Many researchers worked for the solvent extraction of Cu(II) from different solutions. Fletcher et al. [2] used pyridine dicarboxylate esters instead of amines to create a copper-selective extraction system. The chelating component of the extractant mixture was LIX 860. This extractant was selective for copper under conditions of medium acidity ( $\text{H}^+ < 1 \text{ M}$ ), where the solvation mechanism operates. Mishonov and Kyuchoukov [3] used a mixed extractant, comprising of Alamine 336 and LIX 54, to separate copper and zinc from hydrochloric acid. They reported that the metal ions were extracted from hydrochloric acid medium; the extract was scrubbed in two steps, whereas zinc passed from Alamine 336 to LIX 54, in order to remove copper and chloride ions. In the CUPREX process Dalton et al. [4] suggested to oxidize copper to Cu(II) in the leached solution and then to extract with DS5443. Zhou et al. [5] studied the co-extraction of  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  with quaternary ammonium chloride. The redox reaction occurred between  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$

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simultaneously and exists as chloro-coordination ions of  $\text{Cu}^+$  and  $\text{Fe}^{3+}$  in the organic phase. Kogan et al. [6] reported the extraction of copper by tri-butyl phosphate (TBP) from acidic solutions containing  $\text{Cl}^-$  1 mol/L, HCl 10–20 g/L, and  $\text{I}^-$   $2\text{--}5 \times 10^{-3}$  mol/L at room temperature with the flow of roasting gas containing 0.9–1.2% of  $\text{SO}_2$ . Pressure hydrogen reduction was suggested for the recovery of copper from the loaded organic phase. Duggan [7] patented the use of dialkyl ester of pyridine-3,5-dicarboxylic acid for the extraction of Cu(I) from halide or pseudo halide solutions. One reagent with such structure namely aforementioned DS5443 (or Acorga CLX50) was patented, which preferentially extracts Cu(II) instead of Cu(I) [8]. Lee et al. [9] developed a process to recover metals and regenerate the nitrate etch waste (250 g/L  $\text{HNO}_3$ , 30–40 g/L Cu, 30–40 g/L Sn, 30–40 g/L Pb and 20–25 g/L Fe) solution of PCBs using solvent extraction, stripping, electrowinning, precipitation and cementation processes. Nitric acid was selectively extracted by TBP from spent etching solution and pure nitric acid solution was stripped by distilled water. From the acid depleted solution, the pure copper metal was obtained by electrowinning. In order to achieve a high-quality cathode copper, solvent extraction in chloride medium was also tested by several researchers. The extraction of CuCl by alkyl, aryl, and mixed alkyl-aryl tertiary phosphite (S) was studied by Healy and Barton [10]. Complexes of the types  $\text{CuCl}\cdot\text{S}$  and  $\text{CuCl}\cdot 2\text{S}$  were postulated, but most of these phosphite compounds were hydrolysed during the solvent extraction. Demarthe et al. [11] described a process for the solvent extraction and electrowinning of copper from leach solution containing copper(I), copper(II) and iron(II) chlorides. The copper(I) is oxidized to copper(II) before extraction with LIX 65N. Scientists of Murdoch University reported R&D work in the field of the cuprous hydrometallurgy [1], and suggested to use organic nitriles to extract copper(I). Nitrile (RCN) coordinated to the cuprous ions and formed the extract  $\text{Cu}(\text{RCN})_3\text{Cl}$ . When high-boiling nitriles, like benzonitrile, was used, the copper complex in the organic phase was oxidized to copper(II) chloride before stripping by water. And, when the volatile nitriles, like acetonitriles were used, CuCl was recovered by distilling the volatile acetonitrile.

Cu(I) is an important oxidation state of copper, which is significant both in the area of fundamental chemistry and industrial applications. Cuprous ions form stable coordination compound with chloride with high solubility. Compared to the research on cupric solvent extraction, the work on the cuprous extraction is limited. Therefore, in the present work, solvent extraction studies have been carried out to extract Cu(I) from chloride solutions using TBP–1-octanol. The effect of different diluents, contact time, acid concentration of solution, and concentration of TBP, etc. has been studied. The behaviors of extraction and stripping have been discussed, and a comparison with other diluents and extractants has also been made. The obtained data will be useful to widen the knowledge of cuprous solvent extraction and in scaling up the process for the treatment of etch waste water.

## 2. Materials and methods

The colorless synthetic solution of cuprous chloride was prepared by using (i) cupric chloride solution with sodium chloride and (ii) cupric chloride with hydrochloric acid. The fine copper powder was added in excess to both of the solutions and then filtered. Freshly prepared solutions were used for the experimental purpose. The solutions were kept in air-tight bottles to prevent the oxidation of cuprous to cupric. The chemical reagents used for the experimental purposes were of A.R. grade. The extractant TBP supplied by M/s Yakuri Pure Chemicals Co., Japan was used without further purification.

**Table 1**  
Selection of the diluent

Solvent	Raffinate Cu (g/L)	Extraction (%)	Stripping Cu (g/L)	Stripped (%)
Octane	16.3	39.9	8.40	77.3
Chloroform	25.2	7.20	1.96	98.0
Toluene	18.9	32.4	1st stage: 7.28 2nd stage: 0.44	82.7 4.99
Total				87.6
1-Octanol	16.3	40.0	9.34	85.8
Pure TBP	7.05	74.1	1st stage: 7.34 2nd stage: 5.00 3rd stage: 3.25	36.4 24.8 19.4
Total				80.6

Aqueous feed = 27.2 g/L Cu(I), 1 mol/L NaCl, 1 mol/L HCl, little  $\text{Na}_2\text{SO}_3$  as anti-oxidant, organic = 50% of TBP in different diluents, O/A = 1/1, mixing time = 10 min, stripping solution = 0.83 mol/L NaCl, O/A = 5/6 and mixing time = 5 min.

Solvent extraction experiments were carried out in a conical flask. The organic and aqueous phases were mixed by using shaker. Sodium sulphite was used as reductant to prevent the oxidation of cuprous ions present in the solution. In order to avoid any complexity due to the addition of this reagent, experiments of the liquid–liquid extraction were carried out in a pure nitrogen atmosphere. Conventional titration and atomic absorption spectrophotometer were used for the analyses of the samples.

## 3. Results and discussion

### 3.1. Selection of the diluent

The behavior of TBP mixed with different diluents viz. octane, chloroform, toluene and 1-octanol has been studied for the extraction of Cu(I). The aqueous solution containing 27.2 g/L Cu(I), 1 mol/L NaCl, 1 mol/L HCl and small amount of  $\text{Na}_2\text{SO}_3$  as anti-oxidant was contacted with an organic solution of 50% of TBP in different diluents maintaining a phase ratio of O/A = 1/1 for 10 min. The stripping studies were carried out by using 0.83 mol/L NaCl, at phase ratio of O/A = 5/6 and contact time of 5 min. In similar experimental conditions the extraction was found to be 39.9%, 7.20%, 32.4% and 40.0% with diluents octane, chloroform, toluene and 1-octanol, respectively. The results presented in Table 1 show that the chloroform is not a suitable diluent. Other diluents are found effective for TBP. Toluene is not selected due to its toxicity and it needs modifier to prevent the formation of third phase during high loading. Eventually, in the present work, 1-octanol is selected as diluent for TBP due to its good extractability, high polarity, solvation and dissolution properties towards chloro-cuprous compounds.

### 3.2. Effect of contact time

The studies for the kinetics of copper extraction were carried out by equilibrating aqueous solution containing 15.47 g/L Cu(I), 2 mol/L NaCl and 1 mol/L HCl with organic phase of 50% TBP diluted in 1-octanol. The mixing time was varied from 0.5 to 20 min at O/A ratio 1. The extraction of copper was found quite rapid and attained the equilibrium within 30 s. It was also observed that the prolong contact time had no adverse effect on extraction. However, to ensure the maximum equilibrium, 2 min contact time was maintained during further studies.

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