

Solvent Extraction of Copper as a Thiocyanate Complex. Reducing Effect of Thiocyanate[#]

Astrid Gojmerac Ivšić and Biserka Tamhina[†]

Laboratory of Analytical Chemistry, Faculty of Science, University of Zagreb,
Strossmayerov trg 14, 10000 Zagreb, Croatia

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Extraction of copper(II) from sulphuric and hydrochloric acid solutions containing an excess of thiocyanate ions with tetraphenylphosphonium (TPP) chloride and cetyltrimethylammonium (CTMA) bromide in chloroform was investigated. The optimum conditions for quantitative extraction (over 99%) by both extractants were determined. The extraction behaviour of CTMA was found to be more efficacious than that of TPP because a low excess of thiocyanate and extractant was required and extraction was feasible even from a higher concentration of sulphuric acid. The formation of an extractable copper(II) thiocyanate complex with CTMA could also be determined spectrophotometrically by measuring the absorbance of the organic phase at 409 nm. The presence of ascorbic acid decreased the absorbance at 409 nm but the formed copper(I) thiocyanate was quantitatively extracted with CTMA, independently of the ascorbic acid concentration. Thiocyanate ions also exercised a reducing effect on copper(II) at pH > 1.3; with increasing pH and/or prolonged shaking time of the aqueous and organic phases, the reducing effect increased. The composition of the extracted copper(II) complex was determined by the distribution and spectrophotometric methods. The molar ratio Cu:SCN:TPP (CTMA) of the extracted complex was 1:4:2; accordingly, its composition was [TPP]₂ [Cu(SCN)₄] or [CTMA]₂ [Cu(SCN)₄].

Key words: copper, thiocyanate, extraction, spectrophotometry

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[†] Deceased on February 10, 2000.

INTRODUCTION

The formation of a blood-red copper(II) thiocyanate complex in acetone has been proposed as a basis for the spectrophotometric determination of copper.¹ A disadvantage of the method is that the coloured complex is unstable, and that an anhydrous solution is required. The presence of an organic solvent, either miscible or immiscible with water, or extraction into an organic solvent containing an extractant have been considered as a means to stabilize the copper thiocyanate colour.²⁻⁶

Most of those studies deal with the spectrophotometric determination of copper based on the extraction of a copper(II) thiocyanate anion with organic cations as extractants: triphenylmethylarsonium,⁴ tetraphenylarsonium,⁵ tetraphenylphosphonium⁵ and tetrabutylammonium.^{6,7} The extraction of a copper(I) thiocyanate complex with a tetrabutylammonium cation formed in the presence of ascorbic acid has also been reported.^{7,8}

The present experiments were undertaken to study the extraction of copper as a thiocyanate complex with cetyltrimethylammonium (CTMA) bromide, which is a cationic surfactant and an ion-pair extractant, and with tetraphenylphosphonium (TPP) chloride, which is only an ion-pair extractant. The results show that CTMA is a better extractant for copper(II) thiocyanate than TPP. A more efficacious extraction behaviour of CTMA in comparison with TPP is discussed. The dependence of copper extraction on ascorbic acid concentration and the reducing effect of thiocyanate on copper(II) are also described.

EXPERIMENTAL

Reagents

Standard copper solution $c\{\text{Cu(II)}\} = 0.01 \text{ mol dm}^{-3}$ was prepared by dissolving $\text{CuSO}_4 \times 5 \text{ H}_2\text{O}$ (Kemika) in distilled water. The solution was standardized gravimetrically with cuprone.⁹ Solutions of lower concentrations were made by dilution. Tetraphenylphosphonium chloride (analytical grade, Fluka) and cetyltrimethylammonium bromide (cryst. pure, Serva) were dissolved in reagent-grade chloroform. All chemicals used were of the *p.a.* purity grade.

Extraction Procedures

The copper(II) distribution ratio was determined at room temperature by shaking equal volumes (5 mL) of the organic and aqueous phases of a given composition with a mechanical shaker in a 50-mL conical flask for 20 min. After the phases were separated by gravity, aliquots of the organic or aqueous phases were used for each experimental point. Copper concentrations in the aqueous phase were determined after suitable dilution by flame atomic absorption using a Unicam 919 AA spectro-

meter with a specialized computer program. Copper concentrations in the organic phase were calculated from the difference in the copper concentrations in the aqueous phase before and after extraction.

Copper distribution was also determined by absorbance measurements in the organic phase at 409 nm using a Varian Cary 3 spectrometer. Copper concentrations in the aqueous phase were calculated from the difference between the maximum and constant absorbances of the organic phase at 409 nm under optimum extraction conditions (A_o) and the measured absorbance value before reaching complete complex formation in the organic phase (A_x).

RESULTS AND DISCUSSION

Extraction of copper(II) from sulphuric and hydrochloric acid solutions, containing an excess of thiocyanate ions, with TPP chloride and CTMA bromide in chloroform was investigated. A copper(II) thiocyanate complex formed in the aqueous phase was quantitatively extracted (over 99%) with TPP in the whole acidity range from pH 5.5 to $c(\text{H}_2\text{SO}_4 \text{ or } \text{HCl}) = 0.5 \text{ mol dm}^{-3}$ and with CTMA from pH 5.5 to $c(\text{H}_2\text{SO}_4) = 3 \text{ mol dm}^{-3}$ or $c(\text{HCl}) = 0.5 \text{ mol dm}^{-3}$. The pH independence of extraction was to be expected since thiocyanic acid is a strong acid. With increasing acid concentration, the complex extraction decreased very slowly. At a high sulphuric acid concentration in the optimum acidity range for the extraction with CTMA $\{c(\text{H}_2\text{SO}_4) = 2 \text{ mol dm}^{-3}\}$, an increase in the initial chloride ion concentration in the aqueous phase produced a very slow decrease in copper extraction. This decrease was almost as large as the one caused by the addition of hydrochloric acid at a concentration higher than 0.5 mol dm^{-3} and it explained the difference in the optimum acidity range for copper extraction with CTMA from sulphuric and hydrochloric acid solutions. At a low sulphuric acid concentration in the optimum acidity range for extraction with both extractants $\{c(\text{H}_2\text{SO}_4) = 0.2 \text{ mol dm}^{-3}\}$, copper extraction was independent of chloride and sulphate ions concentration over the range of $0\text{--}4 \text{ mol dm}^{-3}$ chloride and $0\text{--}2 \text{ mol dm}^{-3}$ sulphate added in the aqueous phase. Therefore, all investigations were carried out with $c(\text{H}_2\text{SO}_4) = 0.2 \text{ mol dm}^{-3}$ sulphuric acid solutions to eliminate possible influence of chloride ions from hydrochloric acid.

The copper(II) extracted as the thiocyanate complex with TPP or CTMA could be quantitatively stripped with ammonia solution $c(\text{NH}_3)_{\text{aq}} = 1 \text{ mol dm}^{-3}$.

The effect of thiocyanate concentration on the formation and extraction of the copper(II) thiocyanate complex was examined by varying the thiocyanate concentration in the aqueous phase. Extractions started from solutions containing the analytical copper(II) concentration $3 \times 10^{-4} \text{ mol dm}^{-3}$ and sulphuric acid concentration 0.2 mol dm^{-3} using an excess of extrac-

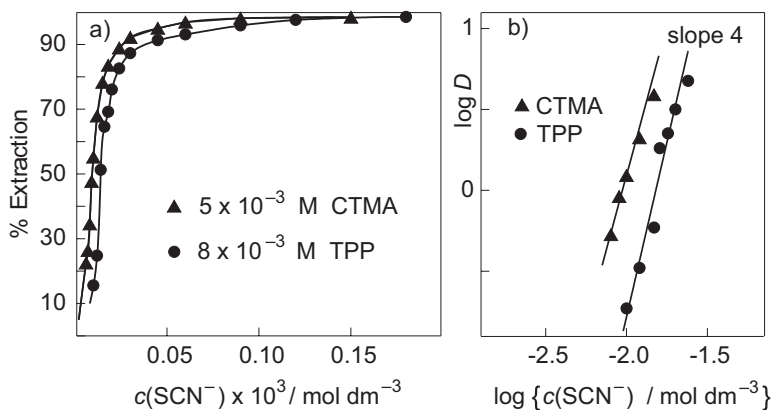


Figure 1. The dependence of the percent of extraction (a) and the distribution ratio (b) of copper(II) on thiocyanate concentration. $c\{\text{Cu(II)}\} = 3 \times 10^{-4} \text{ mol dm}^{-3}$, $c(\text{H}_2\text{SO}_4) = 0.2 \text{ mol dm}^{-3}$.

tants in chloroform (Figure 1a). Copper(II) was quantitatively extracted with TPP from a solution containing more than 0.09 mol dm^{-3} thiocyanate (the minimum molar ratio of thiocyanate to copper was 300:1). For the quantitative extraction of copper(II) with CTMA, a thiocyanate concentration of 0.05 mol dm^{-3} or higher was required (the minimum molar ratio of thiocyanate to copper was 170:1). The influence of TPP and CTMA concentration in the organic phase on the extraction of copper(II) from the aqueous phase at optimum acidity and thiocyanate concentration was also studied (Figure 2a). For the quantitative extraction of copper(II) ($3 \times 10^{-4} \text{ mol dm}^{-3}$),

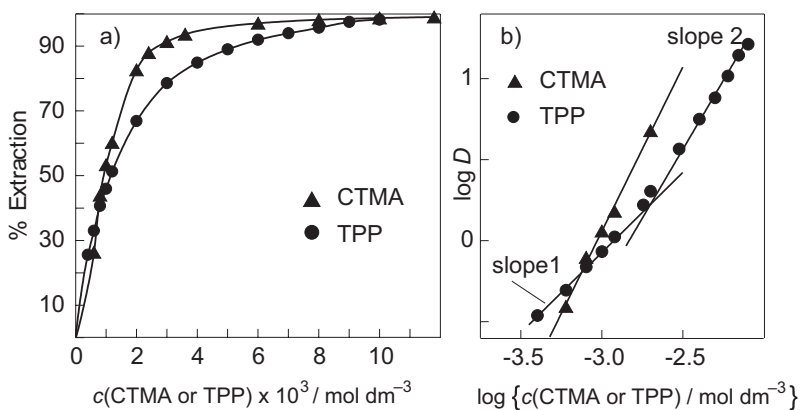


Figure 2. The dependence of the percent of extraction (a) and the distribution ratio (b) of copper(II) on extractant concentration. $c\{\text{Cu(II)}\} = 3 \times 10^{-4} \text{ mol dm}^{-3}$, $c(\text{H}_2\text{SO}_4) = 0.2 \text{ mol dm}^{-3}$, $c(\text{SCN}^-) = 0.1 \text{ mol dm}^{-3}$.

the molar ratio of TPP to Cu(II) had to be at least 27:1 (8×10^{-3} mol dm⁻³ TPP) and of CTMA to Cu(II) 17:1 (5×10^{-3} mol dm⁻³ CTMA).

These results showed that for the quantitative extraction of the copper(II) thiocyanate complex with CTMA, a lower excess of thiocyanate and extractant was required than with TPP and that copper(II) could be extracted with CTMA even from a higher concentration of sulphuric acid.

The dependence of the distribution ratio on the analytical thiocyanate concentration in the aqueous phase was determined by keeping the optimum sulphuric acid concentration in the aqueous phase and the optimum excess of TPP or CTMA concentration in the organic phase constant. A fourth-power thiocyanate dependency was found with both extractants, indicating that four thiocyanate ions were bonded to one atom of copper forming $[\text{Cu}(\text{SCN})_4]^{2-}$, which was transferred into the organic phase after the addition of onium salts (Figure 1b). This was confirmed by determining the dependence of the distribution ratio on analytical extractants concentration by keeping the optimum sulphuric acid concentration and the excess of thiocyanate concentration in the aqueous phase constant (Figure 2b). A second-power extractant dependency was found over the whole investigated range of CTMA and over the TPP concentration range higher than 1.8×10^{-3} mol dm⁻³ (TPP to copper molar ratio higher than 6:1). For solutions containing a molar ratio of TPP to copper lower than 6:1, the distribution ratio was one-power dependent upon TPP concentration. These results showed that two CTMA cations were bonded to one atom of copper irrespective of the CTMA concentration and that two TPP cations were bonded to one atom of copper only in the presence of a high excess of TPP. Thiocyanate was always in high excess and complexes of the formula $[\text{TPP}]_2 [\text{Cu}(\text{SCN})_4]$ or $[\text{CTMA}]_2 [\text{Cu}(\text{SCN})_4]$ were formed and transferred into the organic phase independently of CTMA concentration and at the optimum TPP concentration for the quantitative extraction of copper. These results showed that also in the presence of a high thiocyanate excess, one TPP cation was bonded to one atom of copper in the presence of a low concentration of TPP in the organic phase and a complex of the formula $[\text{TPP}] [\text{Cu}(\text{SCN})_3]$ was formed and transferred into the organic phase. At a high thiocyanate concentration, $[\text{Cu}(\text{SCN})_4]^{2-}$ predominated in the solution¹⁰ thus confirming the existence of the $[\text{Cu}(\text{SCN})_3]^-$ species that could be extracted with TPP but only if its concentration was insufficient for extraction of the $[\text{Cu}(\text{SCN})_4]^{2-}$ species.

In contrast to TPP extraction, the composition of the copper complex extracted with CTMA did not depend on the CTMA concentration and $[\text{Cu}(\text{SCN})_4]^{2-}$ species were extracted also from a solution containing a stoichiometric ratio of CTMA to copper 2:1. A different, more efficacious extraction behaviour of CTMA in comparison with TPP was due to the fact that

CTMA was not only an ion-pair extraction reagent, but also a cationic surfactant. It is known that the presence of a surfactant can influence complex formation.^{11–13} The extracted species could be also formed in a reaction at the phase interface. Since the optimal CTMA concentration for quantitative extraction of Cu(II) is higher than the critical micellar concentration (cmc),¹¹ the possibility of micelle formation could also support the copper extraction.

The absorption spectrum of the complex extracted with CTMA under optimum conditions showed a maximum absorbance at 409 nm. The maximum and constant absorbances were in the same thiocyanate and CTMA concentration range as for quantitative extraction. This showed that the formation of the extractable copper(II) thiocyanate complex with CTMA could be determined spectrophotometrically by measuring the absorbance of the organic phase at 409 nm. Contrary to the absorbance dependence on thiocyanate and CTMA concentration, dependence on acidity showed that the absorbance of the organic phase was constant only in the acidity range $c(\text{H}_2\text{SO}_4) = 0.05$ to 3 mol dm^{-3} . With the decreasing acidity of the aqueous phase, the absorbance of the organic phase, decreased and at pH 5.5 (quantitative extraction) was about 50% (Figure 3). This may have been due to the excess of thiocyanate reducing the copper(II) complex to the copper(I) complex, which was also extractable in chloroform with CTMA. It is known that copper(II) is reduced by thiocyanate in basic solution; reduction in acid solution does not normally occur.¹⁴

The extraction efficiency was not significantly lowered if the extraction took place in the presence of an excess of ascorbic acid as a reducing agent.

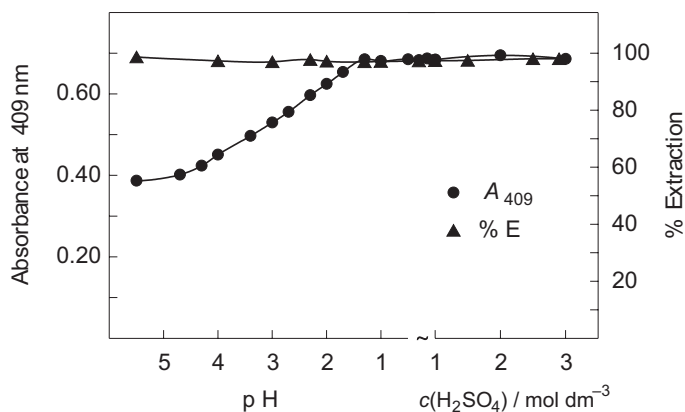


Figure 3. The dependence of the percent of extraction and absorbance at 409 nm on sulphuric acid concentration. $c\{\text{Cu(II)}\} = 3 \times 10^{-4} \text{ mol dm}^{-3}$, $c(\text{SCN}^-) = 0.1 \text{ mol dm}^{-3}$, $c(\text{CTMA}) = 5 \times 10^{-3} \text{ mol dm}^{-3}$.

The formed copper(I) thiocyanate was quantitatively extracted with CTMA independently of ascorbic acid concentration. In contrast, the presence of ascorbic acid decreased the absorbance of the organic phase at 409 nm (Figure 4) because it was due to the formation and extraction of the copper(II) thiocyanate complex in the form of the ion pair $[\text{CTMA}]_2 [\text{Cu}(\text{SCN})_4]$. At an ascorbic acid concentration of $4.5 \times 10^{-4} \text{ mol dm}^{-3}$ (molar ratio of ascorbic acid to analytical concentration of copper(II) = 1.5:1), all copper(II) was reduced to copper(I) and the organic phase showed no absorbance at 409 nm.

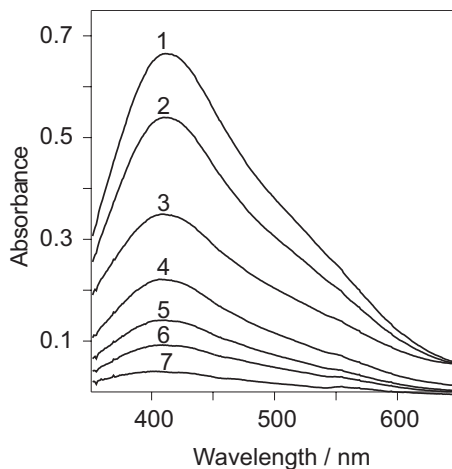


Figure 4. The dependence of the absorption spectrum of the organic phase on ascorbic acid concentration in the aqueous phase. $c\{\text{Cu}(\text{II})\} = 3 \times 10^{-4} \text{ mol dm}^{-3}$, $c(\text{SCN}^-) = 0.1 \text{ mol dm}^{-3}$, $c(\text{H}_2\text{SO}_4) = 0.2 \text{ mol dm}^{-3}$, $c(\text{CTMA}) = 5 \times 10^{-3} \text{ mol dm}^{-3}$, without addition of ascorbic acid(1); conc. of ascorbic acid (mol dm^{-3}): 6×10^{-5} (2); 1.2×10^{-4} (3); 1.8×10^{-4} (4); 2.4×10^{-4} (5); 3×10^{-4} (6); 4.5×10^{-4} (7).

Under optimum extraction conditions in the whole acidity range from pH 5.5 to $c(\text{H}_2\text{SO}_4) = 3 \text{ mol dm}^{-3}$, the distribution equilibrium was attained in less than 5 min. The shaking time of the aqueous and organic phases of 20 min was sufficient to achieve reproducible results by measuring the non-extracted copper in the aqueous phase by atomic absorption spectrometry; the copper extraction efficiency was unaffected by the reduction of copper(II) to copper(I) in the presence of an excess of thiocyanate at pH > 1.3. The absorbance measurements of the organic phase at 409 nm showed it to be independent of the shaking time of the two phases only if extraction was carried out at pH < 1.3 $\{c(\text{H}_2\text{SO}_4) > 0.05 \text{ mol dm}^{-3}\}$. Namely, at this acidity range the excess of thiocyanate did not reduce copper(II) to copper(I) (Table I). In contrast, absorbances of the organic phase at 409 nm decreased with increasing shaking time if extraction was carried out at pH = 5.5 because at

TABLE I

The dependence of absorbance on the shaking time of aqueous and organic phases at different acidity of the aqueous phase

Shaking time (min)	Absorbance at 409 nm	
	pH = 5.50	$c(\text{H}_2\text{SO}_4) = 2 \text{ mol dm}^{-3}$
5	0.465	0.706
10	0.415	0.704
20	0.339	0.706
30	0.313	0.704
40	0.267	0.705
60	0.126	0.706
120	0.094	0.705

that pH copper(II) was reduced to copper(I) by the excess of thiocyanate (Table I). These results confirmed that absorbance at 409 nm decreased with decreasing acidity (Figure 3) because of the reducing effect of thiocyanate on copper(II) and that the copper(II) thiocyanate complex that had been extracted with CTMA into chloroform was reduced to the copper (I) thiocyanate complex due to the excess of thiocyanate during the agitation of the two phases. Absorbances of the organic phase were stable for at least 24 h regardless of the pH of the aqueous phase before extraction.

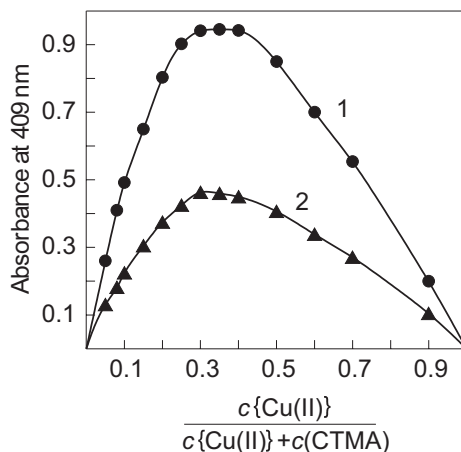


Figure 5. Determination of complex composition by Jobs method of continuous variation. $c(\text{H}_2\text{SO}_4) = 0.2 \text{ mol dm}^{-3}$, $c(\text{SCN}^-) = 1 \text{ mol dm}^{-3}$. $c\{\text{Cu(II)}\} + c(\text{CTMA}) = 3 \times 10^{-3} \text{ mol dm}^{-3}$ (1) and $c\{\text{Cu(II)}\} + c(\text{CTMA}) = 2 \times 10^{-3} \text{ mol dm}^{-3}$ (2).

The composition of the thiocyanato copper(II) complex extracted with CTMA at $c(\text{H}_2\text{SO}_4) = 0.2 \text{ mol dm}^{-3}$ was also determined spectrophotometrically in the organic phase. The results obtained by Job's method of continuous variation (Figure 5) indicated that the molar ratio of Cu(II) to CTMA was 1:2. The results obtained by the equilibrium shift method¹⁵ indicated that the molar ratio of Cu(II) to CTMA was 1:2 and of Cu(II) to thiocyanate 1:4 (Figure 6). The same results were obtained by the distribution (slope analysis) methods (Figures 1b and 2b) and confirmed that the composition of the extracted complex was $[\text{CTMA}]_2 [\text{Cu}(\text{SCN})_4]$ and that the formation of this complex could be determined by absorbance measurement of the organic phase.

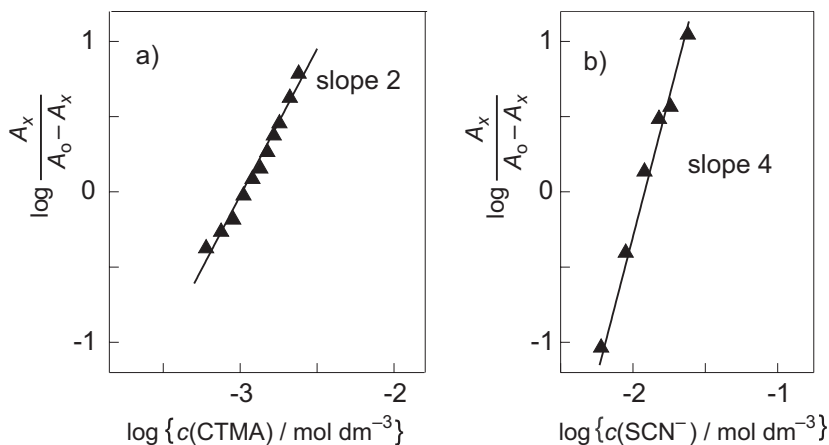


Figure 6. The dependence of $\log A_x/A_0 - A_x$ vs. $\log \{c(\text{CTMA})\}$ (a) and vs. $\log \{c(\text{SCN}^-)\}$ (b). $c\{\text{Cu}(\text{II})\} = 3 \times 10^{-4} \text{ mol dm}^{-3}$, $c(\text{H}_2\text{SO}_4) = 0.2 \text{ mol dm}^{-3}$. (a) $c(\text{SCN}^-) = 0.12 \text{ mol dm}^{-3}$; (b) $c(\text{CTMA}) = 7.5 \times 10^{-3} \text{ mol dm}^{-3}$.

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SAŽETAK

Ekstrakcija bakra u obliku tiocijanatnog kompleksa. Redukcijsko djelovanje tiocijanata

Astrid Gojmerac Ivšić i Biserka Tamhina

Istraživana je ekstrakcija bakra(II) iz sumporno i klorovodično kiselih otopina koje sadrže suvišak tiocijanatnih iona sa tetrafenilfosfonijevim (TPP) kloridom i cetiltrimetilamonijevim (CTMA) bromidom. Određeni su optimalni uvjeti za kvantitativnu ekstrakciju (iznad 99%) s oba ekstraktanta. Ekstrakcijsko ponašanje CTMA povoljnije je nego TPP, jer je potreban manji suvišak tiocijanata i ekstraktanta, a ekstrakcija je moguća pri većoj koncentraciji sumporne kiseline. Ekstrakcija bakrova(II) tiocijanato-kompleksa s CTMA može se pratiti spektrofotometrijski mjerenjem apsorbancije organske faze pri 409 nm. Prisutnost askorbinske kiseline smanjuje apsorbanciju pri 409 nm, ali nastali bakrov(I) tiocijanat kvantitativno se ekstrahira s CTMA, neovisno o koncentraciji askorbinske kiseline. Tiocijanatni ioni reduciraju bakar(II) pri pH > 1.3; s povećanjem pH i/ili produljenjem vremena kontakta vodene i organske faze reducirajuće djelovanje tiocijanata se povećava. Sastav ekstrahiranog bakrova(II) kompleksa određen je distribucijskom i spektrofotometrijskom metodom. Množinski odnos Cu:SCN:TPP (CTMA) u ekstrahiranom kompleksu jest 1:4:2; tj. sastav ekstrahiranog kompleksa je $[\text{TPP}]_2[\text{Cu}(\text{SCN})_4]$, odnosno $[\text{CTMA}]_2[\text{Cu}(\text{SCN})_4]$.