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Solvent Extraction and Separation of Zinc from Copper and Direct Spectrophotometric Determination of Copper (II) by Monooctyl α-Anilinobenzylphosphonate

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Extraction of copper (II) from diluted hydrochloric, nitric and sulphuric acid solutions with monooctyl α-anilinobenzylphosphonate (MOABP) dissolved in chloroform, has been studied. Copper is quantitatively extracted from the solutions at $4.5 \leqslant \text{pH} \leqslant 6.2$. Although zinc is also extracted from diluted mineral acids, the separation of zinc from a large amount of copper is feasible in the presence of cyanide.

Copper (II) and MOABP form a stable yellow colored complex, whose solution in chloroform follows the Lambert-Beer's law. A procedure for rapid spectrophotometric determination of copper has been developed. The influence of various cations and anions on the absorbance of the complex has been investigated.

The ratio of copper to MOABP in the extractable complex has been established spectrophotometrically, and from the dependence of the copper distribution ratio on the MOABP concentration in the organic phase.

A MOABP complex having 2 ligand molecules coordinated to the copper ion has been isolated in pure form.

INTRODUCTION

Monooctyl α-anilinobezylphosphonate (MOABP) has been utilized as a suitable reagent for extraction and separation of certain metals.[1-9] Physical properties of MOABP and its extraction efficiency in different solvents have also been studied.[10,11] This paper describes the use of MOABP as an extractant to separate zinc from a large amount of copper. Since ^{65}Zn is produced in a cyclotron by nuclear reaction ^{65}Cu(d, 2n)^{65}Zn, this separation has a practical importance because it yields radiochemically pure zinc. Although both zinc and copper are extracted under similar conditions, their separation was achieved with the aid of an alkali cyanide.

It has been found that MOABP forms stable colored complexes with some metals. This property has been utilized to determine metal extractable species.[1,8] Copper(II) forms a yellow complex with MOABP whose solution in chloroform follows the Lambert-Beer's law. On the basis of this property a new spectrophotometric determination of copper was developed. The experimental conditions for quantitative extraction of copper and its subsequent determination in the organic phase are described. The influence of various cations and anions on the absorbance of the copper-MOABP complex was investigated. The composition of the extractable copper complex was studied spectrophotometrically and was also established from the dependence of copper distribution ratio, *D*, on the MOABP concentration in the organic phase. A copper-MOABP complex was isolated in pure form and characterized by chemical analysis.

EXPERIMENTAL

Reagents and Apparatus

The radionuclide ^{65}Zn of high specific activity was obtained in chloride form from the Institute »Boris Kidrič«, Vinča, Yugoslavia. Inactive $CuSO_4$, $Cu(NO_3)_2$ and $ZnCl_2$ solutions were standardized gravimetrically and by complexometric titrations. The synthesis of MOABP was described earlier[12]. Its solution in chloroform served as organic phase. All chemicals used were of analytical grade.

The γ-activity of the radioactive zinc was counted on a well-type γ-scintillation counter with a NaI/Tl crystal.

The absorbance measurements were made on a Beckman Spectrophotometer, Model DU-2, using a 1 cm quartz transmission cell. The IR spectra were recorded on a Perkin-Elmer IR Spectrophotometer, model 257.

Isolation of Copper(II)-MOABP Complex

The extractable complex of copper was prepared by shaking equal volumes of a 0.05 M solution of MOABP in chloroform and a 0.1 M solution of a copper (II) salt. The acidity of the aqueous phase was previously adjusted to $pH \approx 5$. The organic phase was separated and the chloroform evaporated *in vacuo*. The yellow-greenish complex was recrystallized from a chloroform-petroleum ether (1 : 1) mixture.

Anal. $C_{42}H_{58}N_2O_6P_2Cu$ (812.39) calc'd: C 62.09; H 7.20; N 3.45; P 7.62; Cu 7.82%.
found: C 62.28; H 7.28; N 3.49; P 7.50; Cu 7.45%.

Procedure for the Spectrophotometric Determination of Copper(II)

An aqueous solution (8 ml), containing 0.05—0.5 mg of copper (II), is adjusted to approximately $5 < pH < 6$ and stabilized with an acetate buffer (2 ml), $pH \approx 5.5$.

It is then extracted with 0.01 M solution of MOABP in chloroform (5 ml) for 2 min. The chloroform layer is transferred into a 10 ml volumetric flack. To extract the remaining traces of copper, the aqueous phase is extracted with chloroform (3 ml), the chloroform extracts are combined, diluted to volume with chloroform, and the absorbance of the complex is measured at 371 nm.

Procedure for the Separation of Zinc from Copper

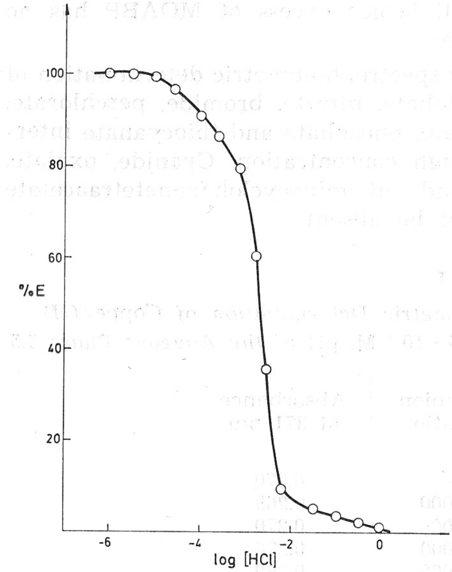
Irradiated metalic copper, used as a target for ^{65}Zn, is disolved in 2 M HNO_3. The excess of the acid is neutralized, and a solution of potassium cyanide is added. To prevent the extraction of copper, the molar ratio of copper to cyanide has to be at least 1 : 50. The solution is adjusted to $pH \approx 5.5$, and is then extracted with an equal volume of 0.05 M solution of MOABP in chloroform for 2 min. Under these circumstances, zinc is quantitatively extracted into the organic phase, while copper remains in the aqueous phase. Reextraction of zinc can be carried out with 1 M hydrochloric or any other mineral acid.

RESULTS AND DISCUSSION

Extraction and Spectrophotometric Determination of Copper

Extraction of copper(II) as a function of hydrochloric acid concentration, with MOABP dissolved in chloroform, is shown in Fig. 1. Copper is quantitatively extracted only from a weakly acidic solution having a pH in the range $4.5 \leqslant pH \leqslant 6.2$. The same results were obtained with sulfuric and nitric acid and are therefore not presented. The reextraction of copper can be carried out with a 1 M mineral acid.

The absorbance of the copper(II)-MOABP complex is also dependent on the acidity of the aqueous solution from which copper is being extracted, and is the highest in the range $4.5 \leqslant pH \leqslant 6.2$, as is shown in Fig. 2. In the experiments this pH was maintained with acetate buffer because it has been found that these anions do not interfere with the extraction of copper. The solution



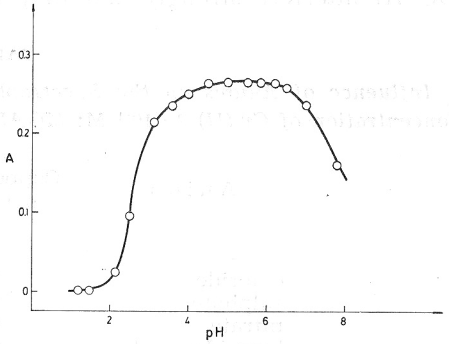


Fig. 1. Extraction of Cu(II) ($2 \cdot 10^{-4}$ M) from hydrochloric acid solution with MOABP ($5 \cdot 10^{-2}$ M) dissolved in chloroform.

Fig. 2. Effect of pH in the aqueous phase on the absorbance of Cu(II)-MOABP complex in chloroform. Concn. of Cu(II) $2 \cdot 10^{-4}$ M; MOABP $5 \cdot 10^{-2}$ M.

of the complex in chloroform is yellow colored with the maximum absorbance at 371 nm (Fig. 3.), and the molar absorptivity 1400. It follows the Lambert-Beer's law in the whole range of concentrations studied. The complex is stable in solution and the absorbance did not change even after several days of standing.

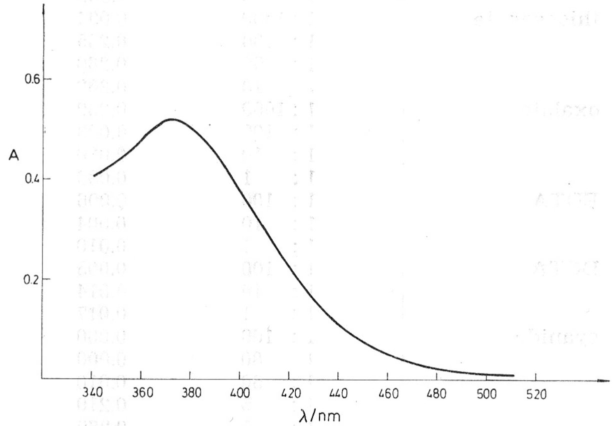


Fig. 3. Absorption spectrum of Cu(II)-MOABP complex in chloroform.

Factors Influencing the Absorbance of Cu(II)-MOABP Complex

In order to obtain the quantitative extraction of copper and the reproducible absorbance readings, the concentration of MOABP must be at least 15 times higher than that of copper. A still larger excess of MOABP has no further influence on the absorbance values.

The influence of various anions on the spectrophotometric determination of copper is shown in Table I. Chloride, sulphate, nitrate, bromide, perchlorate, acetate and tartrate do not interfere. Citrate, phosphate and thiocyanate interfere only when they are present in a high concentration. Cyanide, oxalate, ethylenediaminetetraacetate (EDTA) and diaminocyclohexanetetraacetate (DCTA) interfere strongly and they must be absent.

TABLE I

Influence of Anions on the Spectrophotometric Determination of Copper (II). Concentration of Cu (II) $2 \cdot 10^{-4}$ M; *MOABP* $5 \cdot 10^{-2}$ M. pH *of the Aqueous Phase* 5.5.

Anion	Copper : anion molar ratio	Absorbance at 371 nm
—	—	0.270
chloride	1 : 1000	0.269
sulphate	1 : 1000	0.270
nitrate	1 : 1000	0.270
bromide	1 : 1000	0.269
perchlorate	1 : 1000	0.268
acetate	1 : 1000	0.270
tartrate	1 : 1000	0.270
citrate	1 : 1000	0.050
	1 : 500	0.125
	1 : 100	0.260
	1 : 50	0.265
	1 : 10	0.269
phosphate	1 : 1000	0.140
	1 : 500	0.180
	1 : 200	0.195
	1 : 100	0.265
	1 : 10	0.269
thiocyanate	1 : 1000	0.094
	1 : 100	0.255
	1 : 50	0.260
	1 : 10	0.262
oxalate	1 : 1000	0.030
	1 : 100	0.023
	1 : 10	0.030
	1 : 1	0.030
EDTA	1 : 100	0.006
	1 : 10	0.004
	1 : 1	0.010
DCTA	1 : 100	0.005
	1 : 10	0.014
	1 : 1	0.017
cyanide	1 : 100	0.000
	1 : 80	0.000
	1 : 50	0.010
	1 : 5	0.210
	1 : 1	0.269

The influence of cations on the spectrophotometric determination of copper is presented in Table II. Most of the cations studied do not interfere even when they are present in a moderate excess with respect to copper. Aluminium(III), chromium(III), cobalt(II) and manganese(II) do not exhibit any interference even if their concentration exceeds 50 times that of copper, providing there is an excess of MOABP to prevent the formation of insoluble complexes between metals and MOABP. Cations which are extracted very much under these conditions, like gallium(III), niobium(V), zinc(II) and uranium(VI), compete with the extraction of copper and may therefore bring about a decrease of the absorbance values. This interference could easily be overcome by using a more concentrated MOABP solution. Among all cations investigated only

TABLE II

Influence of Cations on the Spectrophotometric Determination of Copper (II). Concentration of Cu (II) $2 \cdot 10^{-4}$ M; *MOABP* $5 \cdot 10^{-2}$ M. pH *of the Aqueous Phase* 5.5.

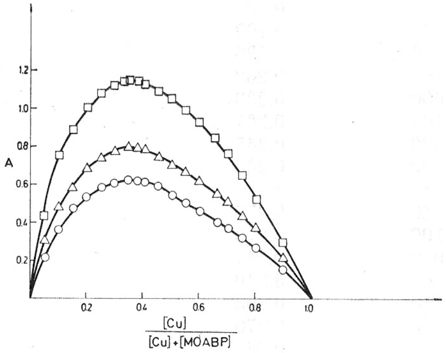
Cation	Copper : cation molar ratio	Absorbance at 371 nm
—	—	0.270
K (I)	1 : 1000	0.269
Na (I)	1 : 1000	0.268
NH_4 (I)	1 : 1000	0.269
Mg (II)	1 : 1000	0.235
	1 : 100	0.268
Ni (II)	1 : 1000	0.233
	1 : 100	0.267
Ba (II)	1 : 1000	0.245
	1 : 100	0.260
	1 : 50	0.267
Al (III)	1 : 50	0.270
Cr (III)	1 : 100	0.270
Ca (II)	1 : 1000	0.147
	1 : 100	0.240
	1 : 10	0.268
Co (II)	1 : 50	0.270
Mn (II)	1 : 50	0.267
Bi (III)	1 : 100	0.240
	1 : 10	0.263
V (V)	1 : 100	0.272
Ti (IV)	1 : 100	0.250
	1 : 10	0.265
Zr (IV)	1 : 100	0.273
Fe (III)	1 : 100	> 2
	1 : 10	1.800
Ga (III)	1 : 10	0.200
	1 : 1	0.269
Nb (V)*	1 : 10	0.225
	1 : 1	0.268
U (VI)	1 : 10	0.225
	1 : 1	0.265
Zn (II)	1 : 10	0.098
	1 : 1	0.267

* Added as tartrate complex

iron(III) influences the determination of copper even if present in smaller quantities.

Determination of Cu(II)-MOABP Ratio in the Extractable Complex

The ratio of copper to MOABP in the extractable complex was determined by three spectrophotometric methods and by extraction dependence study. The ratio was determined by Job's method of continuous variations,[13] by the molar ratio method,[14] and by the slope ratio method.[14] The results obtained are shown in Figs. 4, 5 and 6, respectively. Since MOABP is practically insoluble in water, for all these experiments the appropriate solutions of MOABP in chloroform were shaken with aqueous solution of copper. Then the organic layer was separated and its absorbance measured spectrophotometrically. The experimental results indicate a complex with 1 : 2 ratio of Cu(II) to MOABP, and formula $Cu[C_6H_5NHCH(C_6H_5)PO(OC_8H_{17})O]_2$ (marked



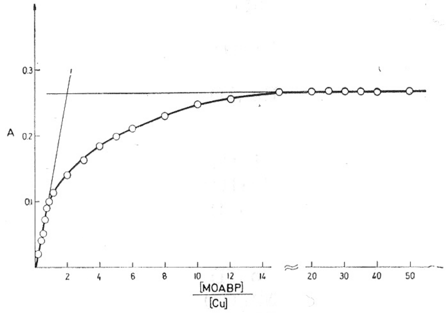


Fig. 4. Determination of composition of (Cu(II)-MOABP complex by Job's method. Concn. of (○) [Cu] + [MOABP] = $3 \cdot 10^{-3}$ M; (△) [Cu] + [MOABP] = $4 \cdot 10^{-3}$ M; (□) [Cu] + [MOABP] = $6 \cdot 10^{-3}$ M; pH of aqueous solution 5.5 (acetate buffer).

Fig. 5. Determination of composition of Cu(II)-MOABP complex by molar ratio method. Concn. of Cu(II) constant $2 \cdot 10^{-4}$ M; concn. of MOABP varied. pH of the aqueous phase 5.5 (acetate buffer).

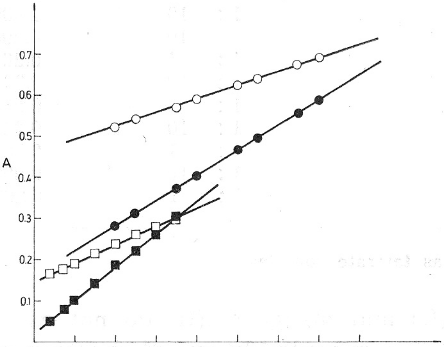


Fig. 6. Determination of composition of Cu(II)-MOABP complex by slope ratio method. (○) MOABP concn. $2 \cdot 10^{-4}$ M. Cu(II) concn. varied, (●) MOABP cocn. varied, Cu(II) concn. $2 \cdot 10^{-4}$ M; (□) MOABP concn. $8 \cdot 10^{-5}$ M, Cu(II) concn. varied; (■) MOABP concn. varied, Cu(II) concn. $8 \cdot 10^{-5}$ M.

later as CuA_2). This complex was also isolated from the organic phase as described in the Experimental Section. The broad shallow absorption of the OH vibration in the 2500—2700 cm^{-1} range characteristic for the ligand molecule is not evident in the IR spectrum of the complex. The P→O frequency shift of 35 cm^{-1} provides support that this group is involved in the complex formation.

The dependence of the distribution ratio, *D*, for copper on the MOABP concentration in the organic phase is shown in Fig. 7. A curve with a slope of 2 was obtained, indicating that *D* is proportional to the second power of the extractant concentration. Taking into account that MOABP is actually dimerized in chloroform[11], the stoichiometry of the copper extraction can be represented as:

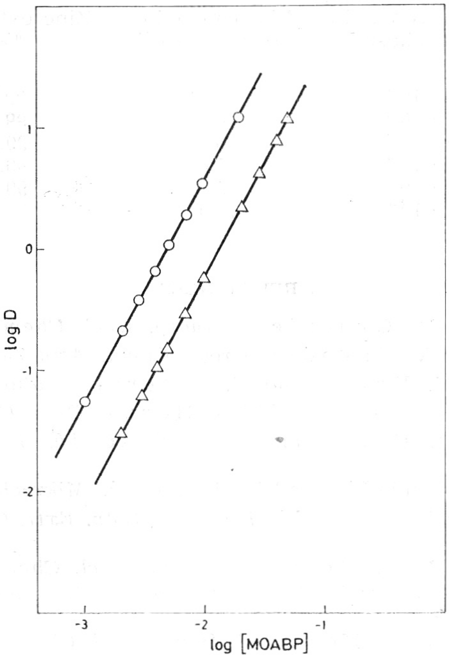


Fig. 7. Dependence of distribution ratio, *D*, of Cu(II) ($2 \cdot 10^{-4}$ M) on the MOABP concn. in the organic phase. Initial acidity of the aqueous phase (○) pH = 2.5; (△) pH = 2.0.

$$Cu^{2+}_{(aq)} + (HA)_{2(o)} \rightleftarrows CuA_{2(o)} + 2H^{+}_{(aq)}$$

where $(HA)_2$ denotes dimeric form of MOABP.

Separation of Zinc from Copper

As shown in Fig. 1, copper is quantitatively extracted from very diluted mineral acids. Zinc is also extracted from the solutions with pH higher than 3.[7] Their separation is, nevertheless, feasible if copper ions are masked with cyanide. The copper cyanide complex is soluble only in water and insoluble in chloroform. To prevent the competition between MOABP and cyanide, the molar concentration of the latter must exceed that of copper at least 50 times (Table I). It is shown in Table III that the excess of cyanide does not interfere with the extraction of zinc. Using this procedure it is possible to extract zinc from the aqueous solutions containing a large amount of copper.

TABLE III

Extraction of Zinc (II) in the Presence of Different Amounts of Copper (II) and Cyanide Ions. Concentration of Zn (II) $1 \cdot 10^{-5}$ M; *MOABP* $5 \cdot 10^{-3}$ M. pH *of the Aqueous Phase* 5.5.

$Cu(NO_3)_2$ concn. in aqueous phase/M	KCN concn. in aqueous phase/M	Zinc extracted %
$1 \cdot 10^{-4}$	0.01	99.9
$1 \cdot 10^{-3}$	0.1	99.9
$5 \cdot 10^{-3}$	0.5	99.9
$1 \cdot 10^{-2}$	1.0	99.9
$5 \cdot 10^{-2}$	5.0	99.9
$1 \cdot 10^{-1}$	10.0	99.9

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IZVOD

Odjeljivanje cinka od bakra metodom ekstrakcije i spektrofotometrijsko određivanje bakra (II) pomoću monooktil-α-anilinobenzilfosfonata

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Proučavana je ekstrakcija bakra (II) iz razrijeđenih otopina klorovodične, dušične i sumporne kiseline pomoću otopine monooktil-α-anilinobenzilfosfonata (MOABP) u kloroformu. Bakar se kvantitativno ekstrahira iz otopina s pH u rasponu $4.5 \leqslant \text{pH} \leqslant 6.2$. Iako se cink također ekstrahira iz razrijeđenih otopina mineralnih kiselina, odjeljivanje cinka od velikih količina bakra izvedivo je u prisutnosti cijanida.

Bakar (II) i MOABP tvore stabilan žuto obojeni kompleks čija otopina u kloroformu slijedi Lambert-Beerov zakon. Razrađen je postupak za spektrofotometrijsko određivanje bakra i ispitan je utjecaj raznih kationa i aniona na apsorpciju kompleksa.

Omjer bakra i MOABP u kompleksu je utvrđen spektrofotometrijski i iz odnosa distribucijskog omjera bakra prema koncentraciji MOABP u organskoj fazi.
U čistom stanju izdvojen je kompleks s MOABP u kojemu su 2 molekule liganda vezane s ionom bakra.

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