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# **REPORT**

**No. M228**

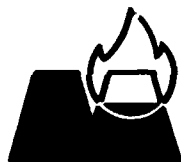
**THE SOLVENT EXTRACTION OF ZINC, IRON, AND INDIUM FROM CHLORIDE SOLUTIONS  
BY NEUTRAL ORGANOPHOSPHORUS COMPOUNDS**

by

J.S. Preston and A.C. du Preez

25th November, 1985

**CCUNCIL FOR MINERAL TECHNOLOGY  
200 Hans Strijdom Road  
RANDBURG  
South Africa**



**MINTEK**

**(MINERAL AND PROCESS CHEMISTRY DIVISION)**

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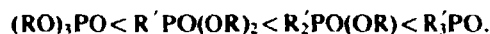
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## SYNOPSIS

The preparation of several neutral organophosphorus compounds and their evaluation as selective extractants for zinc in chloride media are described. The compounds belong to the series trialkyl phosphates  $(RO)_3PO$ , dialkyl alkylphosphonates  $R'PO(OR)_2$ , alkyl dialkylphosphinates  $R_2'PO(OR)$ , and trialkylphosphine oxides  $R_3'PO$ . They were characterized by measurement of their physical properties (melting and boiling points, refractive indices, and densities), and their purities were confirmed by osmometric determination of their molecular masses; by carbon and hydrogen microanalysis; by the titrimetric determination of acidic impurities; and, for liquid products, by comparison of their experimental molar refractivities with empirical values.

Metal-distribution equilibria were determined for solutions of the extractants in xylene and aqueous phases containing 0,5 to 5,0M sodium chloride. Moderately good selectivities were shown for zinc(II) over iron(III), and excellent selectivities were shown for zinc(II) over iron(II), copper(II), lead(II), and cadmium(II). The extraction of indium(III) was similar to that of zinc(II). The extraction of zinc(II), iron(III), and indium(III) increased markedly through the series



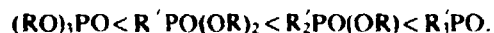
However, no marked effect on extraction or selectivity characteristics was shown when substituent alkyl groups were varied, except when phenyl groups were incorporated into the compounds, which led to much weaker extraction. These results appear to reflect the importance of electron-inductive effects rather than of steric effects. The extracted complexes of zinc(II), iron(III), and indium(III) have the stoichiometries  $ZnCl_2L_2$ ,  $FeCl_3L_2(H_2O)$ , and  $InCl_3L_2(H_2O)$  respectively, where L represents the neutral organophosphorus compound.

## SAMEVATTING

Die bereiding van verskeie organofosforverbindings en hul evaluering as selektiewe ekstraheermiddels vir sink in chloriedmedia word beskryf. Die verbindings behoort tot die reeks trialkielfosfate  $(RO)_3PO$ , dialkielalkielfosfonate  $R'PO(OR)_2$ , alkielalkielfosfinate  $R_2'PO(OR)$  en trialkielfosfienoksiede  $R_3'PO$ . Hulle is gekarakteriseer deur die meting van hul fisiese eienskappe (smelt- en kookpunt, brekingsindeks, en digtheid) en hul suiwerheid is bevestig deur die osmometriese bepaling van hul molekulêre massa; deur koolstof- en waterstofmikroanalise; deur die titrimetriese bepaling van suuron suiwerhede; en, vir vloeistofprodukte, deur die vergelyking van hul eksperimentele molêre refraktiwiteit met empiriese waardes.

Metaaldistribusie-ekwilibriums is bepaal vir oplossings van die ekstraheermiddels in xileen en waterfasies wat 0,5 tot 5,0M natriumchloried bevat. Redelik goeie selektiwiteit vir sink(II) bo yster(III) en uitstekende selektiwiteit vir sink(II) bo yster(II), lood(II) en kadmium(II) is waargeneem. Die ekstraksie van indium(III) is soortgelyk aan dié van sink(II).

Die ekstraksie van sink(II), yster(III) en indium(III) neem merkbaar toe deur die reeks



Daar is geen merkbare effek op die ekstraksie- of selektiwiteitseienskappe waargeneem wanneer substituent-alkielgroepe gevarieer is nie, behalwe wanneer fenielgroepe by die verbindings ingesluit is, wat tot 'n veel laer ekstraksie gelei het.

Hierdie resultate weerspieël blykbaar die belangrikheid van elektron-induktiewe uitwerking eerder as steriese uitwerking. Die stoigiometrie van die geëkstraheerde komplekse van sink(II), yster(III) en indium(III) is respektiewelik  $ZnCl_2L_2$ ,  $FeCl_3L_2(H_2O)$  en  $InCl_3L_2(H_2O)$ , waar L 'n organofosforverbinding is.

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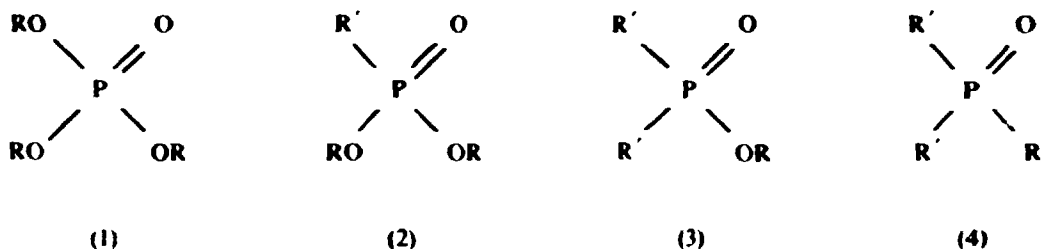
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## 1. INTRODUCTION

The solvent extraction of zinc from chloride solutions by neutral organophosphorus compounds like tributyl phosphate<sup>1</sup>, trioctylphosphine oxide<sup>2</sup>, and dipentyl pentylphosphonate<sup>3,4</sup> has been proposed by several workers as a process that has potential commercial applications. These reagents contain the phosphoryl (P=O) group as the active metal-coordinating function, and form part of a series of compounds comprising trialkyl phosphates (1), dialkyl alkylphosphonates (2), alkyl dialkylphosphinates (3), and trialkylphosphine oxides (4), in which carbon-oxygen-phosphorus linkages are replaced progressively by direct carbon-phosphorus bonds. Such changes in structure have been observed to result in a progressive increase in extractant strength towards metals like uranium(VI) and thorium(IV)<sup>5,6</sup>.



It was therefore considered that it would be interesting for a study to be made of the effect of the nature of compounds (1) to (4) and of changes in the substituent alkyl or aryl groups upon the ability of these compounds to extract zinc from chloride solutions and upon their selectivity for zinc over other metals. In this report, a description is given of the synthesis (or other provenance) and physical properties of the series of compounds (1) to (4) for which  $R = R' = n$ -butyl, the series for which  $R = R' =$  cyclohexyl, and the series for which  $R = R' =$  phenyl. Furthermore, for the dialkyl alkylphosphonates (2) and the alkyl dialkylphosphinates (3), which appear to be the compounds most suited to the recovery of zinc, other examples were synthesized in which the identities of  $R$  and  $R'$  were varied more widely in an attempt to optimize their extraction and selectivity characteristics towards zinc.

For the preliminary assessment of the potential of these extractants in the selective recovery of zinc from chloride solutions, distribution equilibria were obtained for  $Zn^{2+}$  and some associated metal ions ( $Fe^{3+}$ ,  $Fe^{2+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$ , and  $In^{3+}$ ), showing their extraction from solutions of sodium chloride (0.5 to 5.0 M) into solutions of the neutral organophosphorus compounds (0.1 to 1.0 M) in xylene. For zinc(II), iron(III), and indium(III), the stoichiometries of the extracted complexes were determined as an aid in the rationalization of the selectivities observed.

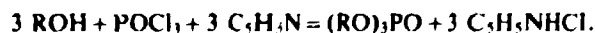
## 2. EXPERIMENTAL METHODS

### 2.1. Reagents

The following neutral organophosphorus compounds were obtained from the sources indicated, and were used as supplied: tri-*n*-butyl phosphate (Aldrich, gold label), di-*n*-butyl butylphosphonate (Daihachi Chemical Industry Co., metal extractant PC-44) triphenyl phosphate (Aldrich, gold label), di-*n*-butyl benzylphosphonate (Mobil Chemical Co.), and triphenylphosphine oxide (Merck-Schuchardt, zur Synthese). Dicyclohexylphosphinic and di-*iso*-butylphosphinic acids were supplied by Cyanamid Canada Inc. for use as starting materials in some of the syntheses.

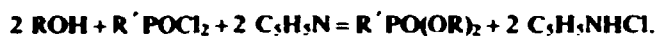
The remaining compounds were synthesized according to the following general methods.

Trialkyl phosphates were prepared by reaction of the appropriate alcohol with phosphorus oxychloride in the presence of pyridine, with toluene as the solvent,

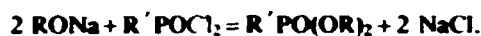


Dialkyl alkylphosphonates, except those in which  $R' = n$ -alkyl, were prepared via the corresponding alkylphosphonic dichlorides,

EXTRACTION OF ZINC, IRON, AND INDIUM



For the compounds where  $\text{R}' = \textit{tert}$ -butyl, the above reaction did not take place, and reaction with the more strongly nucleophilic alkoxide in place of the alcohol was required,



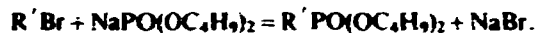
The alkylphosphonic dichlorides themselves were obtained by the reaction of alkyl chlorides with phosphorus trichloride and anhydrous aluminium chloride<sup>7-9</sup>,



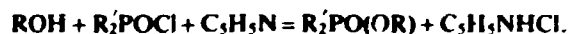
Dialkyl alkylphosphonates in which  $\text{R}' = n$ -alkyl were prepared, in the case of the diethyl esters, by reaction of the alkyl bromide with triethyl phosphite<sup>10</sup>,



and, in the case of the di-*n*-butyl esters, by reaction of the alkyl bromide and the sodium derivative of di-*n*-butyl phosphite<sup>11-13</sup>. The latter compound is traditionally named as the phosphite, but is in fact di-*n*-butyl hydrogen phosphonate, i.e.  $\text{HPO(OC}_4\text{H}_9)_2$  rather than  $\text{HOP(OC}_4\text{H}_9)_2$ .



Alkyl dialkylphosphinates were prepared by reaction of the appropriate alcohol with the dialkylphosphinic chloride in the presence of pyridine,



The acid chlorides required for this reaction were prepared by the action of thionyl chloride or, better, phosphorus pentachloride on the corresponding dialkylphosphinic acids, i.e.



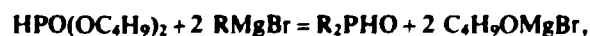
or



The phosphinic acids were obtained commercially or, in the case of di-*n*-octylphosphinic acid, prepared by the reaction of 1-octene with hypophosphorous acid, benzoyl peroxide being used as the free-radical initiator<sup>14,15</sup>,



and, in the case of di-*n*-butylphosphinic acid, prepared by the reaction of *n*-butylmagnesium bromide with di-*n*-butyl phosphite, followed by oxidation of the intermediate phosphine oxide with hydrogen peroxide<sup>14,16,17</sup>,

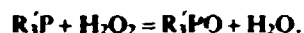


and

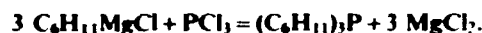




Trialkylphosphine oxides were prepared by the oxidation of the parent phosphine in aqueous ethanol using a 30 per cent solution of hydrogen peroxide,



Of the required phosphines, tri-*n*-butylphosphine was a commercial product, whereas tricyclohexylphosphine was prepared by the reaction of cyclohexylmagnesium chloride with phosphorus trichloride<sup>18</sup>,



Oxidation of this phosphine with hydrogen peroxide was found to represent a much more convenient synthesis of the oxide than the method described in the literature<sup>18</sup>, which uses potassium permanganate in acetone solution.

All the reagents and solvents used in the above-mentioned reactions were dried by appropriate means: molecular sieve (for pyridine, toluene, heptane, and the isomers of butanol), calcium chloride or potassium carbonate (for alkyl halides), distillation under reduced pressure (for cyclohexanol and phenol), and distillation from dispersed sodium (for toluene).

## 2.2. Characterization of Products

The molecular masses of the neutral organophosphorus compounds were determined by vapour-phase osmometry using 0,10 molal solutions in toluene at 35 °C. The measuring cell of the instrument was constructed at the Council for Mineral Technology (Mintek), and the electronic control and measuring unit was designed and built at Mintek. Pure recrystallized samples of benzophenone and benzil were used as calibration solutes.

The densities of liquid products were determined at 20,0 °C, a bottle with a nominal capacity of 10 ml being used, and were corrected<sup>19</sup> relative to the density of water at 4,0 °C by use of the value  $d_4^{20}(H_2O) = 0,998232$ . Refractive indices were determined at 20 °C (or, occasionally, at 25 °C) by use of an American Optical Corporation Abbe-type refractometer calibrated against pure water and several organic liquids of analytical grade.

The melting point (m.p.) of each product purified by recrystallization was determined on a Gallenkamp melting-point apparatus using a thermometer checked against the melting points of pure samples of benzophenone, 8-hydroxyquinoline, benzil, benzoic acid, and salicylic acid. The melting and freezing points of solid products purified by distillation were determined by use of a xylene heating-bath and a thermometer calibrated in 0,1 °C intervals immersed in the sample contained in the flask that had been used as the distillation receiver.

Carbon and hydrogen microanalyses were carried out at Mintek. (Unfortunately, facilities for the microanalysis of phosphorus are not available.)

Acidic impurities in the products were determined by the titration of samples (0,5 to 1,0 g) dissolved in aqueous ethanol against 0,05 M sodium hydroxide solution using a potentiometric end-point.

## 2.3. Metal-Distribution Equilibria

The metal-distribution equilibria were determined at  $24 \pm 2$  °C. Initial aqueous phases usually contained 0,01 to 0,05 M metal chlorides in mixtures of 0,5 to 5,0 M sodium chloride and 0,005 to 0,025 M hydrochloric acid. Organic phases contained 0,02 to 2,00 M extractant in xylene of analytical-reagent grade. Experiments involving iron(II), which is easily oxidized, were carried out with aqueous and organic phases that had been purged with high-purity nitrogen. Stock solutions of metal chlorides were prepared from the A.R.-grade salts or oxides or, in the case of iron(II) and indium(III), from the pure metals.

Equal volumes of organic and aqueous phases were shaken in separating funnels for at least 15 minutes. After clear separation of the phases, the metal contents of the aqueous phases were determined by direct titration against a 0,010 M solution of ethylenediaminetetra-acetic acid (EDTA), except for iron(II), which was titrated against 0,020 M  $(NH_4)_2Ce(SO_4)_4$  solution, and indium(III), which was back-titrated against 0,01 M  $ZnSO_4$  solution after the addition of excess 0,010 M EDTA solution. The indicators used in these titrations were methyl thymol blue for indium(III) and zinc(II) at a pH value of 6, murexide for copper(II) at a pH value of 10, Variamine Blue B for iron(III) at a pH value of 2 to 3, xylenol orange for lead(II)

at a pH value of 6, Eriochrome Black T for cadmium(II) at a pH value of 10, and ferroin redox indicator for iron(II) in dilute sulphuric acid. The difference between the initial and the final aqueous metal concentrations was assumed to be equal to the metal concentrations in the organic phases.

For determination of the chloride-to-metal ratio in the extracted complex, a suitable sample (1 or 2 ml) of the organic phase was dissolved in 1,0M nitric acid (10ml) and ethanol (40ml), and titrated potentiometrically against 0,020M silver nitrate solution.

### 3. RESULTS AND DISCUSSION

#### 3.1. Physical Properties and Purities of the Extractants

The physical properties of the neutral organophosphorus compounds used in the extraction studies are given in Tables 1 to 4, and the properties of some organophosphorus acids and acid chlorides prepared as intermediates in the syntheses in Table 5.

TABLE 1

#### Trialkyl phosphates (RO)<sub>3</sub>PO

R*	$n_D^{20}$	$d_4^{20}$	Melting point °C
<i>n</i> -C <sub>8</sub> H <sub>17</sub>	1,4240	0,9766	-
C <sub>6</sub> H <sub>5</sub>	1,5644†	-	51 to 51,5
C <sub>6</sub> H <sub>11</sub>	-	-	64 to 65

\* Abbreviations used in denoting alkyl groups in the tables are *n* (normal), *i* (iso), *s* (secondary), and *t* (tertiary); C<sub>6</sub>H<sub>11</sub> is cyclohexyl and *i*-C<sub>8</sub>H<sub>17</sub> is C<sub>8</sub>H<sub>17</sub>CH(C<sub>7</sub>H<sub>15</sub>)CH<sub>2</sub>. (This notation as iso-octyl is clearly a misnomer, but is widely accepted in chemical technology)

†  $n_D^{25}$  (supercooled liquid)

TABLE 2

#### Dialkyl alkylphosphonates R'PO(OR)<sub>2</sub>

R'	R	Boiling point °C	Pressure mm Hg	$n_D^{20}$	$d_4^{20}$
<i>n</i> -C <sub>8</sub> H <sub>17</sub>	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	95	0,30	1,4328	0,946
<i>i</i> -C <sub>8</sub> H <sub>17</sub>	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	70	0,03	1,4312	0,945
<i>s</i> -C <sub>8</sub> H <sub>17</sub>	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	75	0,04	1,4328	0,948
<i>s</i> -C <sub>8</sub> H <sub>17</sub>	<i>s</i> -C <sub>8</sub> H <sub>17</sub>	62	0,04	1,4298	0,944
<i>t</i> -C <sub>8</sub> H <sub>17</sub>	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	78	0,30	1,4296	0,940
C <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	104	0,03	1,4854	1,038
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	-	-	-	75,5*
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>11</sub>	180	0,10	1,5196	1,104
C <sub>6</sub> H <sub>11</sub>	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	109	0,10	1,4550	0,991
C <sub>6</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>5</sub>	-	-	1,5518†	62*
C <sub>6</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>11</sub>	170	0,05	-	62,5*
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	ND‡	-	1,4836	1,029
<i>n</i> -C <sub>8</sub> H <sub>17</sub>	C <sub>2</sub> H <sub>5</sub>	100	0,40	1,4335	0,949
<i>n</i> -C <sub>8</sub> H <sub>17</sub>	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	129	0,20	1,4392	0,926
<i>i</i> -C <sub>8</sub> H <sub>17</sub>	C <sub>2</sub> H <sub>5</sub>	77	0,05	1,4345	0,954

\* Melting point (°C)

† Supercooled liquid

‡ Not determined

## EXTRACTION OF ZINC, IRON, AND INDIUM

TABLE 3

*Alkyl dialkylphosphinates R<sub>2</sub>'PO(OR)*

R'	R	Boiling point °C	Pressure mm Hg	$n_D^{20}$	$d_4^{20}$	Melting point °C
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	80	0,03	1,4452	0,922	-
<i>i</i> -C <sub>4</sub> H <sub>9</sub>	<i>i</i> -C <sub>4</sub> H <sub>9</sub>	58	0,01	1,4410	0,913	- 18
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	-	-	-	-	137 to 138
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>11</sub>	-	-	-	-	120
C <sub>6</sub> H <sub>11</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	136	0,1	1,4915*	1,016*	27 to 29
C <sub>6</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>5</sub>	-	-	1,5414*	-	62 to 64
C <sub>6</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>11</sub>	-	-	-	-	86 to 88
<i>n</i> -C <sub>8</sub> H <sub>17</sub>	C <sub>2</sub> H <sub>5</sub>	155	0,15	1,4525*	0,897*†	29,5 to 30

\* Supercooled liquid

†  $d_4^{25}$ 

TABLE 4

*Trialkylphosphine oxides R<sub>3</sub>'PO*

R'	Boiling point °C	Pressure mm Hg	Melting point °C
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	96	0,04	69,5 to 70
C <sub>6</sub> H <sub>5</sub>	-	-	155 to 156
C <sub>6</sub> H <sub>11</sub>	-	-	155,5 to 156,5

TABLE 5

*Intermediate products (acids and acid chlorides)*

Compound	Boiling point °C	Pressure mm Hg	$n_D^{20}$	$d_4^{20}$	Melting point °C
<i>s</i> -C <sub>4</sub> H <sub>9</sub> POCl <sub>2</sub>	91	19	1,4706	1,2525	ND*
<i>t</i> -C <sub>4</sub> H <sub>9</sub> POCl <sub>2</sub>	-	-	-	-	121 to 123
C <sub>6</sub> H <sub>11</sub> POCl <sub>2</sub>	138	19	1,5049†	1,2894†	39 to 40
( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> POOH	-	-	-	-	68 to 68,5
( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> POCl	81	0,14	1,4650	1,0270	- 1,5
( <i>i</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> POOH	-	-	-	-	43,5 to 45,5
( <i>i</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> POCl	75	0,3	1,4614	1,0205	ND
(C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> POCl	-	-	-	-	106 to 108
( <i>n</i> -C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub> POOH	-	-	-	-	85
( <i>n</i> -C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub> POCl	-	-	-	-	42 to 44‡

\* Not determined

† Supercooled liquid (also  $n_D^{25}$  1,5030,  $d_4^{25}$  1,2838)

‡ Freezing point of product (not recrystallized)

Although satisfactory microanalyses for carbon and hydrogen ( $\pm 0,3$  per cent) were obtained in most instances (Table 6), the purity of these compounds cannot be estimated quantitatively, since they behave as neutral entities towards acidic and basic titrants. However, this behaviour enables the presence of acidic impurities to be readily detected by titration against standard alkali. (Such impurities are expected to be mono- and dialkyl esters in phosphates, monoalkyl esters in phosphonates, and phosphinic acids in phosphinates and phosphine oxides.) Table 7 shows the amounts (as mole percentages) of acidic impurities detected in the extractants by the titration of a sample (about 1 g) dissolved in aqueous ethanol against

## EXTRACTION OF ZINC, IRON, AND INDIUM

0,050M aqueous sodium hydroxide to a potentiometric end-point. The commercial extractant tri-*n*-octylphosphine oxide (Cyanamid Co.) was shown to contain a large amount (9 mole per cent) of (presumably) di-*n*-octylphosphinic acid, and was therefore unsuitable for use in the extraction studies.

TABLE 6

*Carbon and hydrogen microanalyses of solid compounds*

R'	R	Carbon, %		Hydrogen, %	
		Obs.	Calc.	Obs.	Calc.
<b>Phosphates (RO)<sub>3</sub>PO</b>					
-	C <sub>6</sub> H <sub>5</sub>	66,2	66,3	4,5	4,6
-	C <sub>8</sub> H <sub>11</sub>	62,7	62,8	9,9	9,7
<b>Phosphonates R'PO(OR)<sub>2</sub></b>					
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	69,4	69,7	4,9	4,9
C <sub>6</sub> H <sub>5</sub>	C <sub>8</sub> H <sub>11</sub>	66,8	67,1	8,8	8,4
C <sub>8</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>5</sub>	68,1	68,3	6,7	6,7
C <sub>8</sub> H <sub>11</sub>	C <sub>8</sub> H <sub>11</sub>	65,9	65,8	10,1	10,1
<b>Phosphinates R<sub>2</sub>P(OR)</b>					
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	73,8	73,5	5,1	5,1
C <sub>6</sub> H <sub>5</sub>	C <sub>8</sub> H <sub>11</sub>	72,3	72,0	7,0	7,0
C <sub>6</sub> H <sub>11</sub>	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	66,8	67,1	11,0	10,9
C <sub>8</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>5</sub>	70,5	70,6	8,8	8,9
C <sub>8</sub> H <sub>11</sub>	C <sub>8</sub> H <sub>11</sub>	69,1	69,2	10,9	10,6
<i>n</i> -C <sub>8</sub> H <sub>17</sub>	C <sub>2</sub> H <sub>5</sub>	68,2	67,9	12,4	12,3
<b>Phosphine oxides R<sub>3</sub>PO</b>					
C <sub>6</sub> H <sub>5</sub>	-	77,7	77,7	5,5	5,4
C <sub>8</sub> H <sub>11</sub>	-	72,5	72,9	11,3	11,2

Obs. Observed      Calc. Calculated

The molecular masses of the compounds determined by vapour-pressure osmometry are given in Table 8. Excellent agreement between the observed and the calculated values is evident.

In Table 9 the melting points of the crystalline products are compared with the values available in the literature. The only apparent anomaly concerns the compound phenyl dicyclohexylphosphinate, which Müller and Padeken<sup>25</sup> reported as being a liquid with a boiling point (b.p.) of 121 to 124 °C at 0,7 mm Hg, and an  $n_D^{20}$  value of 1,4438. They isolated 1,5 g of material by a different route from that used in the present investigation, in which the product was found to be a crystalline solid (m.p. 62 to 64 °C) that can be supercooled to a very viscous liquid with an  $n_D^{20}$  value of 1,5414.

For the compounds that are liquids at room temperature, the molar refractivities,

$$(n^2 - 1) M / (n^2 + 2)d,$$

were calculated as a further criterion of their purity, where  $M$  is the molecular mass of the compound,  $n$  its refractive index, and  $d$  its density at the same temperature.

The experimental molar refractivities at 20 °C are compared in Table 10 with the empirical values calculated by summation of the appropriate atomic constants. For the alkyl groups, the atomic constants determined by Vogel<sup>19</sup> were used, except for the cyclohexyl group (which is not listed), for which a value of 26,83 ( $\pm 0,15$  mean deviation) was calculated from the physical constants<sup>20</sup> of eleven well-characterized cyclohexyl compounds. It is interesting for this value to be compared with that calculated from the atomic constants for (CH<sub>2</sub>)<sub>5</sub>CH, namely 26,85, which indicates that there is no 'ring effect' for a six-membered saturated ring. The atomic constants used for phosphorus in the phosphate and phosphonate groups were those given by Kabachnik<sup>26</sup> (3,75 and 4,27 respectively), as was the value for oxygen in the phosphoryl group (2,21). The value for phosphorus in the phosphinate group was that of Kosolapoff and Watson<sup>17</sup>

TABLE 7

Amounts of acidic impurities in neutral organophosphorus compounds

R'	R	Sample taken mg	Acidic content	
			$\mu\text{mol}$	mole %
<b>Phosphates (RO)<sub>3</sub>PO</b>				
-	<i>i</i> -C <sub>4</sub> H <sub>9</sub>	1181	1,0	0,02
-	C <sub>6</sub> H <sub>5</sub>	835	4,0	0,16
-	C <sub>6</sub> H <sub>11</sub>	500	5,0	0,35
<b>Phosphonates R'PO(OR)<sub>2</sub></b>				
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	892	0,5	0,01
<i>i</i> -C <sub>4</sub> H <sub>9</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	1055	0,5	0,01
<i>s</i> -C <sub>4</sub> H <sub>9</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	1007	0,5	0,01
<i>s</i> -C <sub>4</sub> H <sub>9</sub>	<i>s</i> -C <sub>4</sub> H <sub>9</sub>	811	3,0	0,09
<i>t</i> -C <sub>4</sub> H <sub>9</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	1040	0,5	0,01
C <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	903	1,0	0,03
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	671	1,0	0,05
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>11</sub>	965	3,0	0,10
C <sub>6</sub> H <sub>11</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	865	7,0	0,22
C <sub>6</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>5</sub>	852	0,5	0,01
C <sub>6</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>11</sub>	262	0,5	0,06
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	1197	9,0	0,21
<i>n</i> -C <sub>8</sub> H <sub>17</sub>	C <sub>2</sub> H <sub>5</sub>	913	2,5	0,07
<i>n</i> -C <sub>8</sub> H <sub>17</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	822	3,0	0,11
<i>i</i> -C <sub>8</sub> H <sub>17</sub>	C <sub>2</sub> H <sub>5</sub>	903	1,0	0,03
<b>Phosphinates R<sub>2</sub>PO(OR)</b>				
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	822	0,5	0,01
<i>i</i> -C <sub>4</sub> H <sub>9</sub>	<i>i</i> -C <sub>4</sub> H <sub>9</sub>	561	1,5	0,06
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	459	0,5	0,03
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>11</sub>	754	45,0	1,79
C <sub>6</sub> H <sub>11</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	300	2,0	0,19
C <sub>6</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>5</sub>	450	0,2	0,01
C <sub>6</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>11</sub>	393	11,0	0,87
<i>n</i> -C <sub>8</sub> H <sub>17</sub>	C <sub>2</sub> H <sub>5</sub>	453	1,5	0,10
<b>Phosphine oxides R<sub>3</sub>PO</b>				
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	-	1080	20,0	0,40
C <sub>6</sub> H <sub>5</sub>	-	516	1,0	0,05
C <sub>6</sub> H <sub>11</sub>	-	360	4,5	0,37

(4,79), while the value for the ester oxygens in the PO<sub>4</sub>, PO<sub>3</sub>, and PO<sub>2</sub> groups was that given by Vogel<sup>19</sup> for oxygen in acetals (1,61). Such a summation gave excellent agreement between the calculated value for the PO<sub>4</sub> group and that listed by Vogel (10,79 and 10,77 respectively).

Table 10 shows that there is generally good agreement between the observed and the calculated values of molar refractivities, which suggests that the compounds are of acceptable purity. For the phosphonates, which represent the largest group of compounds prepared, the experimental molar refractivities can be used for the calculation (by subtraction of the values for the substituent alkyl groups) of an average refractivity value for the PO<sub>3</sub> group (9,73 ± 0,07), which compares well with the value obtained by summation of the atomic constants for this group described previously (9,70). A similar calculation for the liquid phosphinates prepared gives a mean value for the PO<sub>2</sub> group of 8,79, compared with the empirical value of 8,61.

Two of the compounds, namely phenyl diphenylphosphinate and cyclohexyl diphenylphosphinate, were not suitable for the extraction of metals because of their low solubility in xylene.

### 3.2. Effect of Reagent Structure on Metal Extraction

The extraction of zinc(II) and iron(III) from chloride solutions by the series of neutral organophosphorus

TABLE 8

*Molecular masses of neutral organophosphorus compounds determined by vapor-phase osmometry*

R'	R	Molecular mass		Difference† %
		Calc.	Obs.*	
<b>Phosphates (RO)<sub>3</sub>PO</b>				
-	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	266,3	266,8	0,2
-	C <sub>6</sub> H <sub>5</sub>	326,3	329,8	1,0
-	C <sub>6</sub> H <sub>11</sub>	344,4	344,4	0,0
<b>Phosphonates R' PO(OR)<sub>2</sub></b>				
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	250,3	248,4	-0,8
<i>i</i> -C <sub>4</sub> H <sub>9</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	250,3	249,9	-0,2
<i>s</i> -C <sub>4</sub> H <sub>9</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	250,3	249,1	-0,5
<i>s</i> -C <sub>4</sub> H <sub>9</sub>	<i>s</i> -C <sub>4</sub> H <sub>9</sub>	250,3	250,3	0,0
<i>t</i> -C <sub>4</sub> H <sub>9</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	250,3	248,7	-0,6
C <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	270,3	270,5	0,1
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	310,3	311,6	0,4
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>11</sub>	322,4	321,5	-0,3
C <sub>6</sub> H <sub>11</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	276,4	274,4	-0,7
C <sub>6</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>5</sub>	316,3	316,3	0,0
C <sub>6</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>11</sub>	328,4	323,8	-1,4
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	284,3	284,4	0,0
<i>n</i> -C <sub>8</sub> H <sub>17</sub>	C <sub>2</sub> H <sub>5</sub>	250,3	251,5	0,5
<i>n</i> -C <sub>8</sub> H <sub>17</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	306,4	306,1	-0,1
<i>i</i> -C <sub>8</sub> H <sub>17</sub>	C <sub>2</sub> H <sub>5</sub>	250,3	252,5	0,9
<b>Phosphinates R<sub>2</sub>PO(OR)</b>				
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	234,3	232,8	-0,6
<i>i</i> -C <sub>4</sub> H <sub>9</sub>	<i>i</i> -C <sub>4</sub> H <sub>9</sub>	234,3	234,0	-0,1
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	294,3	297,2	1,0
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>11</sub>	300,3	306,3	2,0
C <sub>6</sub> H <sub>11</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	286,4	284,4	-0,7
C <sub>6</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>5</sub>	306,4	306,9	0,2
C <sub>6</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>11</sub>	312,4	315,5	1,0
<i>n</i> -C <sub>8</sub> H <sub>17</sub>	C <sub>2</sub> H <sub>5</sub>	318,5	318,9	0,1
<b>Phosphine oxides R<sub>3</sub>PO</b>				
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	-	218,3	220,3	0,9
C <sub>6</sub> H <sub>5</sub>	-	278,3	284,4	2,2
C <sub>6</sub> H <sub>11</sub>	-	296,4	304,5	2,7

\* Mean of 4 to 9 determinations

† Percentage difference between observed and calculated molecular masses; arithmetic mean for 29 compounds 0,66 per cent (154 determinations)

Calc. Calculated      Obs. Observed

compounds (1) to (4) described in Section 1, where R and R' are cyclohexyl groups, is shown in Figures 1 and 2 and, for the compounds where R and R' are *n*-butyl groups, in Figures 3 and 4. It can be seen clearly that the extraction increases through the series from (1) to (4) when alkoxy groups are replaced by alkyl groups. This would appear to reflect the importance of electronic rather than steric effects. When alkoxy groups are replaced by alkyl groups, more electron density is available for the P=O group to coordinate with the appropriate metal, owing to the electron-donating nature of alkyl groups relative to alkoxy groups.

The extraction of zinc(II) and iron(III) with phosphonates increases when phenyl groups are replaced by cyclohexyl groups, as shown in Figure 5. This extraction behaviour is presumably due to electronic rather than steric effects, since the cyclohexyl and phenyl groups are similar in size. Cyclohexyl donates electron density to the P=O coordinating group, whereas phenyl withdraws electron density from the P=O group. The same extraction behaviour was observed in phosphinate extraction, as shown in Figure 6.

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TABLE 9

Melting points of solid compounds and comparison with literature values

R'	R	Melting point, °C		Reference no.
		This work	Literature	
<b>Phosphates (RO)<sub>3</sub>PO</b>				
-	C <sub>6</sub> H <sub>5</sub>	51 to 51,5	50 to 51	20
-	C <sub>6</sub> H <sub>11</sub>	64 to 65	63 to 64	21
<b>Phosphonates R'PO(OR)<sub>2</sub></b>				
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	75 to 75,5	-	-*
C <sub>6</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>5</sub>	61 to 62	62	22
C <sub>6</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>11</sub>	62,5	59 to 60	21
<b>Phosphinates R<sub>2</sub>PO(OR)</b>				
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	137 to 138	{ 135 to 136 139	{ 23 24
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>11</sub>	120	120 to 121	23
C <sub>6</sub> H <sub>11</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	27 to 29	Liquid	1
C <sub>6</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>5</sub>	62 to 64	Liquid	25
C <sub>6</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>11</sub>	86 to 88	85 to 86	21
<i>n</i> -C <sub>8</sub> H <sub>17</sub>	C <sub>2</sub> H <sub>5</sub>	29,5 to 30	-	-*
<b>Phosphine oxides R<sub>3</sub>P(O)</b>				
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	-	69,5 to 70	67 to 69	21
C <sub>6</sub> H <sub>5</sub>	-	155 to 156	156 to 157	20
C <sub>6</sub> H <sub>11</sub>	-	155,5 to 156,5	155 to 157	18, 21

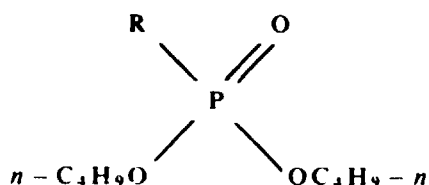
\* Not found in the literature

TABLE 10

Molar refractivities of liquid neutral organophosphorus compounds

R'	R	Molar refractivity	
		Observed	Calculated
<b>Phosphates (RO)<sub>3</sub>PO</b>			
-	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	69,58	69,56
<b>Phosphonates R'PO(OR)<sub>2</sub></b>			
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	68,73	68,47
<i>i</i> -C <sub>4</sub> H <sub>9</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	68,62	68,50
<i>s</i> -C <sub>4</sub> H <sub>9</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	68,54	68,46
<i>s</i> -C <sub>4</sub> H <sub>9</sub>	<i>s</i> -C <sub>4</sub> H <sub>9</sub>	68,43	68,44
<i>t</i> -C <sub>4</sub> H <sub>9</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	68,76	68,73
C <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	74,66	74,22
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>11</sub>	88,73	88,72
C <sub>6</sub> H <sub>11</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	75,63	75,71
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	78,95	78,89
<i>n</i> -C <sub>8</sub> H <sub>17</sub>	C <sub>2</sub> H <sub>5</sub>	68,60	68,44
<i>n</i> -C <sub>8</sub> H <sub>17</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	87,09	87,02
<i>i</i> -C <sub>8</sub> H <sub>17</sub>	C <sub>2</sub> H <sub>5</sub>	68,38	68,44
<b>Phosphinates R<sub>2</sub>PO(OR)</b>			
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	67,67	67,38
<i>i</i> -C <sub>4</sub> H <sub>9</sub>	<i>i</i> -C <sub>4</sub> H <sub>9</sub>	67,75	67,47
C <sub>6</sub> H <sub>11</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	81,69	81,86
<i>n</i> -C <sub>8</sub> H <sub>17</sub>	C <sub>2</sub> H <sub>5</sub>	95,53	95,19

The extraction of zinc(II) and iron(III) with compounds of the structure



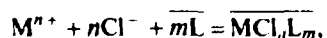
where R represents the *n*-, *iso*-, *sec*-, and *tert*-butyl groups, is shown in Figure 7. The order of extraction observed was *sec*-butyl  $\approx$  *n*-butyl  $>$  *iso*-butyl  $>$  *tert*-butyl, although the differences in extraction were small. This appears to result from an approximate cancelling of the steric and electronic effects through the series. On the basis of the electronic effect of the substituent groups, the extractant strength would be expected to increase in the order *n*-butyl  $<$  *iso*-butyl  $<$  *sec*-butyl  $<$  *tert*-butyl, whereas on the basis of the steric effect of these groups, the reverse order would be expected. Figure 8 shows the extraction of zinc(II) and iron(III) by di-*sec*-butyl *sec*-butylphosphonate. Although this extractant is a relatively sterically hindered compound due to the three *sec*-butyl groups present, there was no significant decrease in extraction as compared with the extractions for the above-mentioned compounds. This fits in with the extraction behaviour explained above for these compounds, since the steric effect is also counteracted by the enhanced electron-donating effect of the *sec*-butyl groups.

The remainder of the extraction curves obtained for the metals extracted by neutral organophosphorus compounds are shown in Figures 9 to 20. Copper(II), cadmium(II), and iron(II) were extracted from chloride solutions with a few selected compounds, and the extraction was very low, as indicated. In the case of lead(II) there was no extraction at all. Indium(III) is extracted strongly by these compounds, as shown in Figure 21.

The lengthening or shortening of the straight-chain groups (R and R-O) in phosphonates has little effect on the extractant strength of the compound. This is illustrated in Figures 9 and 10, which show that the extraction of metals by di-*n*-butyl *n*-octylphosphonate and diethyl *n*-octylphosphonate is virtually the same. However, di-*n*-butyl *n*-octylphosphonate will be commercially more suitable since it is less soluble in water (more carbons present), and the loss of extractant to the aqueous phase is therefore limited. The same applies to the extraction by the corresponding phosphinates.

### 3.3. Stoichiometries of the Extracted Metal Complexes

The general equation for the extraction of a metal  $M^{n+}$  by a neutral organophosphorus compound L is



where the bars denote the presence of the species in the organic phase. The extraction constant K for the reaction is given by the expression.

$$K = \frac{[\overline{MCl_nL_m}]}{[M^{n+}][Cl^-]^n[L]^m},$$

or

$$K = \frac{D}{[Cl^-]^n[L]^m},$$

where

$$D, \text{ the distribution coefficient} = \frac{[\overline{MCl_nL_m}]}{[M^{n+}]}$$

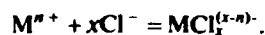


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The taking of logarithms gives

$$\log D = \log K + n \log [Cl^-] + m \log [L].$$

Therefore a plot of  $\log D$  versus  $\log [L]$  at constant chloride concentration is expected to be a straight line with slope  $m$ , and a plot of  $\log D$  versus  $\log [Cl^-]$  at constant extractant concentration is also expected to be a straight line, but with slope  $n$ . However,  $n$  was not determined by this means because of the formation of non-extractable metal chlorocomplexes in the aqueous phase, of the nature



(This is the reason for the decrease in zinc extraction at high chloride concentrations.) So that this complication could be avoided, the value of  $n$  was determined by direct analysis of the metal and chloride contents of loaded organic phases. The chloride-to-metal ratios determined are summarized in Table 11. The reason for one unexpectedly high value for  $n$  in the case of iron(III) is not known.

TABLE 11

*Chloride-to-metal ratios in the complexes extracted by neutral organophosphorus compounds*

Extractant	Zinc(II)*	Iron(III)*	Indium(III)*
Tri- <i>n</i> -butylphosphate	1,95	3,85	-
Di- <i>n</i> -butyl <i>iso</i> -butylphosphonate	1,96	2,89	-
Cyclohexyl dicyclohexylphosphinate	1,97	2,97	-
Ethyl di- <i>n</i> -octylphosphinate	-	-	2,91
Tri- <i>n</i> -butylphosphine oxide	1,98	2,93	3,00

\* Values are the mean of three determinations in each case

Graphs to illustrate plots of  $\log D$  versus  $\log [L]$  at constant chloride concentration are shown in Figures 22 to 24, and the values for slope  $m$  are summarized in Table 12.

TABLE 12

*Extractant-to-metal ratios (m) in the complexes extracted by neutral organophosphorus compounds*

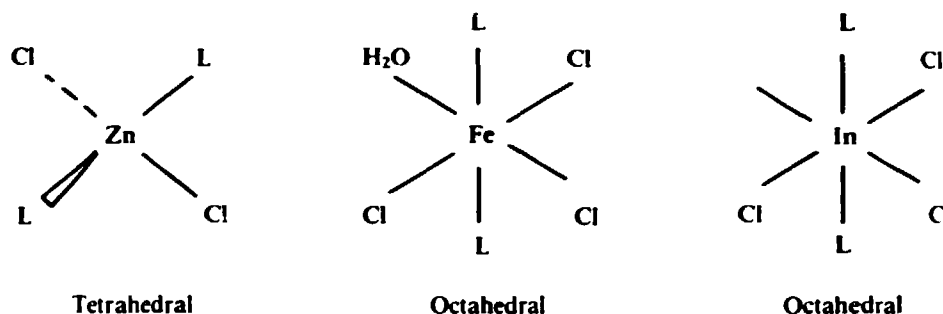
Extractant	Zinc(II)	Iron(III)	Indium(III)
Tri- <i>n</i> -butylphosphate	2,90	4,68	-
Di- <i>n</i> -butyl <i>n</i> -butylphosphonate	2,20	2,00	-
Ethyl di- <i>n</i> -octylphosphinate	1,88	1,72	2,04
Tri- <i>n</i> -butylphosphine oxide	2,23	2,00	-

The other metals studied were too weakly extracted to yield data for the stoichiometries of the complexes formed.

The probable stoichiometries of the complexes formed are therefore  $ZnCl_2L_2$  (tetrahedral),  $FeCl_3L_2(H_2O)$  (octahedral), and  $InCl_3L_2(H_2O)$  (octahedral). It was found that the selectivity for zinc(II) over iron(III) does not change through the series of neutral organophosphorus compounds, which is probably due to the fact that, for both metals, the number of ligand molecules found to be present in the extracted complex is two (Table 12), and therefore any changes in extractant structure affect both metals to a similar extent. The

## EXTRACTION OF ZINC, IRON, AND INDIUM

reason for the unexpectedly high values of  $m$  in the extraction with tributylphosphate is not known. Likely structures for these complexes are



As indium(III) has a larger ionic radius (0,81 Å) than iron(III) (0,64 Å), the dependence of indium(III) extraction on extractant concentration was determined so that the number of ligand molecules in the extracted complex could be compared with that found for iron(III). However, despite the larger size of the indium cation, the complex still contains only two organophosphorus ligand molecules.

### 4. CONCLUSIONS

The following findings arose from the study of the extraction of zinc and some associated metals from chloride solutions by the use of a series of well-characterized neutral organophosphorus compounds.

1. Zinc(II), iron(III), and indium(III) are strongly extracted. The extraction of iron(III) and indium(III) increases monotonically with increase in the chloride concentration in the aqueous phase, whereas that of zinc(II) increases up to a chloride concentration of about 2,5 M and decreases gradually thereafter. Moderate selectivities for zinc(II) over iron(III) are shown for chloride concentrations up to 2,5 M.
2. Iron(II), copper(II), cadmium(II), and lead(II) are weakly extracted, and would not interfere in a process for the recovery of zinc(II).
3. The dialkyl alkylphosphonates and alkyl dialkylphosphinates show the best compromise between the effective extraction of zinc(II) at higher chloride concentrations and effective stripping at the lower concentrations that would be required in practice. The selectivities of these two classes of reagent for zinc(II) over iron(III) are of similar magnitudes.
4. The progressive replacement of alkoxy groups by alkyl groups markedly increases the strength of the extractant through the series of neutral organophosphorus compounds.
5. The progressive increase in chain-branching of the substituent alkyl groups through series such as *n*-butyl, *iso*-butyl, *sec*-butyl, and *tert*-butyl, has little effect on the strength or selectivity of the extractant.
6. The substitution of six-membered aliphatic (cyclohexyl) by six-membered aromatic (phenyl) rings markedly decreases the strength of the extractants.
7. The above observations on the effect of molecular structure upon the strength of extraction appear to reflect the importance of electron-inductive effects rather than steric effects in the systems studied.
8. The extracted complexes of zinc(II), iron(III), and indium(III) have the stoichiometries  $ZnCl_2L_2$ ,  $FeCl_3L_2(H_2O)$ , and  $InCl_3L_2(H_2O)$  respectively, where L represents the neutral organophosphorus compound.

## 5. REFERENCES

1. RITCEY, G.M., LUCAS, B.H., and PRICE, K.T. Evaluation and selection of extractants for the separation of copper and zinc from chloride leach liquor. *Hydrometallurgy*, vol. 8. 1982. p. 197.
2. RICE, N.M., and SMITH, M.R. Recovery of zinc, cadmium and mercury(II) from chloride and sulphate media by solvent extraction. *J. Appl. Chem. Biotechnol.*, vol. 25. 1975. p. 379.
3. SCHLIEBE, R., KASCHUBA, J., ROEYER, W., and SCHMIDT, S. (Bayer AG and Duisburger Kupferhütte). Extraction of zinc, cadmium, and/or indium from solutions containing their salts plus those of other metals. *S.Afr. Pat.* 73/5459. 1973.
4. NOGUEIRA, E.D., and COSMEN, P. The solvent extraction of zinc chloride with di-*n*-pentyl pentaphosphonate. *Hydrometallurgy*, vol. 9. 1983. p. 333.
5. BLAKE, C.A., BAES, C.F. and BROWN, K.B. Solvent extraction with alkylphosphoric compounds. *Ind. Eng. Chem.*, vol. 50. 1958. p. 1763.
6. SIDDALL, T.H. Trialkyl phosphates and dialkyl alkylphosphonates in uranium and thorium extraction. *Ind. Eng. Chem.*, vol. 51. 1959. p. 41.
7. CLAY, J.P. A new method for the preparation of alkane phosphonyl dichlorides. *J. Org. Chem.*, vol. 16. 1951. p. 892.
8. KINNEAR, A.M., and PERREN, E.A. Formation of organophosphorus compounds by the reaction of alkyl chlorides with phosphorus trichloride in the presence of aluminium chloride. *J. Chem. Soc.*, 1952. p. 3437.
9. CROFTS, P.C., and KOSOLAPOFF, G.M. Preparation and determination of apparent dissociation constants of some alkylphosphonic and dialkylphosphinic acids. *J. Am. Chem. Soc.*, vol. 75. 1953. p. 3379.
10. FORD-MOORE, A.H., and WILLIAMS, J.H. The reaction between trialkyl phosphites and alkyl halides. *J. Chem. Soc.*, 1947. p. 1465.
11. KOSOLAPOFF, G.M. Isomerization of alkylphosphites. III. The synthesis of *n*-alkylphosphonic acids. *J. Am. Chem. Soc.*, vol. 67. 1945. p. 1180.
12. GEISELER, G., ASINGER, F., and FEDTKE, M. Substitution ratios in the chlorophosphonylation of paraffinic hydrocarbons. *Chem. Ber.*, vol. 93. 1960. p. 765. (In German.)
13. ZIMMERER, R.E., and LAUGHLIN, R.G. The reaction between dialkylphosphonates and their sodium salts. *J. Org. Chem.*, vol. 27. 1962. p. 3576.
14. WILLIAMS, R.H., and HAMILTON, L.A. Disubstituted phosphine oxides and disubstituted phosphinic acids. II. The di-*n*-alkyl series. *J. Am. Chem. Soc.*, vol. 77. 1955. p. 3411.
15. PEPPARD, D.F., MASON, G.W., and LEWEY, S. Di-*n*-octylphosphinic acid as a selective extractant for metallic cations. Selected M(III) and M(VI) tracer studies. *J. Inorg. Nucl. Chem.*, vol. 27. 1965. p. 2065.
16. WILLIAMS, R.H., and HAMILTON, L.A. Di-*n*-alkylphosphine oxides. I. Synthesis. *J. Am. Chem. Soc.*, vol. 74. 1952. p. 5418.
17. KOSOLAPOFF, G.M., and WATSON, R.M. The anhydrides of di-*n*-propyl- and di-*n*-outylphosphinic acids. *J. Am. Chem. Soc.*, vol. 73. 1951. p. 4101.
18. ISSLEIB, K., and BRACK, A. Preparation of tricyclohexylphosphine and its derivatives. *Z. anorg. allgem. Chemie*, vol. 277. 1954. p. 258. (In German.)
19. VOGEL, A.I. A textbook of practical organic chemistry. 2nd edition. London, Longmans Green, 1951. p. 1035.
20. WEAST, R.C. Handbook of chemistry and physics. 57th edition. Cleveland, CRC Press, 1976.
21. BUCKLER, S.A. Autoxidation of trialkylphosphines. *J. Am. Chem. Soc.*, vol. 84. 1962. p. 3093.
22. GRAF, R. The reaction of alkanes with phosphorus trichloride and oxygen. *Chem. Ber.*, vol. 85. 1952. p. 9. (In German.)
23. BERLIN, K.D., AUSTIN, T.H., and NAGABHUSHANAM, M. A convenient synthesis of esters of diphenylphosphinic acid. III. *J. Org. Chem.*, vol. 30. 1965. p. 1267.
24. SCHINDLBAUER, H. Statements about possible resonance with the phosphoryl groups in organophosphorus compounds on the basis of infrared spectroscopic measurements. *Allg. prakt. Chemie*, vol. 18. 1967. p. 102. (In German.)
25. MULLER, E., and PADEKEN, H.G. Photophosphonylation of cyclohexane. *Chem. Ber.*, vol. 100. 1967. p. 521. (In German.)
26. KABACHNIK, M.I. Organophosphorus compounds. X. Atomic refraction of phosphorus in esters and chlorides of acids of phosphorus. *Chem. Abstr.*, vol. 42, 5736 g. 1948.

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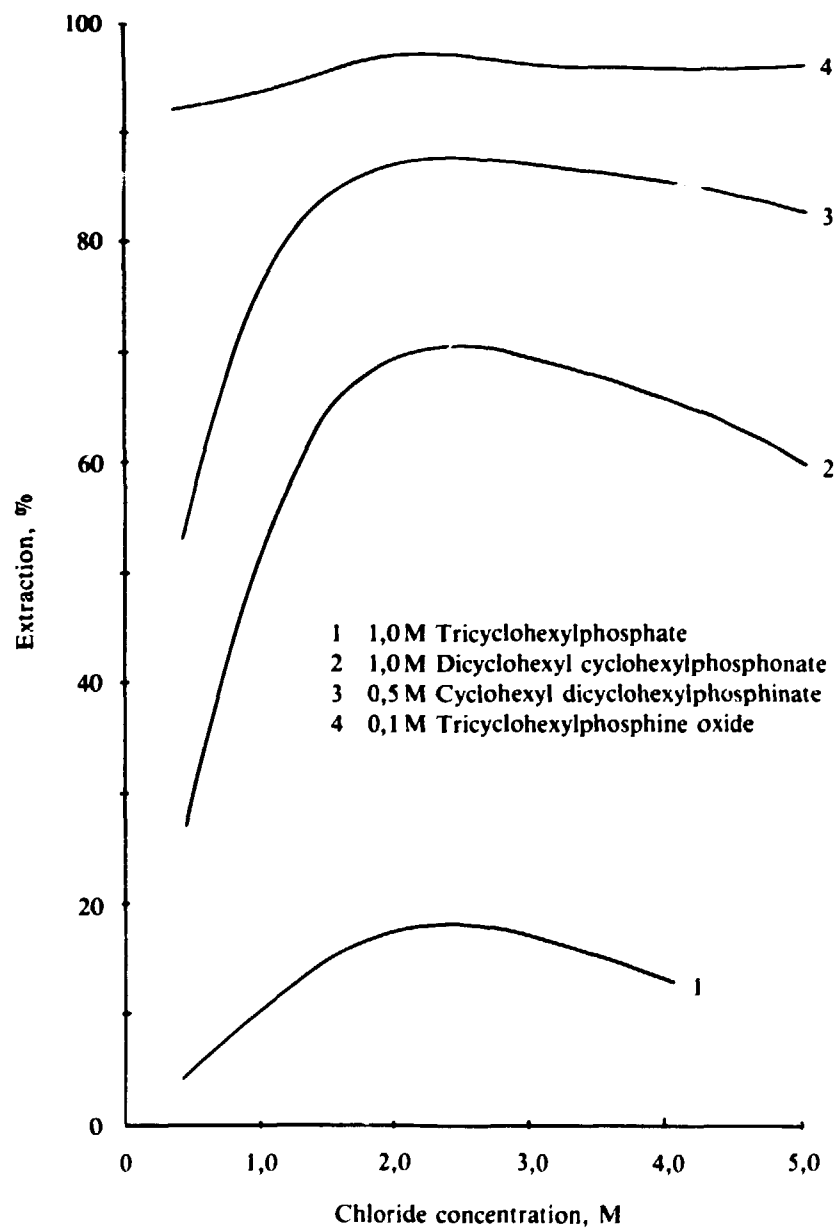


FIGURE 1. Extraction of zinc(II) by the cyclohexyl series of neutral organophosphorus compounds

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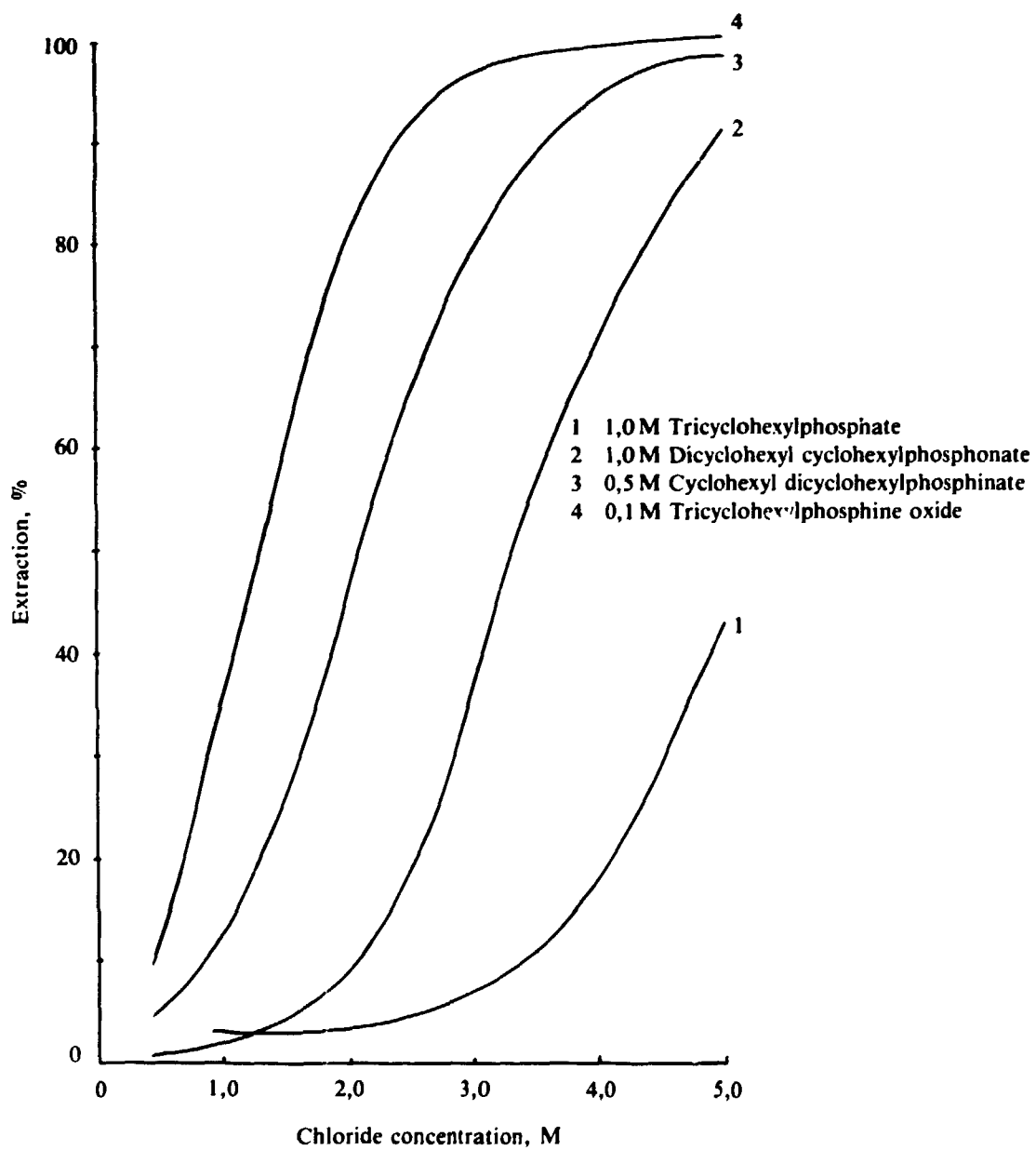


FIGURE 2. Extraction of iron(III) by the cyclohexyl series of neutral organophosphorus compounds

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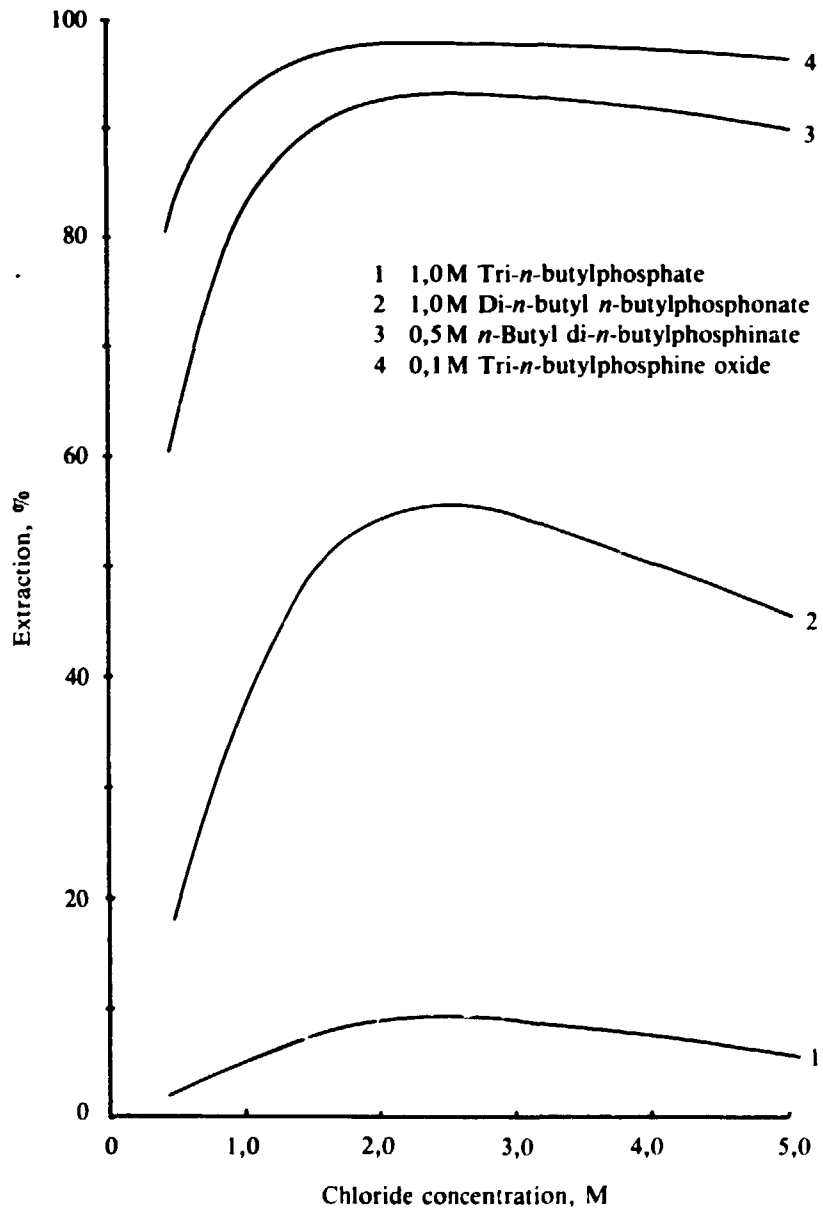


FIGURE 3. Extraction of zinc(II) by the *n*-butyl series of neutral organophosphorus compounds

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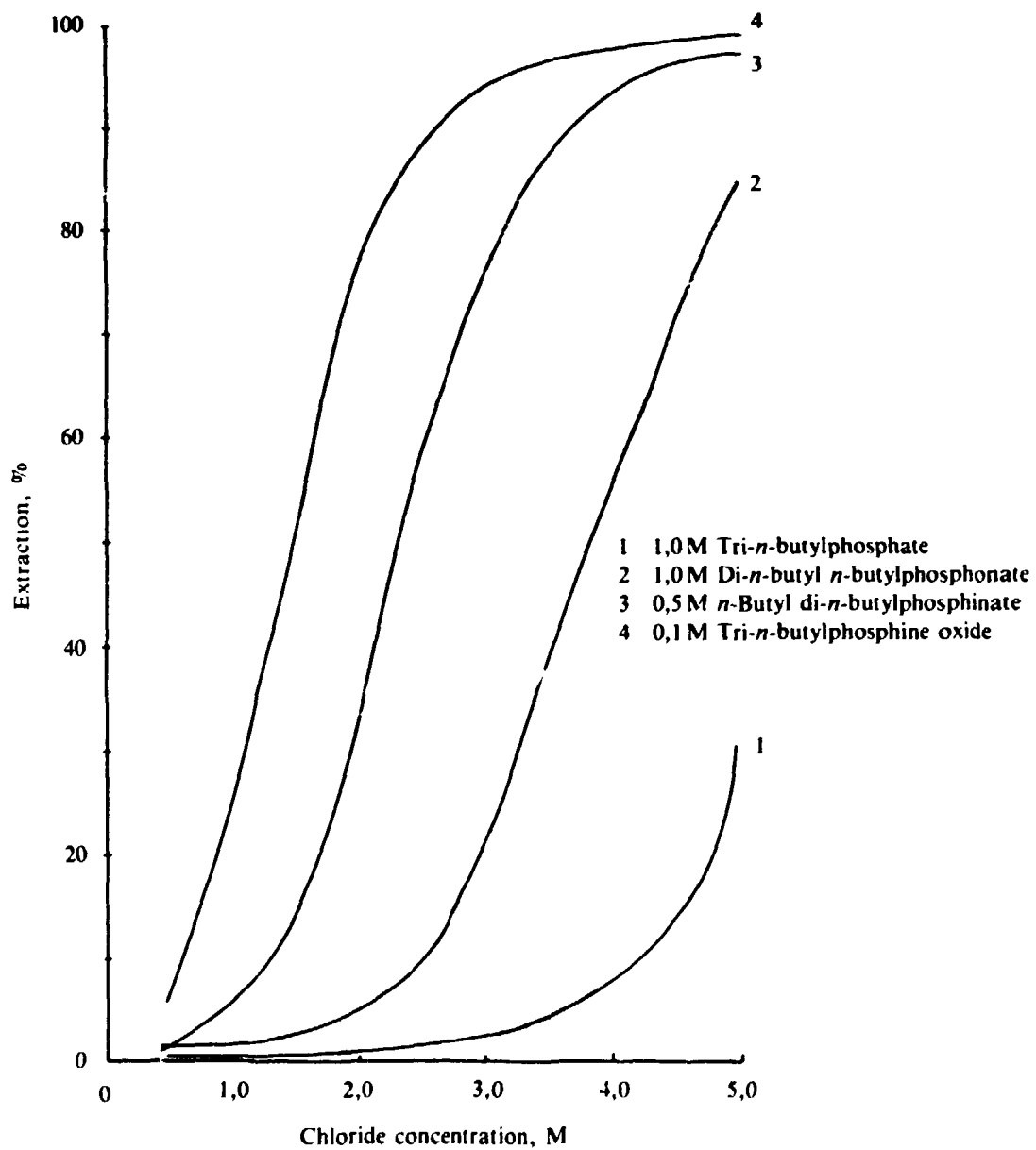


FIGURE 4. Extraction of iron(III) by the *n*-butyl series of neutral organophosphorus compounds

EXTRACTION OF ZINC, IRON, AND INDIUM

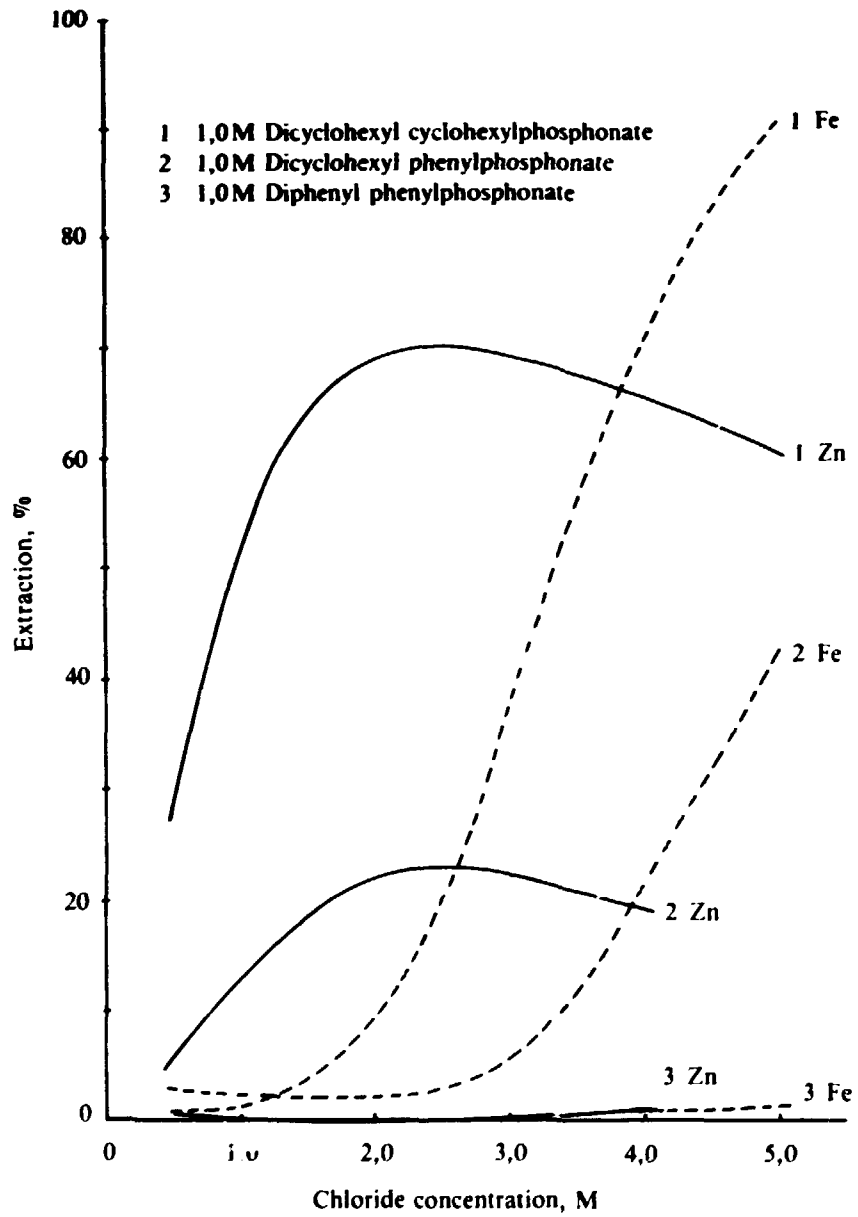


FIGURE 5. Effect of replacement of cyclohexyl groups by phenyl groups on the extraction of zinc(II) and iron(III) by phosphonates



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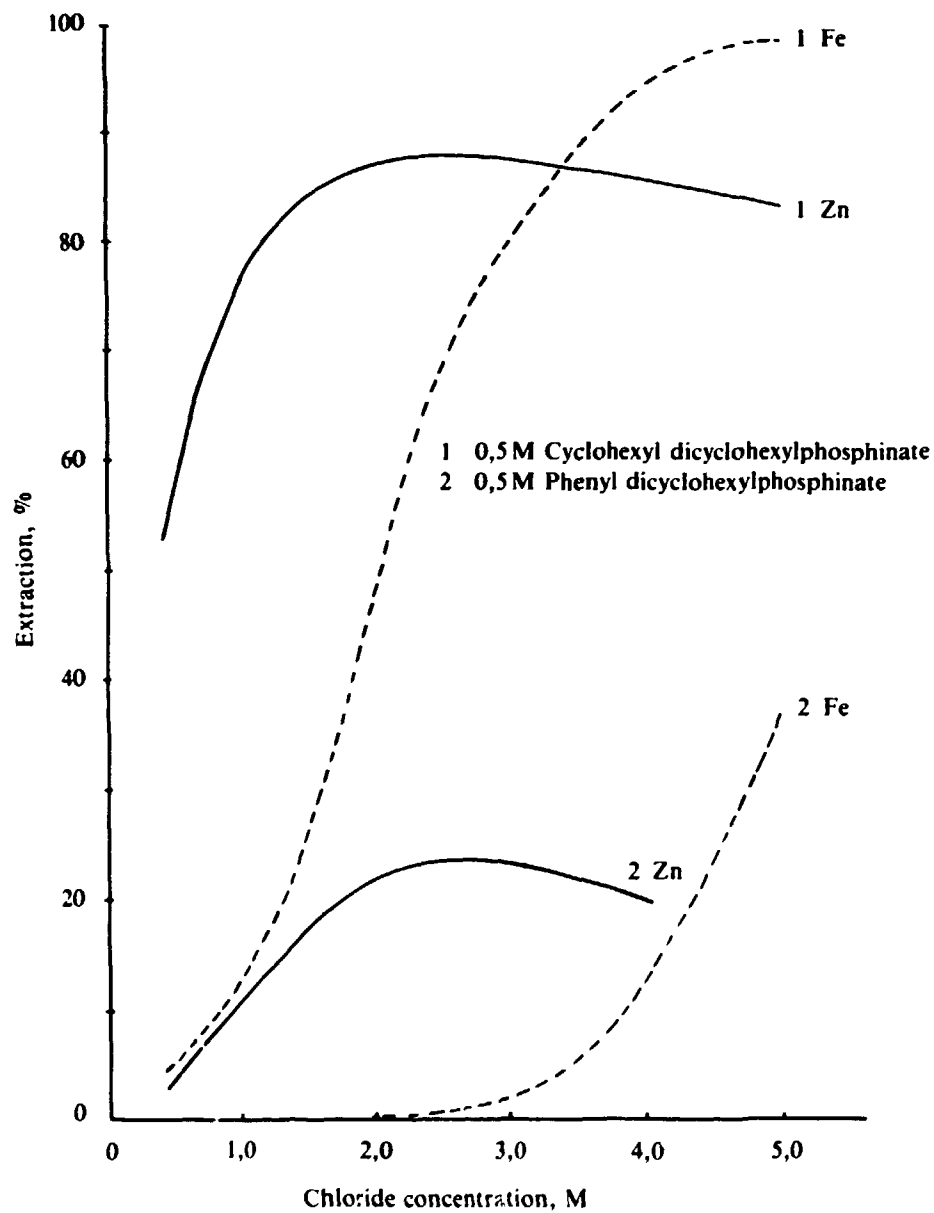


FIGURE 6. Effect of replacement of cyclohexyl groups by phenyl groups on the extraction of zinc(II) and iron(III) by phosphinates

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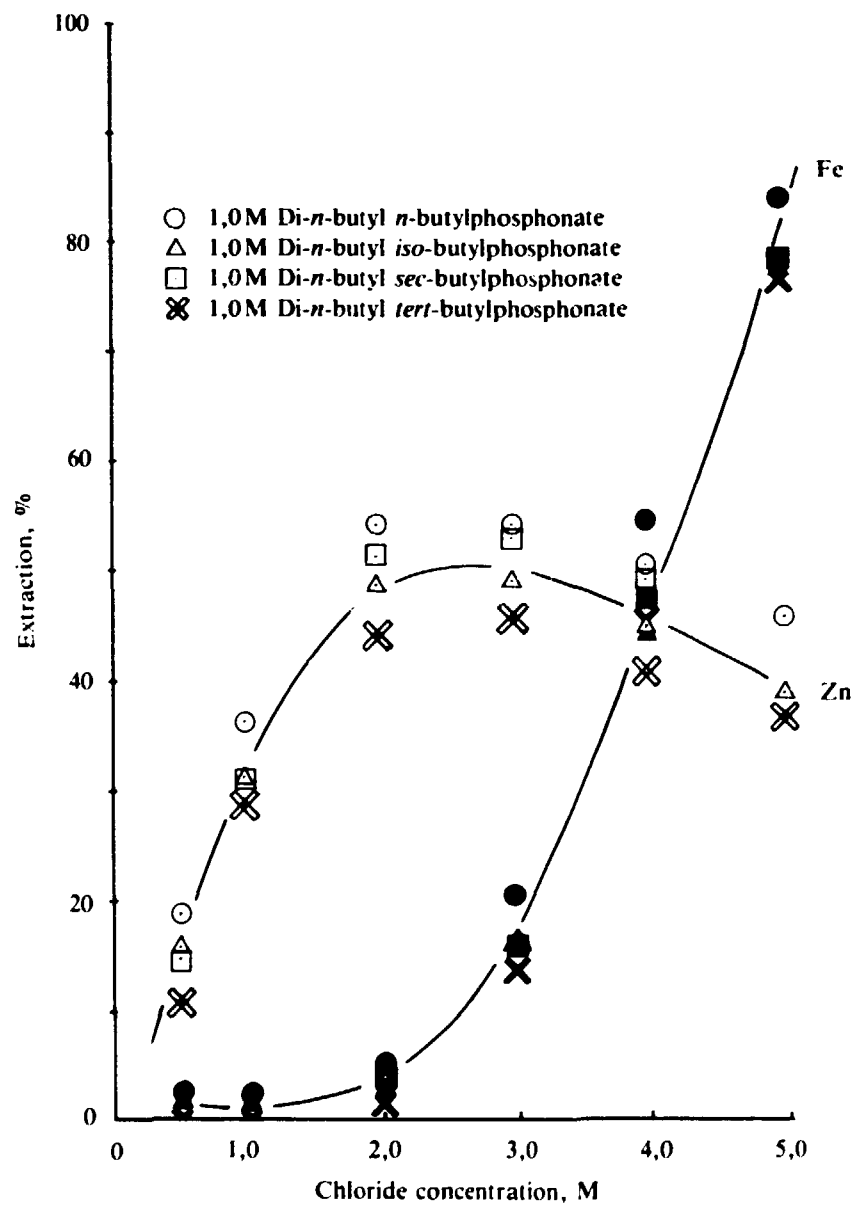


FIGURE 7. The effect of increased chain-branching in the series *n*-butyl, *iso*-butyl, *sec*-butyl, and *tert*-butyl on the extraction of zinc(II) and iron(III) by di-*n*-butyl alkylphosphonates

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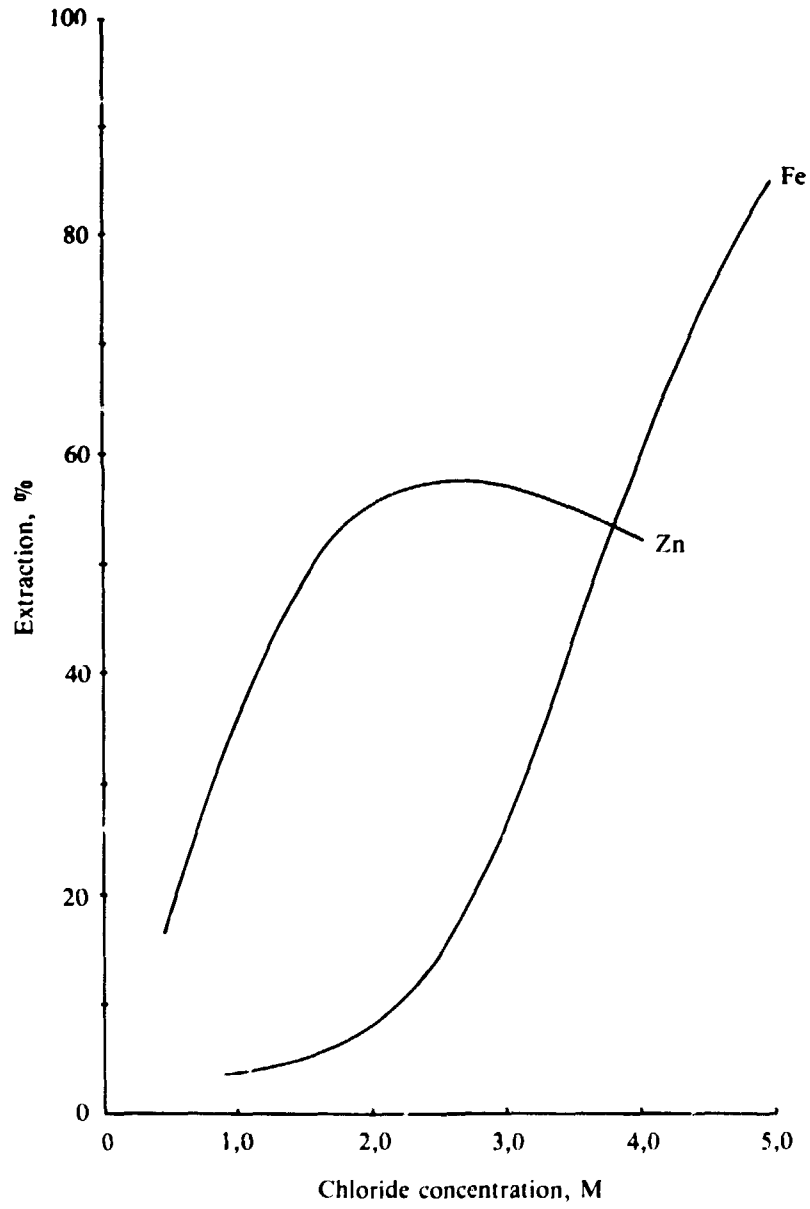


FIGURE 8. Extraction of zinc(II) and iron(III) by 1,0M di-*sec*-butyl *sec*-butylphosphonate

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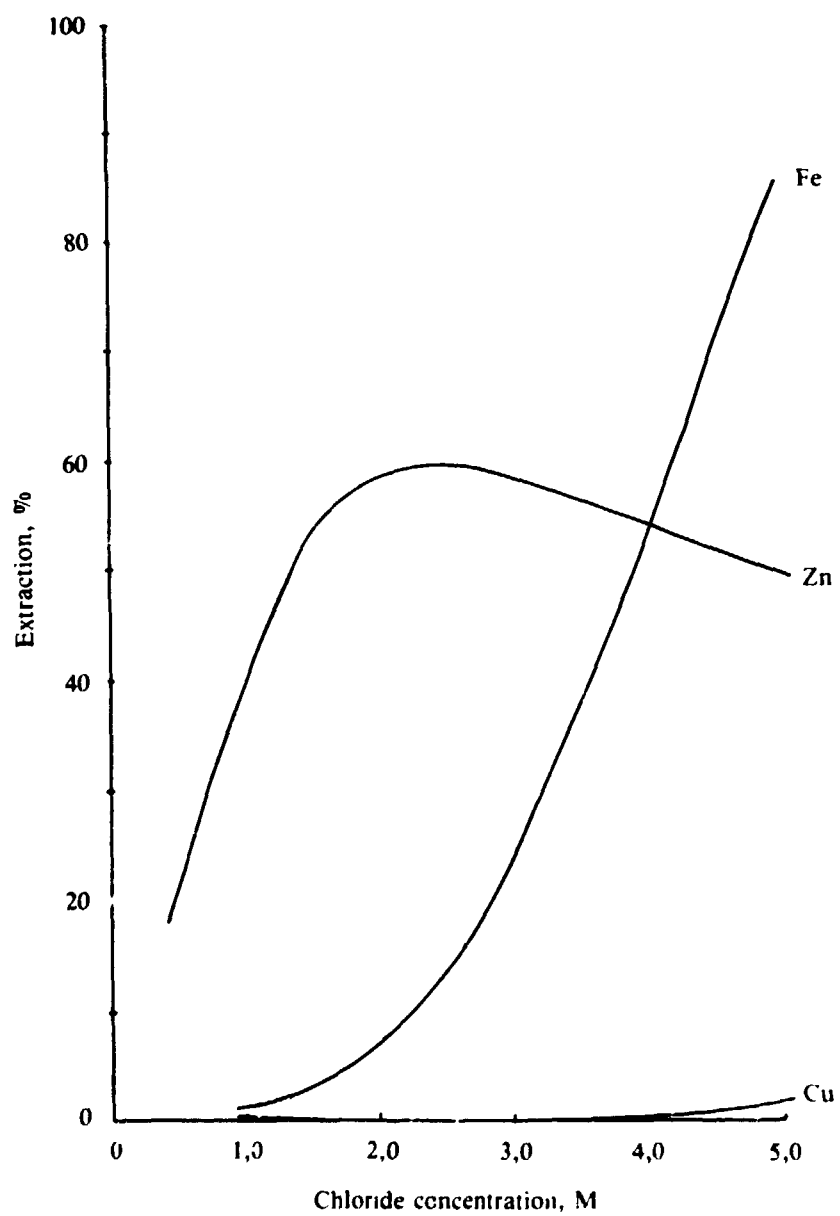


FIGURE 9. Extraction of zinc(II), iron(II), and copper(II) by 1,0M di-*n*-butyl *n*-octylphosphonate

EXTRACTION OF ZINC, IRON, AND INDIUM

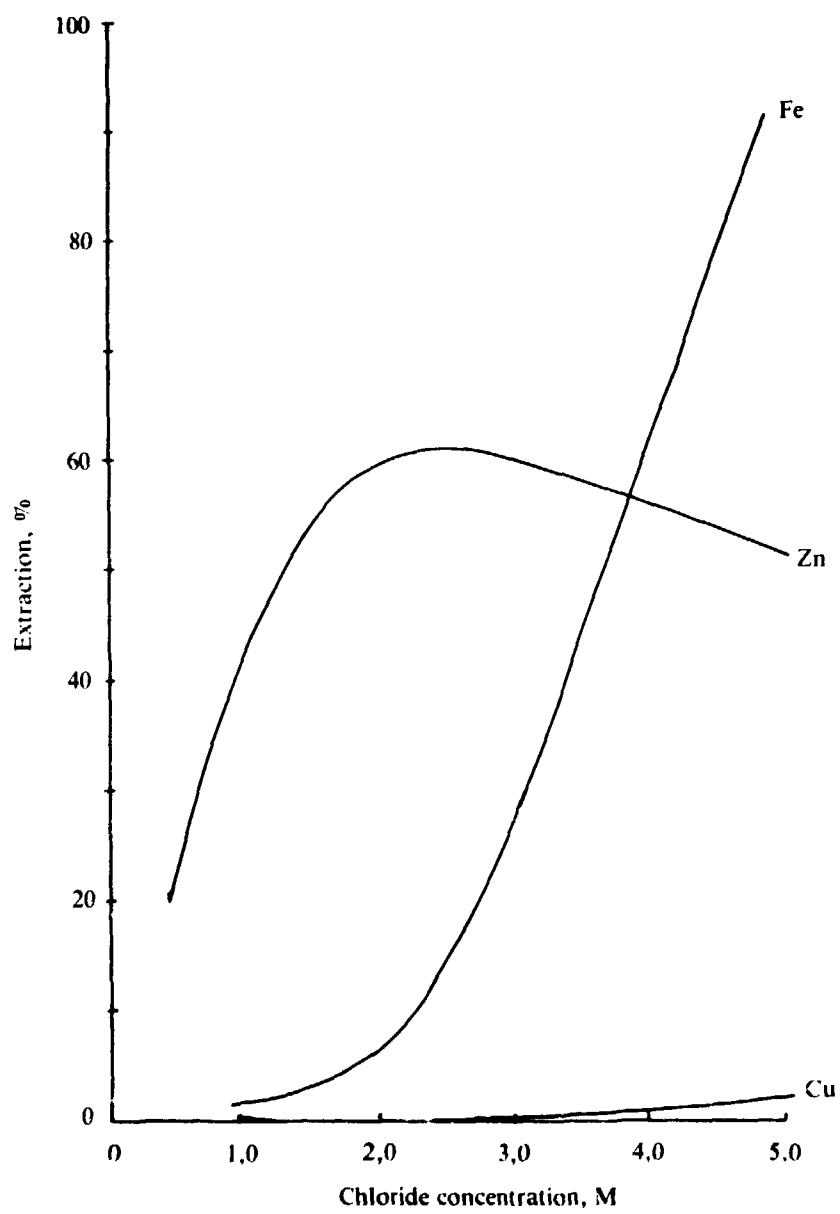


FIGURE 10. Extraction of zinc(II), iron(III), and copper(II) by 1.0M diethyl *n*-octylphosphonate

EXTRACTION OF ZINC, IRON, AND INDIUM

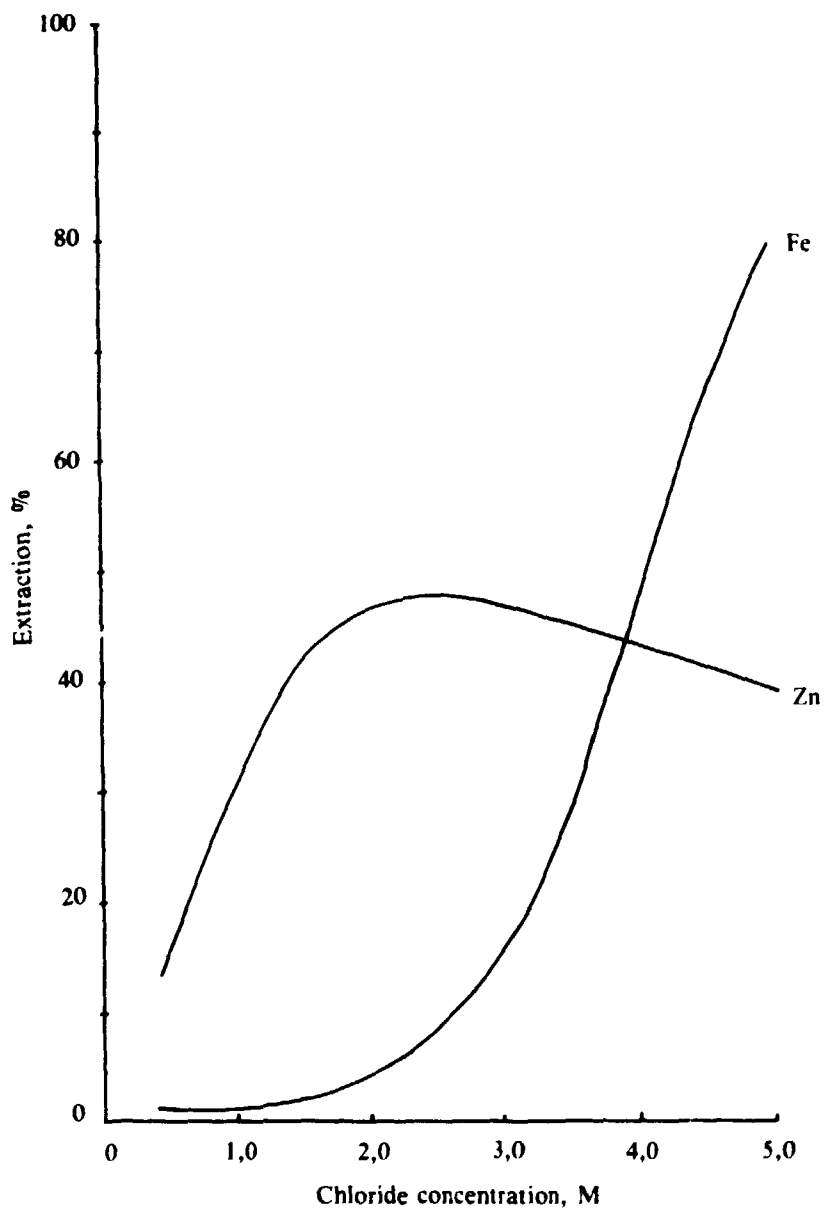


FIGURE 11. Extraction of zinc(II) and iron(III) by 1.0M diethyl 2-ethylhexylphosphonate

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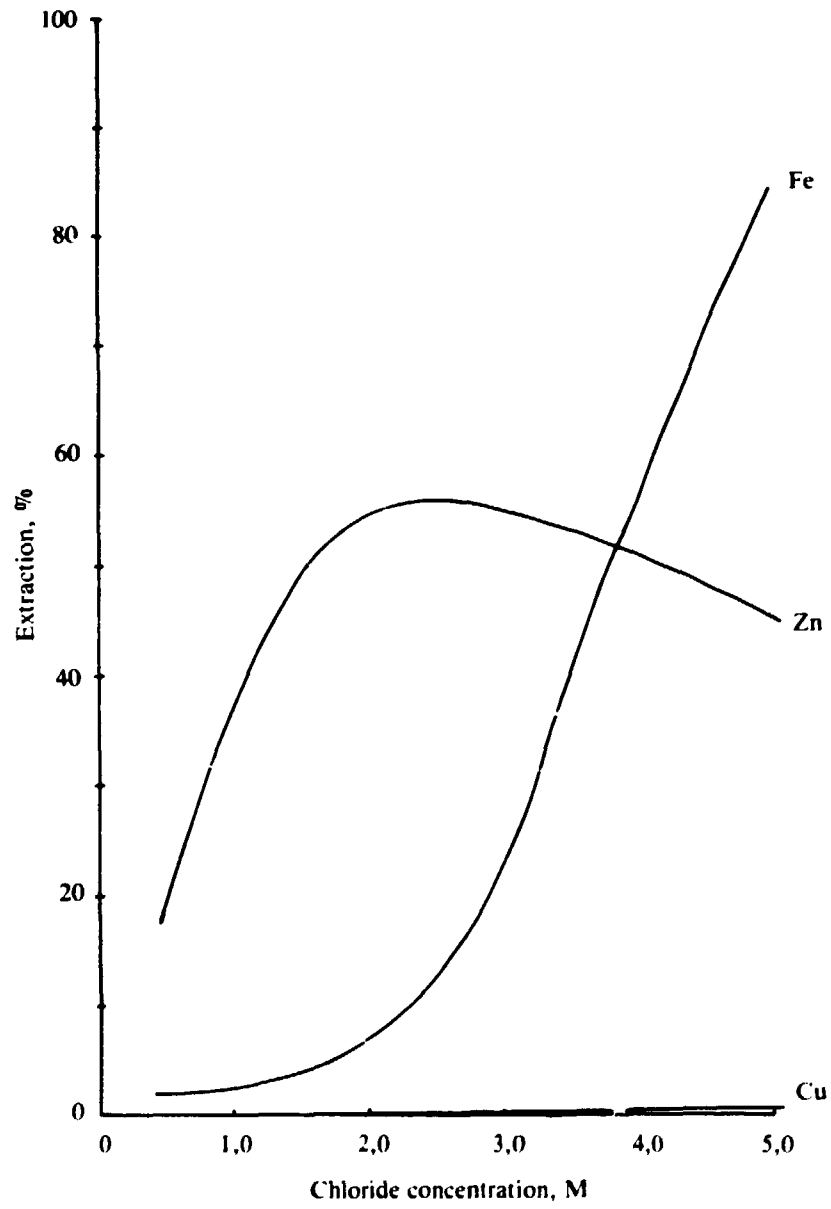


FIGURE 12. Extraction of zinc(II), iron(III), and copper(II) by 1.0 M di-*n*-butyl cyclohexylphosphonate

EXTRACTION OF ZINC, IRON, AND INDIUM

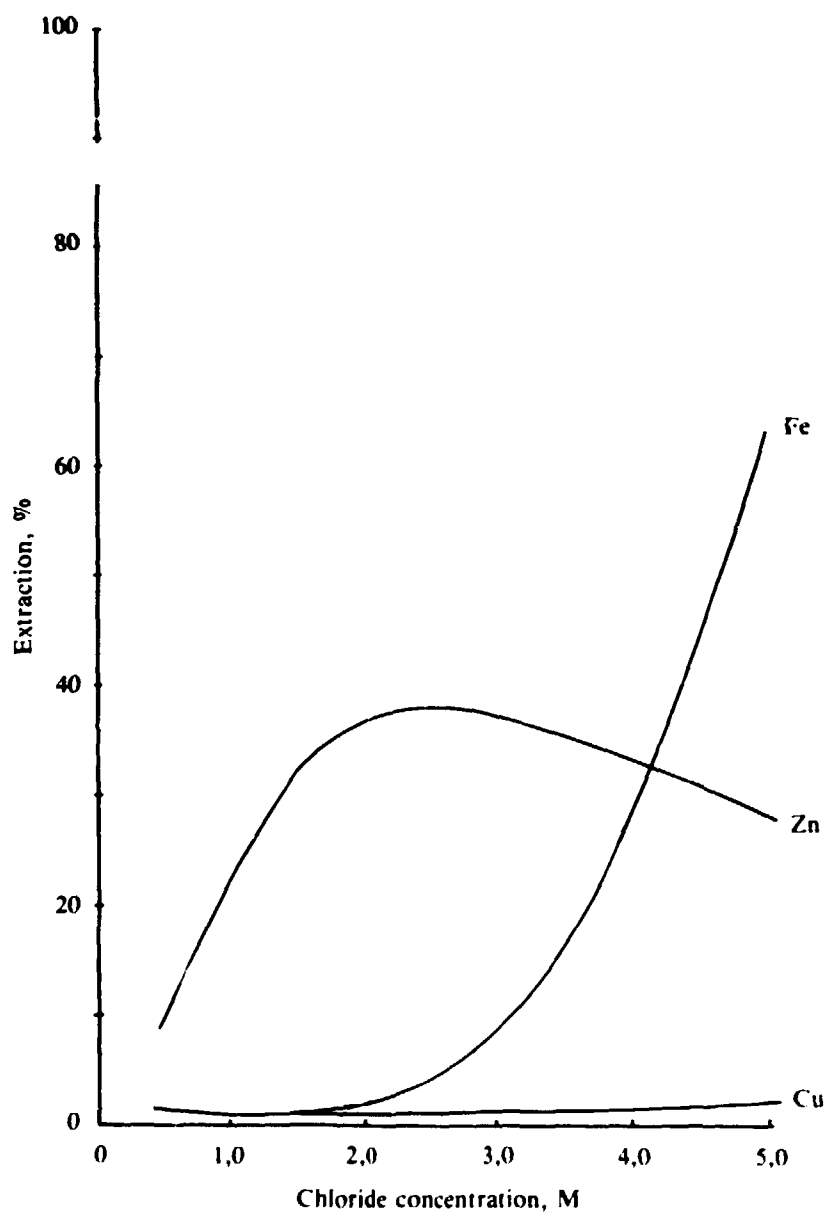


FIGURE 13. Extraction of zinc(II), iron(III), and copper(II) by 1,0M di-*n*-butyl benzylphosphonate



EXTRACTION OF ZINC, IRON, AND INDIUM

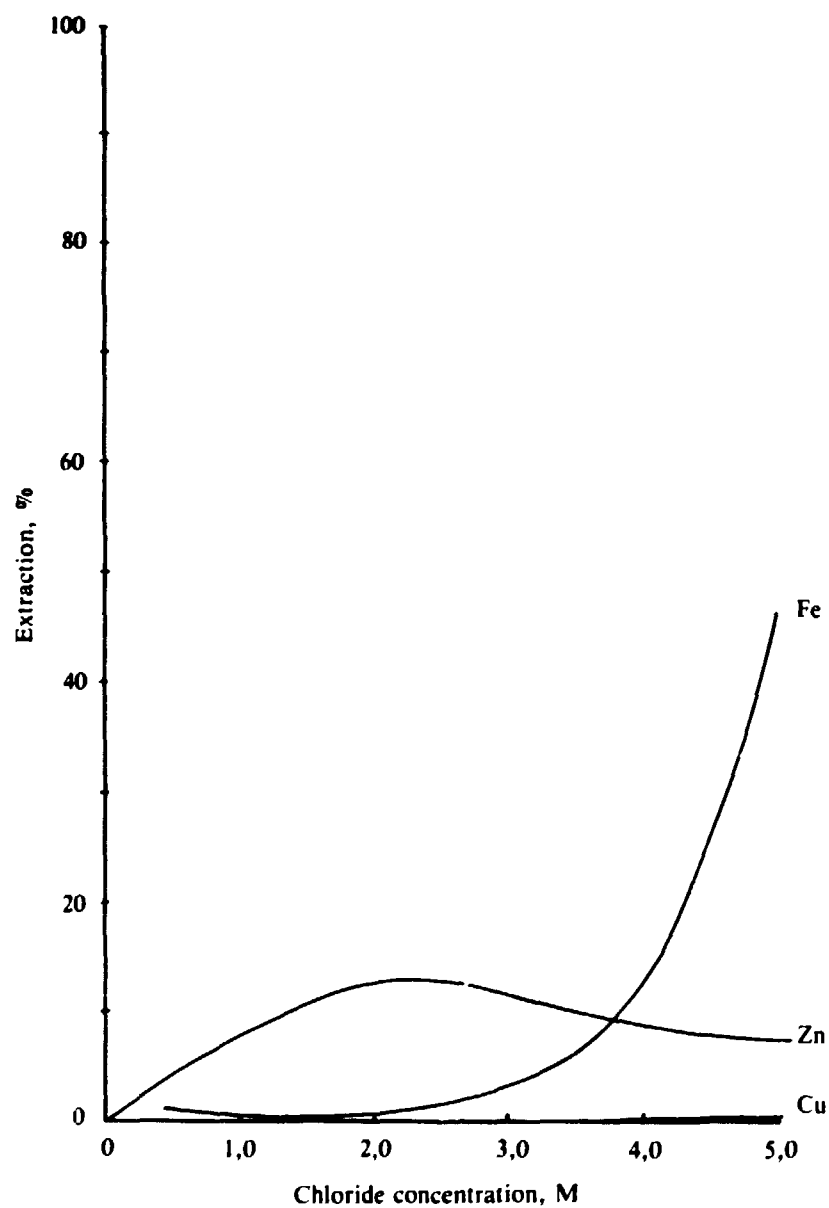


FIGURE 14. Extraction of zinc(II), iron(III), and copper(II) by 1.0M di-*n*-butyl phenylphosphonate

EXTRACTION OF ZINC, IRON, AND INDIUM

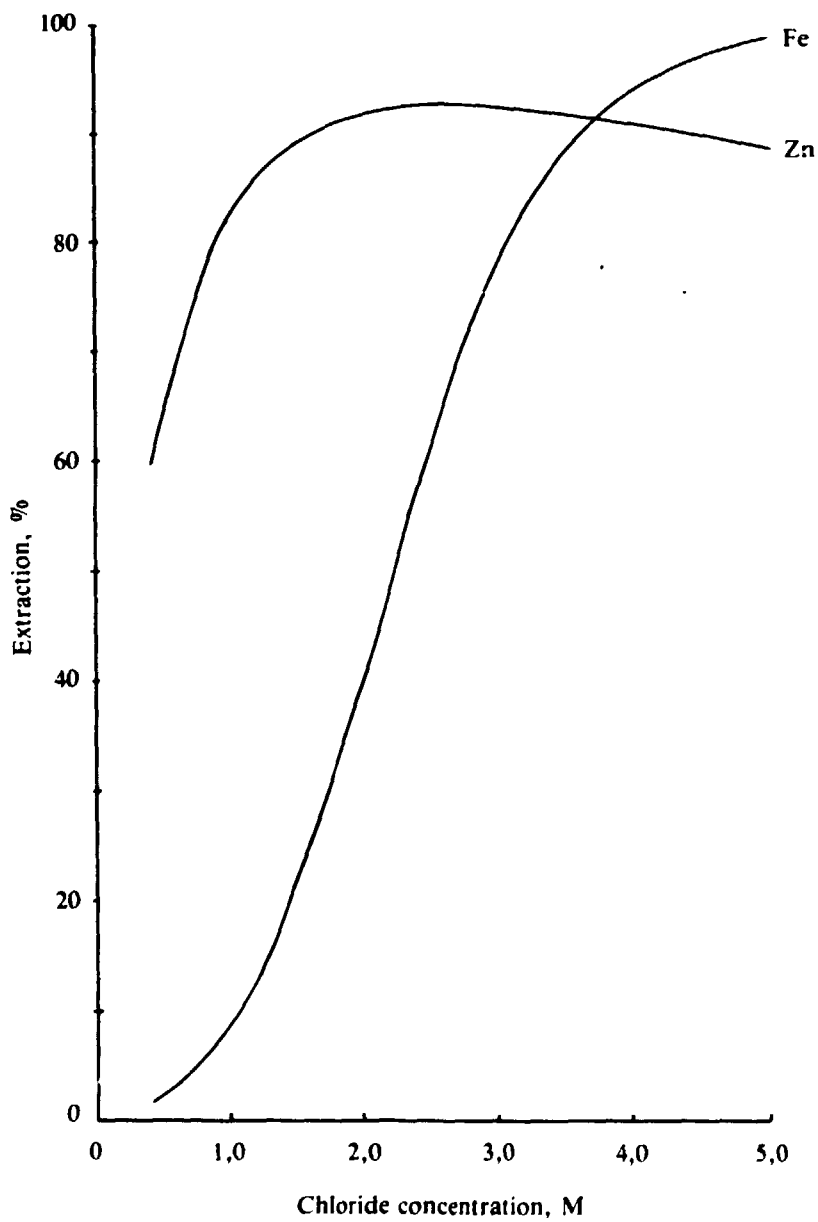


FIGURE 15. Extraction of zinc(II) and iron(III) by 0,5 M ethyl di-*n*-octylphosphinate

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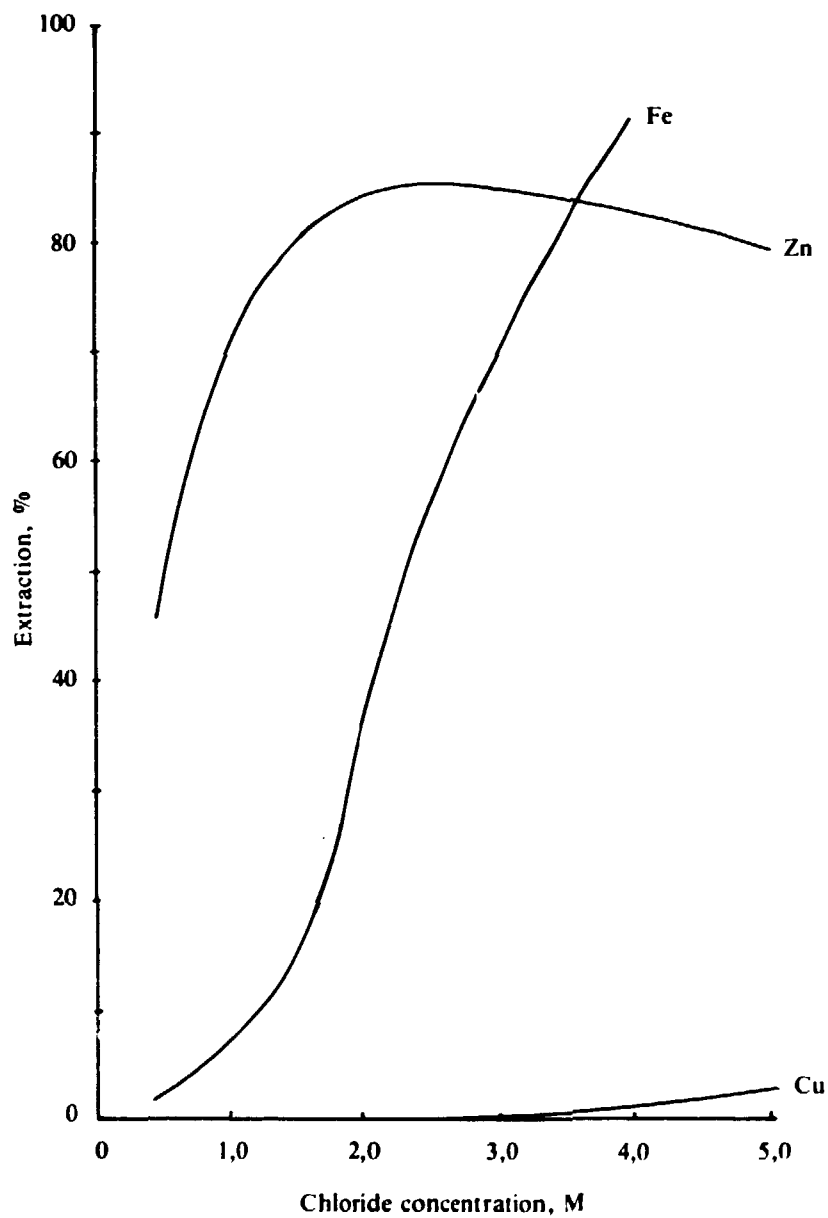


FIGURE 16. Extraction of zinc(II), iron(III), and copper(II) by 0,5M *n*-butyl dicyclohexylphosphinate

EXTRACTION OF ZINC, IRON, AND INDIUM

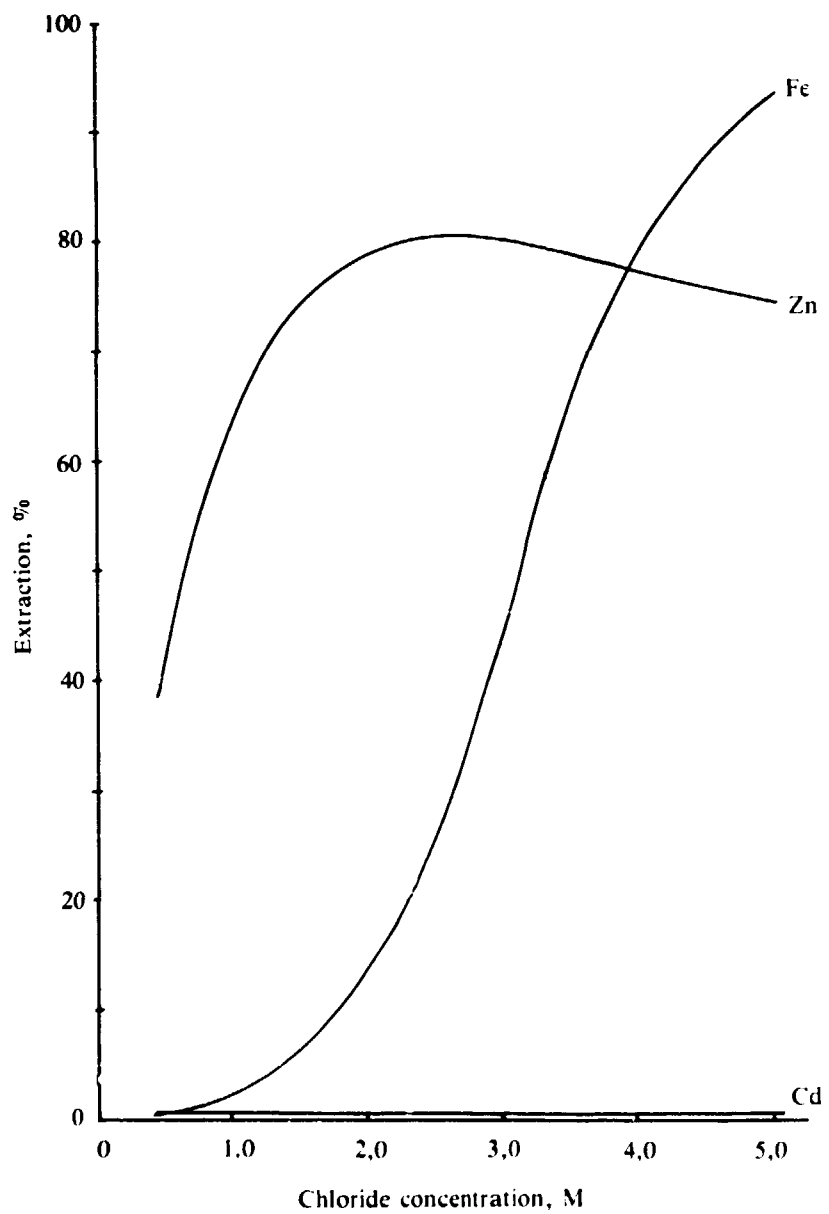


FIGURE 17. Extraction of zinc(II), iron(III), and cadmium(II) by 0.5M *iso*-butyl di-*iso*-butylphosphinate

EXTRACTION OF ZINC, IRON, AND INDIUM

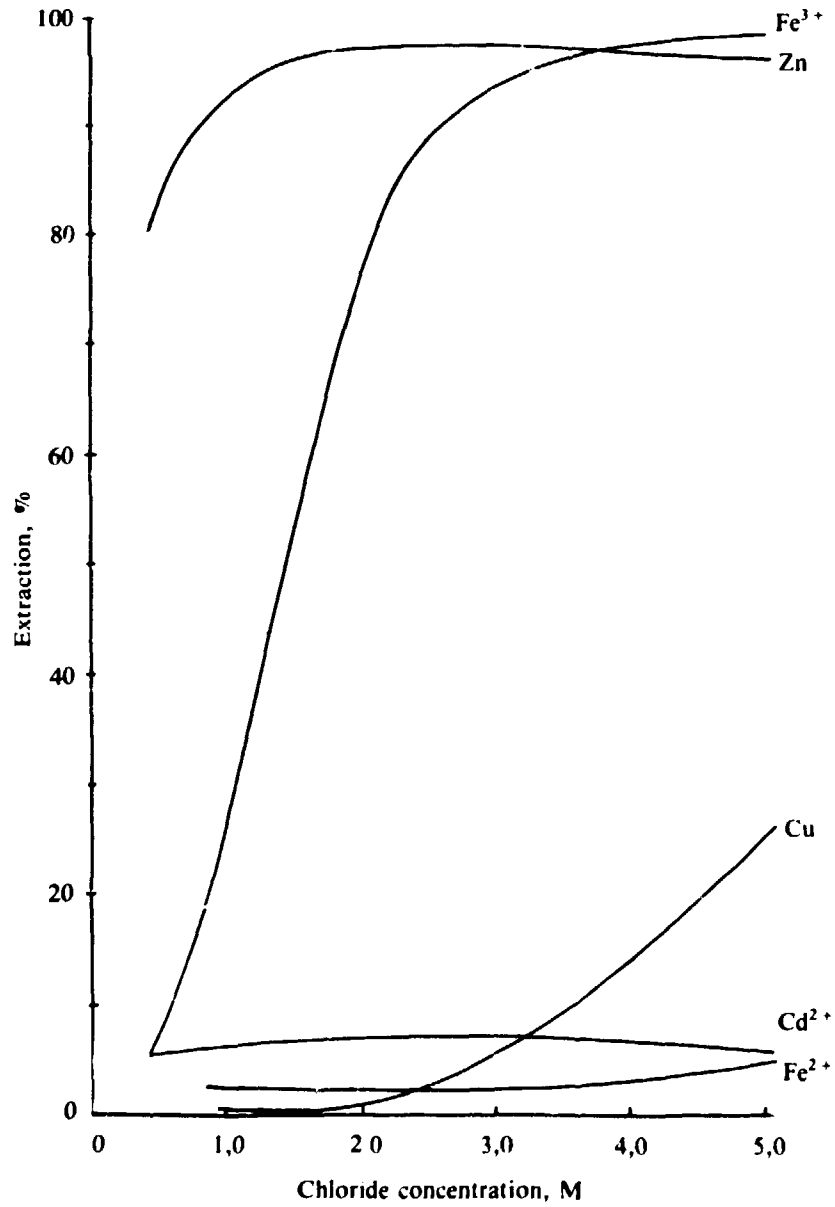


FIGURE 18. Extraction of zinc(II), iron(III), copper(II), cadmium(II), and iron(II) by 0.1M tri-*n*-butylphosphine oxide

EXTRACTION OF ZINC, IRON, AND INDIUM

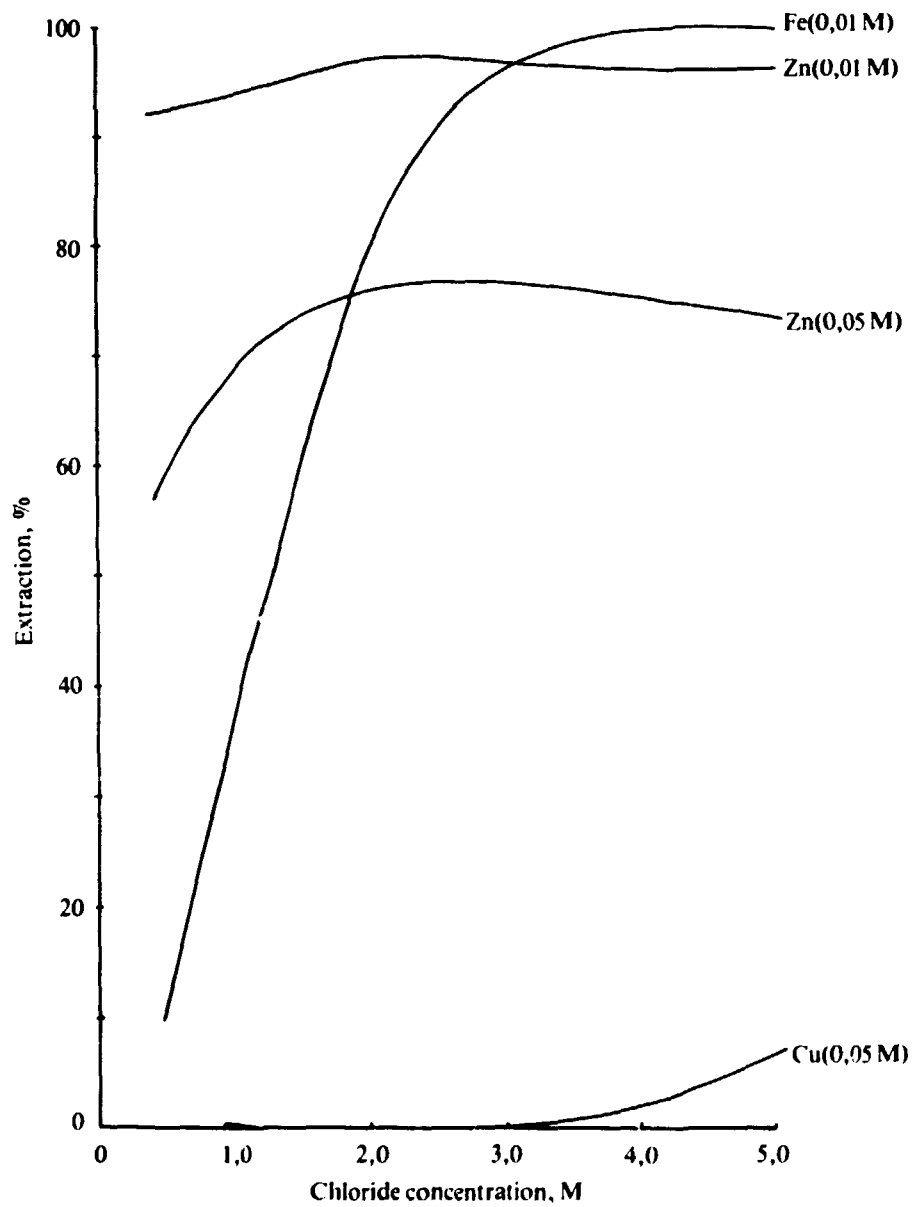


FIGURE 19. Extraction of zinc(II), iron(III), and copper(II) by 0,1 M tricyclohexylphosphine oxide

EXTRACTION OF ZINC, IRON, AND INDIUM

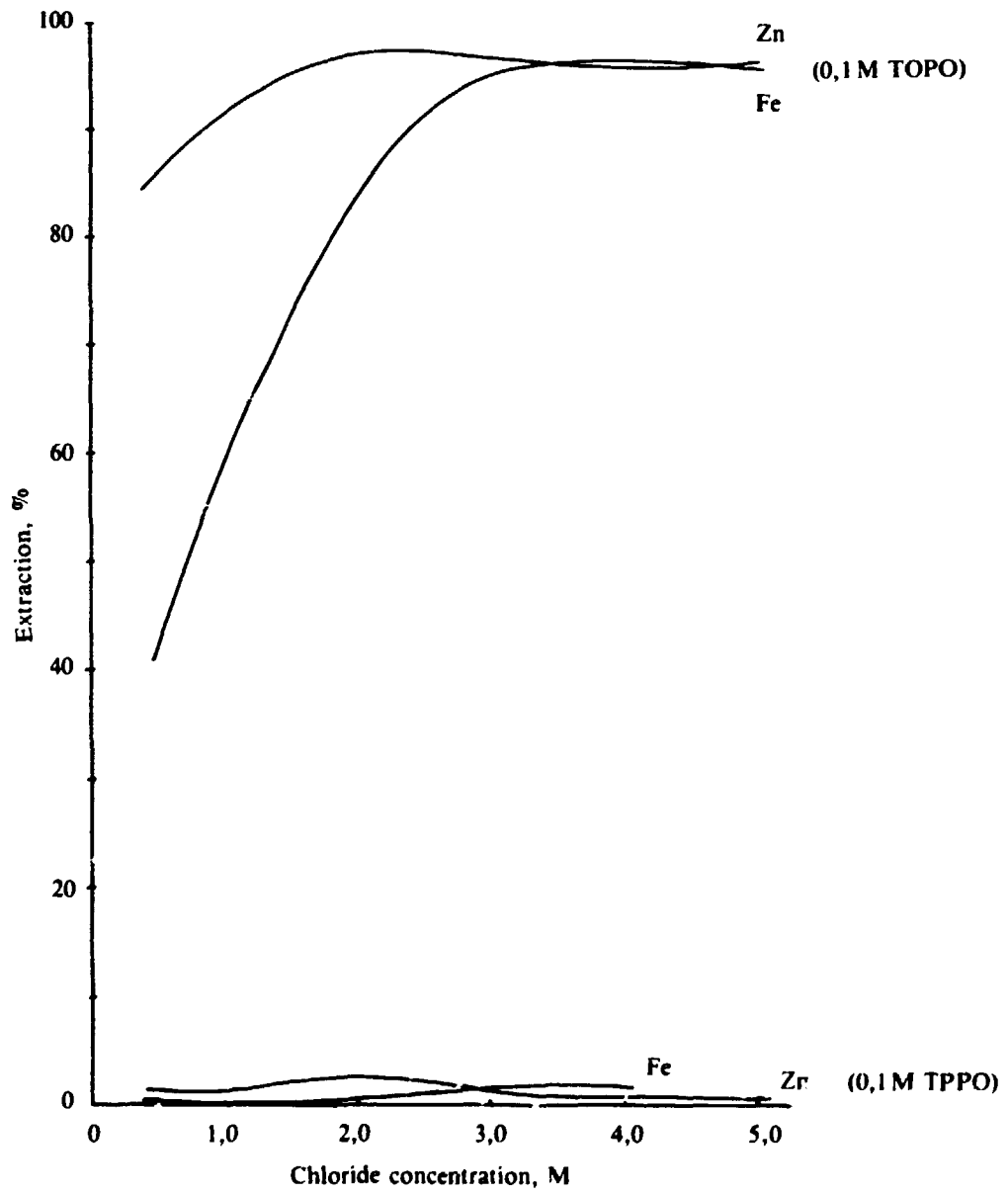


FIGURE 20. Extraction of zinc(II) and iron(II) by 0,1 M triphenylphosphine oxide (TPPO) and by 0,1 M tri-*n*-octylphosphine oxide (TOPO) (commercial)

EXTRACTION OF ZINC, IRON, AND INDIUM

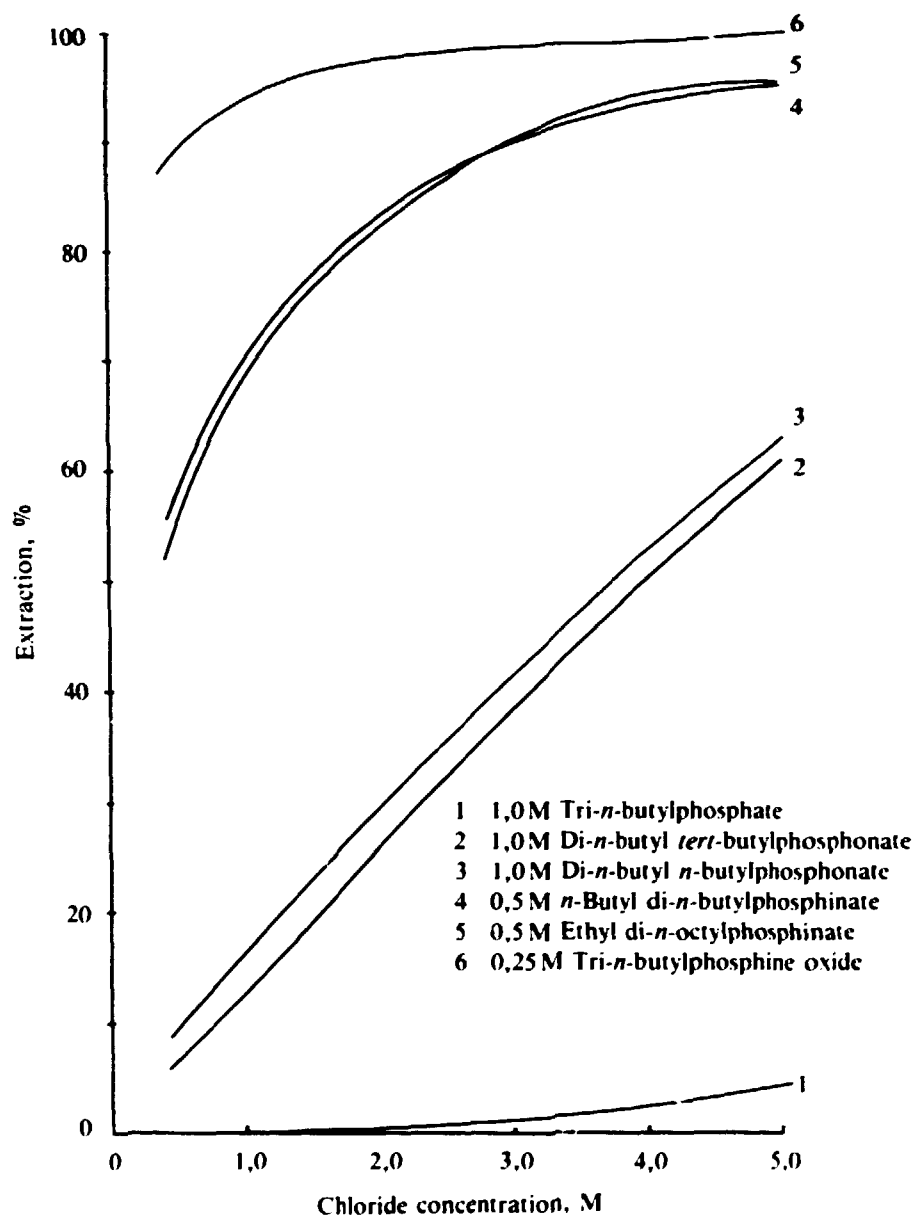


FIGURE 21. Extraction of indium(III) by neutral organophosphorus compounds



EXTRACTION OF ZINC, IRON, AND INDIUM

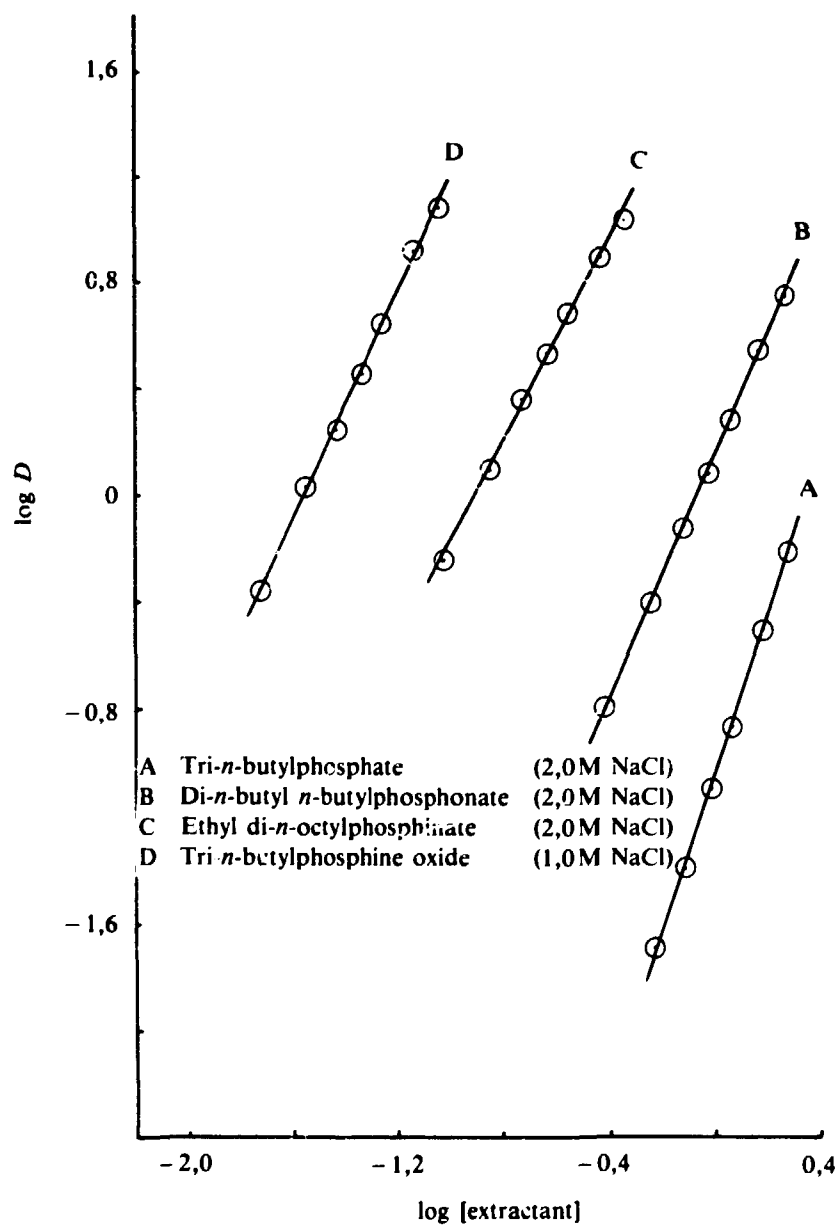


FIGURE 22. Extraction of zinc(II) by neutral organophosphorus compounds: dependence on extractant concentration

EXTRACTION OF ZINC, IRON, AND INDIUM

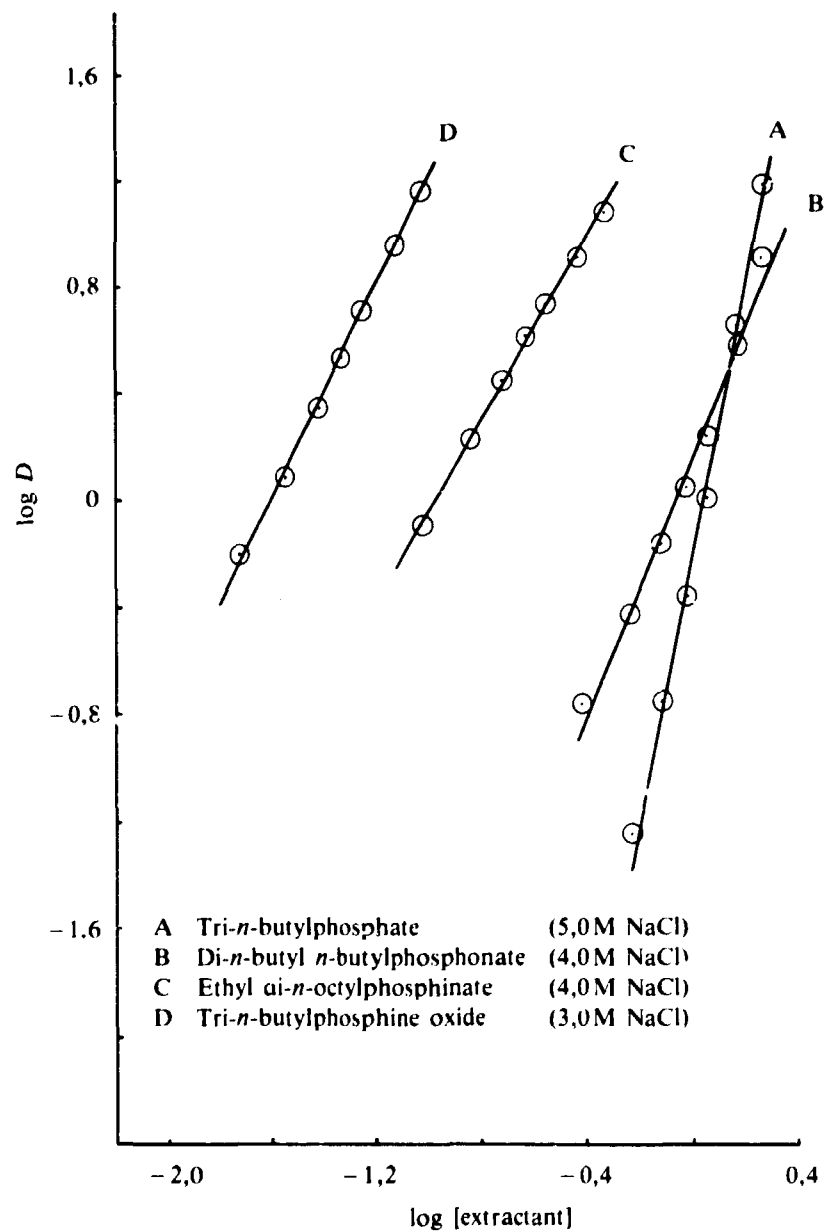


FIGURE 23. Extraction of iron(III) by neutral organophosphorus compounds: dependence on extractant concentration

EXTRACTION OF ZINC, IRON, AND INDIUM

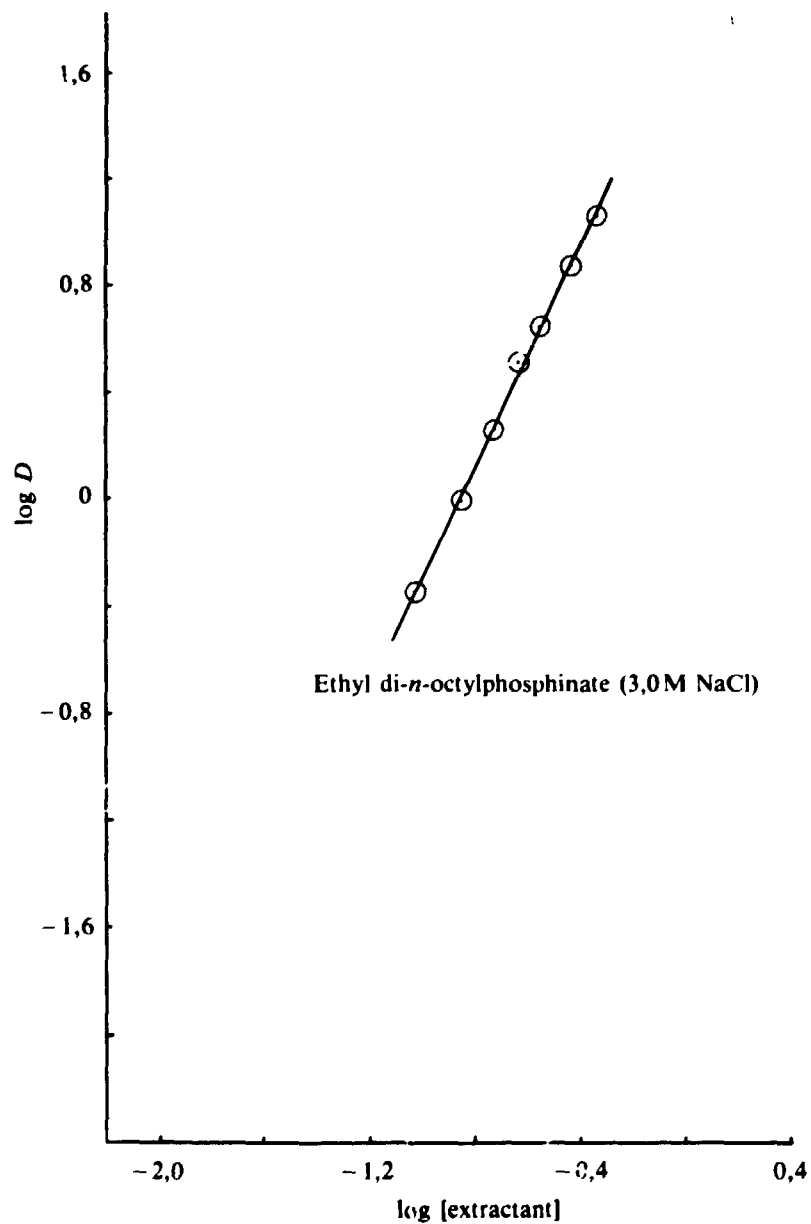


FIGURE 24. Extraction of indium(III) by neutral organophosphorus compounds: dependence on extractant concentration