Translated from *Uspekhi Khimii* **58** 1500–1527 (1989) U.D.C. 541.49:542.61:54.412.2

Extraction with thio and dithio phosphorus acids

I P Alimarin, T V Rodionova, V M Ivanov
Lomonosov Moscow State University

ABSTRACT. The main physicochemical characteristics of thio and dithio phosphorus acids—acid and redox properties, stability in solution, tautomerism, association and solubility in nonaqueous media, distribution in water–organic solvent systems—are reviewed. The effect of the structure of the reagents on their properties is analysed. The optimum conditions and chemical nature of extraction, the effect of substituents and diluents on the extract of metal dialkyldithiophosphates is discussed. Examples are given of the effective use of thio and dithio phosphorus acids for the separation of elements and the isolation of Cu, Hg(II), Tl(I), Sn(II), As(III), and Bi from other elements. The potential application of the extraction of elements with thio and dithio phosphorus acids is examined.

The bibliography includes 157 references.

Contents

I. Introduction 863
II. Properties of thio and dithio phosphorus acids 864
III. Extraction with thio and dithio phosphorus acids 866
IV. The use of dithio phosphorus acids for the separation of elements 874

I. Introduction

There is no standard nomenclature for dithio phosphorus acids. In the English literature dithio phosphorus acids are more frequently called dialkyldithiophosphoric acids or dialkyl dithiophosphates. The term "dialkyl dithiophosphates" emphasises that they are classed as partial esters of dithiophosphoric acid. Correspondingly for thio acids, the terms dialkylthiophosphoric acids and dialkyl thiophosphates are more widely used. In the German literature these reagents are called dithiophosphate esters. In the Russian literature the terms dialkyl- and diaryl-dithiophosphoric acids have become established, *O*,*O*-dialkyl- and *O*,*O*-diaryl-dithiophosphoric acids are to be found less often. In the Russian literature the term dialkyldithiophosphates relates to complex compounds such as nickel diethyldithiophosphate, etc. In this review we have used the terms dialkyl- and diaryl-dithiophosphoric acids and dialkyl- and diaryl-thiophosphoric acids respectively. Complex compounds of elements with these reagents are to be known as dialkyldithiophosphates.

The ability of complex compounds of metals with organic thio and dithio phosphorus acids to be extracted into various solvents was established back in 1949,[1,2] and in 1965 a review on the extraction of these complexes was published.[3] A large amount of material on the extraction of thiophosphates and dithiophosphates has been collected up to the present time and it requires classification. The range of extractants has been extended, the mechanism of extraction has been studied, and schemes for the separation of elements have been developed. In particular, the optimum conditions for extracting many elements with diethyldithiophosphoric acid (DEDTPA),[3–9] di-n-butyldithiophosphoric acid (DBDTPA),[5,6] diphenyldithiophosphoric acid (DPDTPA),[10] and di-2-ethylhexyldithiophosphoric acid (D2EHDTPA)[5,7] have been found. For the extraction of heavy metals, salts of dialkyldithiophosphoric acids have also been used; these contain alkali metals,[9,11] zinc,[12] and nickel.[12,13] Metal dialkyldithiophosphates are more stable than the corresponding acids both in aqueous solution and in organic solvents, and they are also more selective, so their future use is promising.

In addition, the possible use of full esters of dialkyldithiophosphoric acids—*O*,*O*,*S*-trialkyl dithiophosphates,[14–17]—amides,[28,29] bis(dialkyldithiophosphoryl) disulphide,[30] and other derivatives as extractants has been examined.

The use of the extraction of dithiophosphates in a large group of combined methods is of interest.

Almost all dialkyldithiophosphates do not absorb light in the visible or near UV region of the spectrum. This is the reason why extraction spectrophotometry has not been widely developed. Only the determinations carried out on different compounds of copper,[31,32] bismuth,[33,34] and palladium,[35,36] which are based on the ability of Cu(II), Bi(III), and Pd(II) dialkyldithiophosphates to absorb in the visible region of the spectrum, constitute an exception.

The extraction of dithiophosphates is used on a large scale in extraction polarography. By combining extraction with polarography it is possible to determine metals that are present together without initially separating them. Thus, for example, Zn, Co(II), and Ni dithiophosphates are co-extracted, but they can be determined separately by polarography in a benzene–ethanol mixture with 0.2 M $LiClO_4$ as the supporting electrolyte.[37] The polarographic properties of the diethyldithiophosphates of Zn, Cd, Sb(III), Bi(III), Cr(III), U(VI), Mn(II), Fe(II), Ni,[38] Cu(II)[39,40] Pb(II), ^{12}Fe(II)[41], and Pd[42] have been studied. Complexes of elements with full d^{10} shells give reversible polarographic waves in the solvent mixture benzene–ethanol.

The electrolytic oxidation of heteroligand complexes of Cu, Co(II), and Ni with diethyldithiophosphoric acid and bases—2,2′-dipyridyl, 1,10-phenanthroline, and aminopyridine[43,44]—has been studied. Extraction polarography has been widely applied; the main theoretical conclusions and practical recommendations for its use are covered in a review.[45]

The trends towards the use of dialkyldithiophosphoric acids in extraction atomic absorption analysis have been outlined. Elements are determined after their initial extractive or adsorptive concentration (on active carbon) as dialkyldithiophosphates.

Diethyldithiophosphoric acid has been used for extractive concentration of As, Sb, and Bi from industrial nickel electrolytes,[46] for concentration of Cd, Pb, and Bi from sea-water on active carbon,[47] and of Cu, Cd, In, Tl, and Bi in the analysis of metallic aluminium and gallium.[48] Dibutyldithiophosphoric acid is a good reagent for the combined extraction and adsorptive concentration from sea-water of Cu, Zn, Cd, Pb, and Bi, which are then determined by atomic absorption spectroscopy.[49,50]

The first studies on the use of dialkyldithiophosphates in high-performance liquid chromatography indicate that it is possible to use the most stable of them, for example, silver dialkyldithiophosphates,[51] for concentration and separation from associated ions.

The aim of the present review is to correlate the data on the extraction of dithio- and thio-dithiophosphates and to identify the most important aspects of using them in analytical chemistry and the ways of developing them further.

II. Properties of thio and dithio phosphorus acids

1. Acid properties

Thio and dithio phosphorus acids are quite strong acids.[11,52–57] Aqueous solutions of recrystallised dialkyldithiophosphates of alkali and alkaline earth metals have a pH of 7, and as salts of strong acids, they are virtually unhydrolysed.[54] An aqueous 0.109 M solution of DEDTPA has a pH of 1, $K_a = 2.4 \times 10^{-2}$. The potentiometric titration curve of an aqueous solution of DEDTPA against a solution of NaOH is characteristic of strong monobasic acids. The centre of rapid change in potential corresponds exactly to pH 7. Potentiometric titration curves of aqueous solutions of DEDTPA and H_2SO_4 with the same molarity against a solution of NaOH virtually coincide in form and magnitude of sudden change at the equivalence point.[11]

Substituents on the phosphorus atom have little effect on the pK_a values of dialkyldithiophosphoric acids.[56–58] It was found by pH titration of dithio acids in aqueous ethanol solutions containing 40 vol. % ethanol with a constant ionic strength of 0.3 (KNO_3) and at a temperature of 25 ± 0.1 °C that the pK_a values of dithio acids have virtually no dependence on the nature of the substituents, and they are equal to 2.00–2.25.[58] The lack of dependence of the acid strength on the structure of alkyl and alkoxyl groups has been confirmed by a determination of pK_a in aqueous isopropanol solutions containing 90 vol. % isopropanol (pK_a values vary from 2.75 to 2.85).[59] According to other results the pK_a values of acids that have different substituents do not remain constant. Thus, an increase in the length of carbon chain of the substituents leads to a reduction in the acid strength: for DEDTPA $pK_a = -1.10$, while for DBDTPA $pK_a = 0.22$.[62] In absolute ethanol and aqueous ethanol mixtures the solvation conditions are not the same, causing a variation in acid strength by a factor of almost $10^{2.5}$ [53,60] (Table 1). Moreover, the difference in acid strengths may partly be due to a change in function of the glass electrode in absolute ethanol. The pK_a values of some dithio acids have also been determined in other solvents—for aliphatic dithio phosphorus acids they range from 3.60 to 4.40 in benzene and from 2.30 to 2.90 in anisole.[63] Acids with cyclic substituents on the phosphorus atom in benzene ($pK_a = 1.90–3.23$) or anisole ($pK_a = 0.62$-1.65) are stronger than acids that contain aliphatic groups.[63,64]

The dissociation constants of some acids in the presence of different salts ($NaClO_4$, NaCl) were determined spectrophotometrically. It was recorded[65] that compounds containing $P(S)S^-$ have a maximum absorption at 225 nm. A study of the absorption spectra of potassium dibutyldithiophosphate in perchloric and hydrochloric acid in relation to the acidity of the aqueous solution showed that the intensity of light absorption at 225 nm decreases as the concentration of mineral acid increases; this is due to the equilibrium being shifted towards formation of the undissociated form (HA) of the acid. The undissociated form (HA) and the conjugated form—dibutyldithiophosphate ion (A^-)—have different molar absorption coefficients ($\varepsilon_{HA} = 3.9 \times 10^3$ and $\varepsilon_{A^-} = 4.15 \times 10^3$). The average molar absorption coefficients of DBDTPA at 225 nm in solutions of different acidity ($\mu = 1.0$; $NaClO_4$) are given below:[65]

c_{H^+}, M	1.03	0.72	0.31	0.185	0.103
$\bar{\varepsilon}$	4039	4062	4097	4116	4130 .

Table 1. Dissociation constants of dithio and thio phosphorus acids in aqueous ethanol solutions and in anhydrous ethanol.

Acid	pK_a values for ethanol content (vol.%)				Refs.
	7	40 (μ=0,3)	80	100	
$HS(S)P(OC_2H_5)_2$	1.64		2.65	2.84	[60]
		2.00			[55]
$HO(S)P(OC_2H_5)_2$		1.83			[55]
$HS(S)P(C_2H_5)_2$	1.74		2.62	5.06	[60]
		2.62			[55]
$HO(S)P(C_2H_5)_2$		3.60			[55]
$HS(S)P(OC_2H_5)(CH_3)$				3.46	[60]
$HS(S)P(n\text{-}C_3H_7)_2$		2.55			[61]
$HS(S)P(iso\text{-}C_3H_7)_2$	1.85		2.74	2.83	[60]
$HO(S)P(n\text{-}C_3H_7)_2$		2.61			[61]
$HS(S)P(C_2H_5)(n\text{-}OC_3H_7)$		2.82			[61]
$HS(S)P(C_2H_5)(n\text{-}OC_4H_9)$		2.89			[61]
$HS(S)P(OC_6H_5)_2$	1.84		2.75	2.41	[60]
$HS(S)P(C_6H_5)_2$	1.77		2.69	3.48	[60]
$HS(S)P(n\text{-}C_6H_4CH_3)_2$	1.84		2.74	3.93	[60]

In $HClO_4$ the dissociation constant of DBDTPA is equal to −0.24 and in HCl it is equal to −0.09 (in pK_a units) (spectrophotometric determination).[65] These values are not in agreement with those found by the distribution method: 0.28 and 0.22 in $HClO_4$ and HCl respectively.[65,66] For dimethyldithiophosphoric acid (DMDTPA), $pK_a = -0.33$.[67]

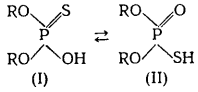
2. Stability in solution

Dialkyldithiophosphoric acids can decompose in aqueous solution with elimination of H_2S and alcohol, but they are more stable than diethyldithiocarbamic acid and xanthic acid.[11] It is assumed that thio phosphorus acids in aqueous solution are hydrolysed on the thiol group. The salts of these acids in aqueous solution are more stable. Thus, the concentration of the sodium salt of DEDTPA remains constant (120 μg ml^{-1}) for a month, while there is 9% decomposition of DEDTPA during this time. In 1 M HCl the decomposition half-life of DEDTPA is 250 h[11] while in 10 M HCl it is 4.8 h. For comparison, diethyldithiocarbamic acid has a decomposition half-life of 1–2 h. DEDTPA decomposes

more slowly in sulphuric acid than in hydrochloric acid of the same concentration.[11,68] Diphenyldithiophosphoric acid does not decompose in neutral or acidic solutions over a period of two months.[69] The decomposition of dialkyldithiophosphoric acids is a first-order reaction. Dialkyldithiophosphoric acids are stable in organic solvents.[11]

3. Tautomerism

A tautomeric conversion of the thione form (I) ⇄ thiol form (II) is characteristic of thio phosphoric acids:[53]



In aqueous solution the equilibrium is shifted towards the thiol form; in ethanol the thione form predominates.

4. Distribution in the system water–organic solvent

The behaviour of dithio acids in water–organic solvent systems has not been studied in sufficient detail and is only known for acids that are used as extractants. In particular, the extraction of diethyl–, diisopropyl-, di-n-butyl-, diisobutyl- and di-2-ethylhexyl-dithiophosphoric acids has been studied.[52,70] The acid distribution constants and the acidic dissociation constants have been determined in the system HCl–CCl_4 (Table 2). An increase in the length of the hydrocarbon group leads to some reduction in acidic properties, which is in agreement with other results;[62] this applies particularly to DEDTPA and D2EHDTPA (Table 2).

Table 2. Distribution constants and dissociation constants (in pK_a units) of some dialkyldithiophosphoric acids when μ = 1 at 25 °C.[52,70]

Alkyl group	Solvent	$pH_{1/2}$*	$\lg K_D$	pK_a**
Ethyl-	Carbon tetrachloride	0.35	0.45	−0.10
Isopropyl-	"	1.89	1.90	0.00
n-Butyl-	"	2.70	2.52	−0.22
	Methyl isobutyl ketone	2.77	2.54	−0.25
	n-Amyl acetate	2.40	2.23	−0.18
Isobutyl-	Carbon tetrachloride	2.74	2.63	−0.10
2-Ethylhexyl-	"	4.17	5.42	−1.25
	n-Heptane	—	5.43	—
	Benzene	—	5.39	—

*$pH_{1/2} = pK_a + \log K_D$, where K_D is the distribution constant of dialkyldithiophosphoric acid (organic phase saturated with the aqueous phase and aqueous phase saturated with the organic phase); **K_a is acid dissociation constant in water saturated with the organic solvent.

The extraction of DBDTPA into CCl_4 decreases at an acid concentration of 6 M regardless of the nature of the mineral acid (HCl, HBr, H_2SO_4, $HClO_4$, HNO_3).[52] The effect of ionic strength on the distribution of dithio acids is complex in nature. For example, in the extraction of DBDTPA from solutions with a constant HCl content, the addition of NaCl initially leads to a reduction and then to a marked increase in distribution coefficient of the reagent.[52] Dithio acids are not extracted from weakly alkaline and neutral solutions; this is due to the formation of dithiophosphate anions. The extraction of DPDTPA from solutions of HCl, HNO_3, and H_2SO_4 has been studied. It is at a maximum when 2–7 M solutions are used. However, the distribution constants and dissociation constants have not been determined.[10] These values are generally difficult to determine separately for dialkyldithiophosphoric acids, therefore the ratio K_D/K_a, that is, the two-phase stability constant, is frequently determined (Tables 3 and 4).

Table 3. Logarithms of two-phase stability constants $\log(K_{D,HA}/K_{a,HA})$ of dithio phosphorus acids $(RO)_2P(S)SH$ in the system water–nonpolar organic solvent[71,72]

R	$\lg(K_{D,HA}/K_{a,HA})$ in		
	heptane	CCl_4	toluene
C_3H_7-	—	1.71	1.88
iso-C_3H_7-	—	1.99	2.12
C_4H_9-	2.10	2.98	3.12
iso-C_4H_9-	2.00	2.93	3.01
sec-C_4H_9-	2.48	3.36	3.44
C_5H_{11}-	3.36	4.23	4.38
iso-C_5H_{11}-	3.10	4.02	4.11
sec-C_5H_{11}-	3.80	4.64	4.71

Table 4. Logarithms of two-phase stability constants $\log(K_{D,HA}/K_{a,HA})$ of DBDTPA and MHDTPA in the system 1 M $HClO_4$–organic solvent.[72]

Solvent	$\lg(K_{D,HA}/K_{a,HA})$	
	DBDTPA	MHDTPA
Toluene	3.12	3.05
Carbon tetrachloride	2.98	2.89
	3.05*	2.88*
Cyclohexane	2.40	—
Heptane	2.10	1.97
Dodecane	1.94	—

*$\log(K_{D,HA}/K_{a,HA})$ values determined in the system CCl_4–1 M NaCl.

5. Polymerisation and solubility in nonaqueous media

Dialkyldithiophosphoric acids, in contrast to phosphoric acids, have no tendency to polymerise in nonaqueous media.[73] However, the association of dithio and thio phosphorus acids in nonaqueous solvents has not been studied in sufficient detail. It is known that DBDTPA does not form dimers or polymers in CCl_4, methyl isobutyl ketone, and amyl acetate.[52] It was also established by cryoscopy that there were no dimers or more complex associated forms of DEDTPA in benzene.[74] D2EHDTPA also does not polymerise in nonaqueous media.[74] An analysis of the IR spectra of DMDTPA and DEDTPA showed that in dilute solutions in CCl_4 these acids were present to a considerable extent as

monomers.[75]

On the basis of the results of a two-phase titration of DBDTPA and methylheptyldithiophosphoric acid (MHDTPA) in cyclohexane and dodecane, a solubility parameter was calculated, which can be applied to all acids with unbranched groups when the number of carbon atoms does not exceed eight.[76] Compounds with a P(S)SH group are characterised by a lower intermolecular interaction energy than the corresponding oxygen-containing compounds. Thus, dithio phosphorus acids have a lower tendency to dimerise through formation of intermolecular hydrogen bonds than, for example, dibutylphosphoric acid.[73] However, the high polarisability of the sulphur atoms assists the interaction of dithio acids with a polar solvent. Therefore, it may be assumed that it is possible to determine solubility parameters more accurately in a nonpolar solvent than in a polar one which is subject to the inductive effect.[76]

6. Redox properties

Dialkyldithiophosphoric acids exhibit reducing properties and are readily oxidised with mild oxidising agents such as iodine to form bis(dialkyldithiophosphoryl) disulphides $[(RO)_2P(S)S]_2$, which are solid, low-melting compounds that are slightly soluble in water.[77] For example, the solubility of bis(dimethyldithiophosphoryl) disulphide in water at 25 °C is 4×10^{-5} M.[78] When dithio acids are treated with chlorine, the following reaction occurs[79]

$$2\,(RO)_2P\begin{matrix}\diagup S\\ \diagdown SH\end{matrix} + 3\,Cl_2 \rightarrow 2\,(RO)_2P\begin{matrix}\diagup S\\ \diagdown Cl\end{matrix} + S_2Cl_2 + 2\,HCl.$$

Anions of dialkyldithiophosphoric acids are oxidised on dropping mercury and platinum electrodes. The half-wave potential for diethyldithiophosphate ion (10^{-3} M) is -0.062 V on a dropping mercury electrode (relative to a saturated calomel electrode) and $+0.696$ V on a rotating platinum microelectrode.[80]

Dialkyldithiophosphate ions and their oxidation products form reversible redox systems for which the Nernst equation is valid.[78] Their reduction takes place in accordance with the following equation:

$$(RO)_2P(S)S\text{—}S(S)P(OR)_2 + 2e \rightleftarrows 2\,(RO)_2P(S)S^-.$$

The potential of a system containing dialkyldithiophosphate ions and their insoluble oxidation products is given by the following equation:

$$E = E_0 - 0.058 \lg a_{(RO)_2P(S)S^-}.$$

As bis(dialkyldithiophosphoryl) disulphides are only slightly soluble in water, their saturated solution can be readily obtained by the addition of small quantities of iodine or previously synthesised bis(dialkyldithiophosphoryl) disulphide to a solution of dithiophosphate ions. In practice there is no need to introduce the oxidation product of dialkyldithiophosphate since the platinum electrode maintains a constant potential even in freshly prepared solutions of dialkyldithiophosphates; this is probably due to the presence of traces of reagent oxidation products in them. The measurement of redox potentials by a balancing method in the circuit

$$Pt\,|\,KS(S)P(OR)_2\ (m)\ |\,[(RO)_2P(S)S]_2\ (s),\ 0.1M\ KCl\,\|\,0.1\,M\ KCl,\ Hg_2Cl_2\,|\,Hg$$

gave the following results:[78]

R	E_0, V	R	E_0, V
CH_3	+0.315	C_6H_{13}	−0.015
C_2H_5	+0.255	iso-C_3H_7	+0.196
C_3H_7	+0.187	iso-C_4H_9	+0.158
C_4H_9	+0.122	iso-C_5H_{11}	+0.086
C_5H_{11}	+0.050		

As the length of the carbon chain of the RO group increases, the redox potential of the acid decreases. Dithio acids with branched substituents and also with a long unbranched chain are oxidised with somewhat greater difficulty than dithiophosphates with a small unbranched carbon chain.

The redox potentials found from potentiometric titration of aqueous ethanol solutions of dithiophosphinic acids against a 0.1 M solution of I_2 in 40% ethanol at pH 6.5 (phosphate buffer solution) have been determined.[61]

III. Extraction with thio and dithio phosphorus acids

1. Reagents used and optimum extraction conditions

The use of DMDTPA as an extractant has been studied less than the others. It is the most soluble in water and passes into the organic phase less effectively than the other acids. Moreover, DMDTPA complexes with metal ions are the least stable and are fairly readily soluble. This is likely to account for the limited use of DMDTPA in extraction chemistry.

A study of the extraction of nickel dimethyldithiophosphate $Ni[S_2P(OCH_3)_2]_2$ with toluene from a 1 M solution of a mixture of $Na[S_2P(OCH_3)_2]$ and $NaClO_4$ showed that the distribution coefficients of the complexes were low and varied from -2 to $+1$ (in $\log K_D$ units).[67] In the system water—toluene the equilibrium stops after 30 min. In the opinion of Wingefors[67] the extraction of nickel dimethyldithiophosphate from weakly acidic solutions is effected because of the large value of the distribution constant of the complex ($\log K_{D,2} > 2$). The complex is not associated in the organic phase even when there is a large concentration of nickel in the initial aqueous solution.

DMDTPA forms a complex with palladium that is insoluble in water but soluble in CCl_4, diethyl ether, and chloroform[35] and which is suitable for the extraction and photometric determination of palladium. The same acid can be used to extract uranyl ions from 0.005—0.01 M $HClO_4$ into benzene, but the distribution coefficients of the complex are very low.[81]

The extraction of diethyldithiophosphates of copper,[13,82,83] silver and gold,[9,82,84,85] bismuth,[86] iron(III),[83] noble metals,[9] ruthenium and osmium,[9,87] and palladium[42,88] has been extensively studied. The extraction conditions using DEDTPA from 0.1—10 M solutions of HCl and 0.05—7.5 M H_2SO_4 into CCl_4 for many elements have been described.[9]

Elements of Groups I—III as well as Zn, V(III), V(V), Nb, Ta, Sn(II), Cr(III), and rare earth elements do not form sparingly soluble compounds with DEDTPA and are not extracted.

Copper(II) is quantitatively extracted from 0.1—5 M solutions of HCl or 0.05—6 M solutions of H_2SO_4,[9] as well as from weakly acidic and neutral solutions.[13] At pH 9 it remains almost completely in aqueous solution. This was used as a basis for the successive extraction of copper and silver with a solution of DEDTPA into CCl_4.[2] Copper diethyldithiophosphate was used for a photometric determination of copper.[83] Silver was completely extracted with DEDTPA from a 0.1—3 M solution of HCl into CCl_4.[9] In a more recent study[82] it was shown that it can also be extracted from less acid solutions up to pH 11. Depending on the ratio of the component concentrations, gold(III) forms different products with DEDTPA. Gold(I) is completely extracted from acid

and neutral media, so DEDTPA has been used in an extraction-atomic absorption determination of gold (and silver) in natural water.[85]

Alkaline earth elements and zinc do not form complexes that can be extracted with DEDTPA. Cadmium is incompletely extracted from 0.1 – 10 M solutions of HCl or 0.05 – 5 M solutions of H_2SO_4, but is completely extracted from media with pH 3.0 – 7.0, and in the presence of 2,2′-dipyridyl it is extracted at pH 6.5 – 8.5.[41] Mercury(II) is quantitatively extracted from 0.1 – 5 M solutions of HCl or 0.1 – 7.5 M H_2SO_4, while mercury(I) is reduced to the metal.[9] A more recent study[89] showed that mercury(II) is extracted from media containing 5 M HCl (or 8 M H_2SO_4) up to pH 7. In this case the complex exists in the organic phase in monomeric form.

Indium is not completely extracted with DEDTPA from a 0.1 M solution of HCl, and thallium(I) is only extracted to the extent of 5%. Thallium(I) is readily extracted from weakly acidic solutions,[9] and in the presence of 2,2′-dipyridyl it is extracted at pH 6.5 – 7.0.[45] Thallium(III) is reduced to thallium(I) by the reagent (sometimes the reduction takes place over several hours).[9]

Germanium(IV) is not extracted from 3 M solutions of HCl, while from solutions with a lower HCl concentration the extraction is not quantitative.[9] Tin(II) and tin(IV) are also incompletely extracted from 0.1 – 10 M HCl or 0.05 – 5 M H_2SO_4.[9] Lead(II) is extracted with DEDTPA from acid, neutral, and alkaline solutions.[9]

Arsenic(III) is quantitatively extracted with DEDTPA from weakly acidic and strongly acidic solutions while arsenic(V) is not extracted under these conditions. Antimony(III) is effectively extracted from 0.1 – 12 M solutions of HCl or 0.05 – 2.5 M H_2SO_4; antimony(V) in this case is first reduced and then extracted as the diethyldithiophosphate.[4,9] Bismuth diethyldithiophosphate is extracted over an acidity range from 5 M HCl (2.5 M H_2SO_4) to pH 2.5.[9,34,86]

Selenium(IV) and tellurium(IV) are extracted with DEDTPA from weakly acidic and strongly acidic solutions. Selenium(VI) is only extracted from strongly acidic solutions, probably being reduced initially to selenium(IV). Tellurium(VI) is only 60% extracted even from a 10 M solution of HCl.[9] Uranyl ions are extracted from 0.0005 – 0.01 M solutions of $HClO_4$ into benzene in the form of uranyl diethyldithiophosphate with very low distribution coefficients.[81]

Rhenium(VII) is extracted as its diethyldithiophosphate to the extent of 20% from a 0.1 M solution of HCl to which has been added a 15% solution of $TiCl_3$, whereas it is not extracted at all from 6 M HCl. From a mixture of potassium perrhenate – sodium diethyldithiophosphate — $SnCl_2$ containing 1 – 3 M HCl, rhenium is extracted with benzene, chloroform, diethyl ether, ethyl acetate, isoamyl acetate, and isobutanol.[9]

Iron(III) is quantitatively extracted at pH 2 – 3 while at lower pH values it is reduced to iron(II).[9] In order to prevent the reduction of iron(III) the extraction is carried out in the presence of H_2O_2. The distribution constant of iron(III) diethyldithiophosphate for passage of the latter into hexane is equal to 51.9.[83] At low concentrations cobalt(II) does not react with sodium diethyldithiophosphate in aqueous solution, but on extraction from solutions with a high cobalt concentration the extract changes to a green colour[4] which is characteristic of a complex of cobalt(III) with DEDTPA. Cobalt(II) diethyldithiophosphate in the extract is oxidised with atmospheric oxygen after several hours.[9] In the presence of 2,2′-dipyridyl, cobalt(II) is extracted with DEDTPA at pH 5.5 – 10.0.[45] Nickel(II) is incompletely extracted from 50% CH_3COOH with sodium diethyldithiophosphate.[4] The extraction becomes quantitative when the operation is repeated four times. In the presence of 2,2′-dipyridyl, Ni(II) is extracted at pH 0.5 – 2.0.[41]

Ruthenium(III) is extracted with carbon tetrachloride at room temperature in the presence of diethyldithiophosphate ions from a 0.1 – 10 M solution of HCl or a 0.05 – 7.5 M solution of H_2SO_4.[9] Osmium(IV) is not quantitatively extracted with DEDTPA from a 0.1 – 8 M solution of HCl or a 0.05 – 6 M solution of H_2SO_4 into carbon tetrachloride. Iridium(III) and rhodium(III) are not extracted from media containing HCl or H_2SO_4.[9] Iridium(IV) is reduced by the reagent to iridium(III), but iridium(III) diethyldithiophosphate precipitates out incompletely. The precipitate is extracted with chloroform and carbon tetrachloride.[4]

Platinum(II) is effectively extracted from acid solutions.[4] If platinum(IV) is reduced to platinum(II) in the presence of diethyldithiophosphate ions using $SnCl_2$, it is rapidly extracted from 1 – 10 M solutions of HCl into CCl_4 as a complex with the ratio $Pt:A^- = 1:2$.[90] Palladium is extracted from neutral and weakly alkaline solutions.[4,9] The reagent has been used to determine palladium in ore.[88]

Diethyldithiophosphates form the following series of extractability: As(III) > Bi > Pb > Zn > Ni > Co > Cd.[9,61,73] However, this series, which corresponds to the optimum extraction conditions, needs to be adjusted (this concerns, for instance, the positions of Cd and Zn) and requires a quantitative characterisation.

Diisopropyldithiophosphoric acid (DIPDTPA), like the other acids, forms coloured compounds with Cu(II), Bi, Pd(II), and Pt(II) ion.[35] The extraction of copper with zinc diisopropyldithiophosphate into CCl_4 is quantitative from 0.1 – 5 M HCl, 0.05 – 2.5 M H_2SO_4, 0.1 – 5 M $HClO_4$, 0.1 – 1.5 M H_3PO_4, or 0.1 – 2 M HNO_3.[91] The extraction of copper from less acid solutions has not been studied. Bismuth diisopropyldithiophosphate is also extracted from acid solutions. The extracts are characterised by a maximum absorption of light at 350 nm. It is possible to determine photometrically 5 – 70 μg of bismuth in 5 ml of chloroform.[92] Uranyl ions are extracted with DIPDTPA from 0.0005 – 0.01 M solutions of $HClO_4$ into benzene but the distribution coefficients are very low.[81]

Dibutyldithiophosphoric acid (DBDTPA) has been studied as an extractant fairly comprehensively.[5] Out of 42 elements studied, 22 have been satisfactorily extracted from media containing 0.03 – 9 M HCl or 0.1 – 18 M H_2SO_4. The extraction only requires a few minutes and is carried out in a single operation. The concentrations of metal can vary over a wide range from submicrogram to milligram quantities per ml of solution.[5] Ag and Bi(III) ions are quantitatively extracted with DBDTPA even from 1×10^{-7} M solutions of their salts. The maximum extractable quantity of metal depends on the initial concentration of DBDTPA in the organic phase, the ratio of volumes of the phases, and the solubility of the complex formed in the organic solvent.

According to the results of Handley and Dean,[5] Ag and Hg(II) are extracted with DBDTPA from an acid medium up to pH 10. Copper(II) and palladium are extracted from ammonia solutions with pH 8. The extraction of silver and palladium cannot solely be attributed to an exchange reaction with DBDTPA and its salts.[6,8] Evidently a coordination and ionic interaction is also occurring in this case. The passage of zinc dibutyldithiophosphate into CCl_4 and heptane from perchloric acid[93] and hydrochloric acid[94] has been characterised in considerable detail (Table 5). For comparison, in the extraction of a complex of cadmium with DBDTPA using carbon tetrachloride from a 1 M solution of HCl with an ionic

strength of 1, $\log K_{ex} = 5.3$; $\log \beta_2 = 9.7$; $\log K_D = 0.9$; $\log(K_{D,2}\beta_2) = 10.6$ [here, $\log(K_{D,2}\beta_2)$ is the two-phase stability constant].[95]

Table 5. The distribution of zinc dialkyldithiophosphate in different systems.

Alkyl	lg K_{ex}	lg β_2	lg K_D	lg $(K_{D,2}\beta_2)$
		CCl_4 – 1 M HCl (Ref.94)		
Ethyl-	—10			—9.3
Butyl-	1.22	3.81	2.77	6.57
Isobutyl-	1.29	4.00	2.70	5.77
sec-Butyl-	1.37		2.77	
2-Ethylhexyl-	1.40		2.86	
		CCl_4 – $HClO_4$ (Ref.93)		
Butyl-	1.67	2.27	5.37	6.05
		Heptane – $HClO_4$ (Ref.93)		
Butyl-	1.85	2.27	3.78	

Zinc dibutyldithiophosphate was used as an extractant for the extraction of mercury(II), which was then determined in the extract by polarography.[12] Nickel dibutyldithiophosphate is extracted into heptane with very high distribution coefficients ($\log D > 3$), but the extraction takes place slowly and re-extraction is not quantitative.[67] Uranyl ions can be extracted from perchloric acid solutions into benzene using DBDTPA.[81]

Dibutyldithiophosphate form the following series of extractability:[5,73]

$$\text{Pd(II)} > \text{Au(III)} > \text{Cu(I)} > \text{Hg(II)} > \text{Ag} > \text{Cu(II)} > \text{Sb(III)} > \\ > \text{Bi(III)} > \text{Pb} > \text{Cd} > \text{Ni} > \text{Zn}.$$

The use of zinc isobutyl-2-ethylhexyldithiophosphate in the form of a 50% solution in a mineral oil (industrial name DF-II) as an extractant for copper has been proposed. This compound is used as an oil additive.[96] The availability of the reagent, its high copper capacity, low viscosity, and good compatibility with kerosine have determined its use in hydrometallurgy.[96] In a single extraction the distribution coefficients of copper are higher by 3–5 orders than for associated elements.

The extraction metals with di-2-ethylhexyldithiophosphoric acid has been studied in the greatest detail. A considerable amount of attention has been given not only to the conditions but also the extraction mechanism, a determination of the extraction constants and distribution constants of the complexes, and the effect of diluents. The extraction of Cu(II),[97–101] Ag,[102] Au(III),[103] Ca,[104] In,[105,106] Tl(I),[107,109] As(III),[110,111] and Bi[112,113] has been studied.

Other dialkyldithiophosphoric acids with large alkyl groups—n-hexyl-, n-octyl-, dodecyl-, and isododecyl-dithiophosphoric acids, and other acids with unbranched C_9–C_{18} groups—have also been tested as extractants. These acids are virtually insoluble in water and in acid and alkali solutions. For example, the solubility of D2EHDTPA in water is 0.0088 g litre^{-1}, in 1 M H_2SO_4 it is 0.022 g litre^{-1}, and in 2 M NaOH 0.114 g litre^{-1}. Out of the acids listed it is best to use D2EHDTPA, since the extraction of metals with its solutions in organic solvents occurs with sufficient rapidity.[114] In contrast to acids synthesised from C_8–C_{18} alcohols, D2EHDTPA does not form stable emulsions. These extractants are not decomposed by solutions of 7–9 M HNO_3, H_2O_2 (in the presence of HCl or H_2SO_4), Br_2, Tl(III), and other oxidising agents.[114] In the absence of oxidising agents, solutions of D2EHDTPA are stable and their extractive capacity does not change with time.[114] The reagent D2EHDTPA forms such stable complexes with metal ions that even compounds of alkali and alkaline earth metals can be extracted. The extraction constants of ammonium and sodium ions into heptane ($\mu = 1$) are equal to -3.50 ± 0.06 and -3.70 ± 0.01 (in $\log K$ units) respectively.[115] The use of the polar solvent 2-ethylhexanol markedly improves the extraction of ammonium ions; in this case $\log K_{ex} = -1.55 \pm 0.10$. Systems with sodium ions separate into phases slowly (20–24 h) while with ammonium ions they separate after a few minutes. Sodium ions are evidently strongly hydrated in the organic phase. The solubility of D2EHDTPA in ammonia solutions is low. After mixing equal volumes of a 1 M solution of NH_3 and $(NH_4)_2CO_3$ with a 0.22 M solution of D2EHDTPA in heptane, 0.05 g litre^{-1} of D2EHDTPA and its anion is extracted into the aqueous phase.

Copper(II) is quantitatively extracted with solutions of D2EHDTPA in saturated hydrocarbons from media containing 0.05–11 M H_2SO_4, 0.1–8.7 M $HClO_4$, 0.1–12 M CH_3COOH, 0.1–12 M HCl, or 0.1–7 M HBr.[97,98] The extraction is virtually complete after 2 min. The extraction of copper with solutions of D2EHDTPA in the presence of diethylenetriaminepentaacetic acid has been studied.[9]

The extraction of copper(II) is made difficult by its partial reduction to copper(I).[100,116] This process has received very little study and is sometimes completely ignored. In dilute solutions reduction takes place quite slowly and after brief contact (30 s) of a solution of D2EHDTPA in toluene with a 1–2 M solution of $CuSO_4$, CuA_2 passes into the organic phase (pH of solution not specified). The electronic spectra of CuA_2 and CuA differ considerably. It is assumed that a dynamic equilibrium is established during extraction

$$2CuA_2 \rightleftarrows 2CuA + A_2.$$

The CuA complex is associated in solution (degree of association 4–5) when the concentration of Cu(I) is 1 mg ml^{-1}.

In the extraction of large quantities of Cu(II) the process can also be complicated by polymerisation of the CuA_2 complex in the organic phase.[97,117] Copper is not re-extracted with a 2.5 M solution of H_2SO_4 or with solutions of $Na_2S_2O_3$, $H_2C_2O_4$, and phosphoric acid salts.[101] Re-extraction can be carried out using 5 M NH_3 or 10 M HNO_3. NaOH solutions are unsuitable for re-extraction, 7–10% solutions of thiourea in 1–3 M solutions of a mineral acid are used for this purpose.[97]

Silver is completely extracted with a 0.01 M solution of D2EHDTPA in octane from media containing 0.1–8.7 M $HClO_4$, 0.05–9 M H_2SO_4 ($D > 2 \times 10^3$), 0.1–8 M HCl, or 0.1–3 M HBr.[102]

The extraction of gold(III) with the reagent D2EHDTPA from solutions of mineral acids has been studied. During extraction from HNO_3 solutions there is a sharply defined minimum when the concentration of acid is 9 M. Gold is extracted from solutions of mineral acids regardless of its form in the initial solution. The distribution coefficients of gold during extraction from HCl solutions are higher than from HBr solutions. They attain a maximum value when the concentration of mineral acids ranges from 0.1 to 10 M. The extractant is decomposed by the mixture

$HCl + H_2O_2$ (9:1); gold is not extracted from this mixture. Another good re-extraction agent is a 0.5 M solution of thiourea in 0.1 N HCl, HBr, or H_2SO_4.[103]

The extraction of calcium with solutions of ammonium di-2-ethylhexyldithiophosphate in heptane, octanol, TBP, and hexadecane has been studied.[104] The equilibrium stops after 2–3 minutes. In the extraction of calcium with this reagent from 0.5–4 M solutions of its salts, $\log K_{ex} = 0.73 \pm 0.05$. Calcium ions are extracted even more effectively with the sodium salt of the acid. The Ca–Na exchange constant is higher than the Ca–NH_4 exchange constant: $\log K_{Ca-Na} = 1.05 \pm 0.04$; $\log K_{Ca-NH_4} = 0.64 \pm 0.06$. D2EHDTPA appears to extract the ammonium ion more effectively than the sodium ion. A solution of D2EHDTPA in n-decane (0.1 M) extracts Mg, Ca, Sr, and Ba. The degree of extraction depends on the pH of the aqueous phase; at pH > 4 extraction is quantitative.[118]

The distribution coefficients of indium are sufficiently high to ensure its almost quantitative extraction with 0.3–0.5 M solutions of D2EHDTPA in saturated hydrocarbons (heptane, toluene, octane) from solutions of $HClO_4$ and H_2SO_4 of any concentration and from solutions of hydrohalic acids up to 3 M HCl, 4 M HBr, and 5 M HI. Extraction decreases in the series HCl > HBr > HI.[106] The extraction constant of indium ($\log K_{ex} = 10.3$) is very high. The distribution coefficients of indium remain high even for extraction with dilute solutions of D2EHDTPA (0.02 M) from solutions of oxoacids. Extraction decreases in the series $HClO_4$ > H_2SO_4 > H_3PO_4 > $H_2C_2O_4$. Indium is also extracted from alkaline and ammonia solutions. For media containing 0.5–5 M NH_3 or NaOH, the distribution coefficients of indium are constant, and they are much higher for the former than for the latter.

A solution of D2EHDTPA in decane (0.1 M) effectively extracts Tl(I) from solutions of oxoacids and from solutions of hydrohalic acids of low concentration. In extraction from isomolar solutions the distribution coefficients increase in the series $HClO_4$ > H_3PO_4 > H_2SO_4 > HNO_3 > HCl. The largest reduction in distribution coefficients occurs in the presence of chlorides; sulphates and phosphates have virtually no effect on this property. Thallium(I) can be re-extracted with an 8–9 M solution of HNO_3. High concentrations of oxalic and citric acids have comparatively little effect on the extraction of Tl(I). Thallium(I) is extracted with high distribution coefficients not only from buffer solutions with pH 5–10 but also from highly concentrated solutions of NH_3 and alkalis; $\log D$ has a constant value up to a concentration of 5 M NH_3 or NaOH.[107] Thallium(I) is quantitatively extracted with a 1 M solution of D2EHDTPA in 2-ethylhexanol from 0.05–2.5 M H_2SO_4.[108]

The extraction of tin(II) with solutions of D2EHDTPA has been studied in detail.[119,120] It occurs quantitatively over a wide concentration range of H_2SO_4 and from HCl solutions up to an acidity corresponding to 3 M HCl. Tin is quantitatively re-extracted with an 8–9 M solution of HCl. It was shown by saturation of the organic phase that the ratio of metal to reagent in the extract was 1:2. The distribution coefficient of tin when it is extracted from sulphuric and hydrochloric acid solutions and HBr solutions with a solution of D2EHDTPA in octane, decane, cyclohexane, benzene, toluene, CCl_4, and chloroform is directly proportional to the square of the concentration of extractant in the organic phase and inversely proportional to the square of the hydrogen ion concentration in the aqueous phase.

A solution of D2EHDTPA in octane (0.05 M) can quantitatively extract bismuth from a 0.1–8.7 M solution of $HClO_4$ and a 0.05–15 M solution of H_2SO_4; with a concentration of bismuth of 5×10^{-3} M, $\log D > 3$.[113] It is extracted in a more acidic medium from solutions of HCl or HBr. As the concentration of hydrohalic acid in the aqueous phase increases, the distribution coefficients are reduced, the decrease being more substantial in extraction from HBr solutions, which is due to the differing stabilities of halide complexes of bismuth.[113] From among cation-exchange extractants — dialkyldithiophosphoric, dialkylthiophosphoric, alkylphosphoric, and naphthenic acids, and alkyl mercaptans — the most effective for bismuth are D2EHDTPA and dioctylthiophosphoric acid. Bismuth is quantitatively extracted with a 0.05 M solution of D2EHDTPA in octane from media containing 0.1–6 M HNO_3 ($\log D > 3$).[112]

The extraction of arsenic(III) from solutions of HNO_3, $HClO_4$, H_2SO_4, HCl, and HBr over a wide concentration range with a solution of D2EHDTPA in decane has been studied.[110] Extraction from strongly acidic media ($\leqslant 5$ M H^+) is complete, while arsenic is not extracted from solutions with pH 6–7. Acetates, tartrates, fluorides, iodides, and EDPTA do not inhibit extraction.[110,121] The highest distribution coefficients are attained in extraction from media containing 8 M H_2SO_4 (up to pH 2) and from a 1–10M solution of HCl. A feature of the extraction of arsenic(III) is the increase in the distribution coefficient as the concentration of the acid in the aqueous phase increases. Levin et al[111] attribute this to the increase in concentration of the extractable species:

$$AsO_3^{3-} + 6H^+ = As^{3+} + 3H_2O.$$

The extraction of nickel and cobalt with solutions of D2EHDTPA in decane has been studied.[122] Nickel extracts have a green colour. The highest distribution coefficients occur in the extraction of nickel from solutions in the region of pH 2 to 0.5 M H_2SO_4 or 1 M HCl. Cobalt has lower distribution coefficients, its maximum extraction is reached at pH 1.6–1.2. The extraction constants of nickel and cobalt are equal to 1.4×10^3 and 0.9 respectively when $\mu = 4.8$; $\log K_{ex} = 2.29 \pm 0.07$. The elements are quantitatively re-extracted with 6-10 M HCl.

Solutions of D2EHDTPA have also been used for extraction of platinum metals. Palladium(II) forms a complex with D2EHDTPA in 2–3 M HCl without heating in the presence of acetone; the complex is quantitatively extracted into the organic solvent. Silver and gold are extracted under the same conditions, but platinum and rhodium are not extracted. After addition of 0.01 M $SnCl_2$ to an aqueous solution of this type, platinum and rhodium are extracted on standing for 2 h, but iridium is not extracted.[123] By using a 0.01 M solution of extractant in toluene it is possible to extract palladium almost completely from a 0.1–10 M solution of NH_3 or a 0.1–5.3 M solution of NH_4Cl. Toluene, CCl_4, and saturated hydrocarbons can be used as diluents. With a ratio of $V_{org}:V_{aq} = 1:50$ and a palladium concentration of 0.02 μg ml^{-1}, more than 98% of palladium was extracted from 1 M NH_3 and NH_4Cl.[124] The extraction constant of palladium with D2EHDTPA is very high ($\sim 10^{20}$). The inhibiting effect of Cu, Pb, Mn, and Co is eliminated by the addition of excess EDTA.[124]

Iridium(III) is quantitatively extracted into the organic phase from an aqueous solution containing 1–4 M HCl when a 100-fold excess of D2EHDTPA is used (when the concentration of iridium is 1×10^{-3} M) in the presence of acetone, heating being required in this case. The optimum extraction conditions are: 2–3 M HCl, 0.1 M solution of extractant in acetone, acetone content 50 vol. %, heating at 100 °C for 30–40 min. The extraction constant of the complex using chloroform is quite high ($\log K_{ex} = 4.41 \pm 0.1$).[123]

Iridium is not re-extracted with 6 M NaOH, 1 M EDTA, or hydrochloric or sulphuric acid solutions of thiourea because of the formation of kinetically inert iridium complexes. Under the optimum conditions the extraction of iridium is not inhibited by the presence of the following metals (in excess quantities): Fe(III) 20; Cu 3×10^3; Ni 1×10^4; Co 3×10^4. The extraction of iridium becomes complicated in the presence of tin(II), which under these conditions evidently forms tin chloride-containing complexes of iridium of different compositions.

The elements can be arranged in the following series in relation to their ability to be extracted with D2EHDTPA from HCl solutions:[125]

$$Bi > Cu(II) > Pb \geqslant As > Cd \geqslant In > Fe > Ni > Zn.$$

A more complete series based on extraction constants is given in another study[126]

$$Au(I) > Ag(I) > Hg(II) > Pt(II) > Pd(II) > Cu(II) > Ir(III) > > Bi(III) > As(III) > Ru(III) > In(III) > Pb(II) > Sn(II) > > Cd(II) > Fe(III) > Tl(I) > Ni(II) > Zn(II) > Co(II).$$

Table 6. Exchange constants and extraction from perchloric acid solutions.[125]

System M_1-M_2	$\log K_{exch}$	System M−H	$\log K_{ex}$
Zn^{2+}—In^{3+}	11.0±0.3	Zn^{2+}—H	2.25±0.03
Zn^{2+}—Ni^{2+}	0.75±0.03	Ni^{2+}—H	3.14
As^{3+}—Pb^{2+}	−0.67±0.05	Fe^{3+}—H	8.62±0.08
In^{3+}—As^{3+}	1.7±0.1	In^{3+}—H	10.22±0.3
Cd^{2+}—As^{3+}	2.82±0.07	Cd^{2+}—H	7.01±0.07
Fe^{3+}—In^{3+}	1.6±0.08	Pb^{2+}—H	8.09±0.05
As^{3+}—Cu^{2+}	12.94	As^{3+}—H	11.93
		Cu^{2+}—H	12.3
		Bi^{3+}—H	20.1±0.06

There is considerable interest in the exchange reactions of metal di-2-ethylhexyldithiophosphates in the presence of anions that have a tendency towards complex formation with exchangable cations. The extraction constants of metals that form complexes with anions of mineral acids and other complex-forming ligands are equal to $K/(1 + \beta_i c^i)$, where K is the extraction constant in the absence of complex-forming ligand, β_i is the stability constant of the ith complex, c is the concentration of ligand. Depending on the conditions, the exchange constants can vary over a wide range, as a result of which many metals alter their position in the exchange-extraction series. Table 6 lists the exchange constants and extraction constants of certain metals from perchloric acid solutions. In hydrochloric acid solutions these constants have different values.

The exchange constants of the pairs Bi−As and As−Cu when $\mu = 5$ (LiCl) and at an H^+ concentration of 1 M are 0.78 and 5.32 respectively, while the $\log K_{ex}$ values for bismuth and copper complexes are 11.5 and 10.01.[125] As arsenic does not form acido-complexes, the value of K_{ex} at a constant acidity of 1 M H^+ remains unchanged ($\log K_{As-H} = 11.9$) if the extraction is carried out from either perchloric acid or hydrochloric acid solutions.

The extraction of metals with diphenyldithiophosphoric acid (DPDTPA) has been well studied.[127] The latter can be used to extract Cu(II), Pd,[35] Bi,[92] and Pt(II).[128] For example, platinum(II) is quantitatively extracted from a 2.5 M solution of HCl or 1.25 M solution of H_2SO_4.[128] Selenium(IV) is extracted with DPDTPA in chloroform from solutions in the region pH 1 to 10 M HCl.[129] The extraction of cadmium from a 0.05 M solution of H_2SO_4 was used for a subsequent titrimetric determination of cadmium in the presence of Zn, Al, Cr, Co, Mn, and Fe(III).[130]

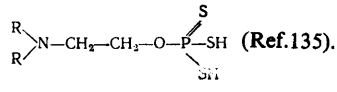
Amongst cyclic alkylidenedithiophosphoric acids, 1,3- and 2,3-butylenedithiophosphoric acids have been studied as extractants for the selective isolation of copper.[13] Solutions of these in chloroform (0.3 M) completely extract copper from acidic media ranging from 2.5 M H_2SO_4 to pH 5. The extraction time in the presence of extraneous elements is 30 min. Using these acids at pH 2, the following may be extracted (in %): Fe(III) 0.3−0.4; Co, Mn, Zn 0.1−0.2. These acids are more selective than isobutylethylhexyldithiophosphoric acid, a 0.15 M solution of which in chloroform at pH 2 extracts 46% iron(III) and 90% nickel. A 0.25 M solution of H_2SO_4 containing 0.5−11.0 M thiourea or a 0.025−0.1 M solution of EDTA in 5% ammonia are suitable for re-extraction of copper. In the presence of Na_2SO_3 copper(I) is quantitatively extracted while there is 1% extraction of iron(II). A 2.5 M solution of H_2SO_4 can be used to re-extract copper(I). The distribution coefficients of 1,3- and 2,3-butylidenedithiophosphoric acids in the system water−$CHCl_3$ at pH > 2 are very small and do not change as the pH increases, which is due to anions of the acids being present in aqueous solution.

Dibutylthiophosphoric acid has been studied from amongst thiophosphoric acids. The extraction of 30 elements using a 0.2 M solution of this acid in CCl_4 from sulphuric acid, hydrochloric acid,[132] and nitric acid[133] solutions has been studied. Ag, Au(I), Pb(II), Hg(II), Bi, and Pd(II) are effectively extracted from solutions of 0.005−5 M H_2SO_4 and 0.01−10 M HCl. Cadmium and zinc are completely extracted from solutions of sulphuric or hydrochloric acid with a concentration of less than 0.05 M. The extraction of As(III), In, Ga, Tl(I), Se(IV), Sn(II), and Fe(III) is characterised by high distribution coefficients. Y, La, Sb(III), Nb, and Mo(VI) are only slightly extracted and Cr(III), Mn(II), Fe(II), Co(II), Ni, alkali metals, and alkaline earth metals are not extracted at all.[132]

Extraction from nitric acid solutions is complicated by oxidation of the reagent, which is marked when the concentration of HNO_3 is more than 6 M. The extractant can be used to separate different groups of elements: Cu, Sc, Se(IV), Pd, Cd, Bi, Sb(V), Zn, In, Te(IV), Tl(I) are extracted from a 1 M HNO_3 solution; Cu, Sc, Se(IV), Pd, Cd, Sb(V), and Bi are extracted from a 3 M solution; and Pd, Bi, and Sb(V) are extracted from a 5 M solution.[133]

Cyclic pinacolinethiophosphoric acid in $CHCl_3$ quantitatively extracts palladium from 0.5−1.0 M HCl. On boiling the extract for 10−15 minutes, the complex decomposes to give PdS.[134]

There has been a qualitative study[135] of the extraction of heavy and platinum metals with dithiophosphoric acids $(RO)_2P(S)SH$, where R are unsaturated groups (allyl, β-methylallyl, propargyl) and also trithiophosphoric acid derivatives such as dimethyl-aminomethyl- and diethylaminoethyl-trithiophosphoric acids with the general formula



(Ref.135).

2. Chemical nature of extraction

Dialkyldithiophosphoric acids extract elements from acidic aqueous solutions by a cation-exchange mechanism, which has been studied in the greatest detail in the case of D2EHDTPA.[136-140] The absence of anions of mineral acids in the extract whatever the type of acid is typical for the extraction of Cu(II),[99] Ag,[102] Ca,[118] In,[105] Tl(I),[109] As,[111] Be,[113] U(VI),[81] Ni,[122] and Pd.[123,124] It has been established using a saturation method that compounds with the composition MA_n which are not solvated with molecules of free acid[99,105,113,122,124] and not hydrated[122,136] are extracted into the organic phase. However, in certain cases the complexes can add on molecules of free acid. For example, complexes of magnesium and alkaline earth elements are solvated with a single D2EHDTPA molecule.[118] The results of elemental analysis of complexes between iridium(III) and D2EHDTPA isolated using thin layer chromatography indicate that they have the composition $Ir_2A_3 \cdot HA$.[123]

The electronic spectra of the organic phases obtained by extraction of metals from solutions of different mineral acids ($HClO_4$, H_2SO_4, HCl, etc.) are identical whatever the nature of the diluent and the concentration of the acid.[105,109,111,113,119,124] The reduction in distribution coefficients as the concentration of acid in the aqueous phase increases [with the exception of As(III)[137]] suggests that there is a cation-exchange mechanism for extraction.

A detailed study of the IR spectra of metal-containing extracts obtained when D2EHDTPA and DPDTPA are used in saturated hydrocarbons also points to a cation-exchange mechanism for extraction. In the IR spectrum of pure D2EHDTPA there is a band with a maximum at 2460 cm^{-1} and two bands with maxima at 2560 and 2595 cm^{-1}. In nonpolar solvents the intensity of the latter two bands increases while the intensity of the band at 2460 cm^{-1} decreases. The bands at 2560 and 2595 cm^{-1} are attributed to (P)—S—H stretching vibrations of the monomeric acid molecules. In the spectrum of the deuterated extractant the $O_2P(S)SD$ maxima at 2560 and 2595 cm^{-1} are shifted to lower frequency. It is assumed that the band at 2460 cm^{-1} is an indication of the presence of dimeric acid molecules.[114] The presence of an asymmetric band with a maximum at 675 cm^{-1} is due to vibrations of the P=S group. Bands in the region 700—400 cm^{-1} are attributed to P—S vibrations, but their interpretation is ambiguous because these bands can correspond to the vibrations of a hydrocarbon group.[114]

In the IR spectrum of the pure acid there is a broad band at 2460 cm^{-1} and two sharp maxima at 2560 and 2595 cm^{-1} due to vibrations of the S—H group; these disappear if the extract contains Ag,[102] In,[105] Tl(I),[109] Sn(II),[119] As(III),[111] Bi,[113] and Pd.[114,124] This phenomenon indicates that the hydrogen ion of the S—H group is replaced by a metal ion, namely, that there is a cation-exchange mechanism for extraction.

The occurrence of an interaction between the sulphur atom of the P=S group and metal ions is supported by the change in position and shape of this band in the spectra of extracts containing complexes compared to its position and shape in the IR spectra of the pure acids. Instead of an intense band at 675 cm^{-1} due to asymmetric vibrations of the P=S group,[114] in the spectrum of an extract that contains bismuth a new band of medium intensity with two clearly defined maxima at 627 and 640 cm^{-1} appears.[113] In the spectrum of an extract of silver complex a band with a maximum at 635 cm^{-1} and a weak shoulder at 645—650 cm^{-1} appears.[124] Similar changes in the vibration bands of the P=S and (P)—S—H groups also occur in the IR spectra of extracts of other metals: In,[105] Tl(I),[109] Sn(II),[114,119] and As(III).[111]

A comparison of the IR spectra of solutions of the reagent in heptane and in TBP with the spectra of extracts saturated with calcium showed that the position of the absorption band due to the P=S group (681 cm^{-1}) did not change. Some broadening of the bands was an indication of a weak interaction between the thione sulphur of the P=S group and the metal.[104] The vibrational bands of the P—S bond (400—700 cm^{-1}) change considerably. The weak maxima at 600, 580, and 535 cm^{-1} and the shoulder at 490 cm^{-1} in the spectrum of the extract of free reagent are shifted to shorter wavelength at 610, 590, and 550 cm^{-1} respectively in the spectrum of the extract of bismuth while the shoulder maintains its position at 490 cm^{-1}.[113] The position of the bands from the P—S bond also change in the spectra of extracts of complexes of Ag,[102] Sn(II),[114,119] As(III),[111] and U(VI),[66] but an interpretation of these shifts is ambiguous.

An asymmetric band with a maximum at 1015 cm^{-1} and poorly defined shoulders at 985 and 1035 cm^{-1} is attributed to vibrations of the (P)—O—C bonds.[114] This band undergoes considerable changes in the spectra of extracts of complexes of Sn(II),[119] As(III),[111] Bi,[113] and other metals[66,114] compared to its position in the spectrum of the free acid. The nature of the changes depends on the degree of ionic character of the P—S—M bond.

The band due to asymmetric vibrations of Pd—S in the Raman spectrum of a complex of palladium with D2EHDTPA is situated at 330 cm^{-1} while in the spectrum of palladium diethyldithiophosphate it occurs at 317 cm^{-1}.[124]

The IR spectra of extracts of bismuth[111] and tin(IV)[119] after they have been diluted with free reagent have also been studied.

The IR spectra of complexes of iridium, rhodium, platinum, and palladium with D2EHDTPA are similar to the spectra of other dithiophosphates. The absorption bands due to vibrations from S—H groups (2560 and 2595 cm^{-1}) disappear, while the band from the P=S group at 673 cm^{-1} in the free reagent is shifted in complexes of these metals to lower frequency by 41, 42, 39, and 40 cm^{-1} respectively.[138] The band from the coordinate P=S group has a doublet structure for all dithiophosphates; this is due to the existence of two rotational isomers.[138] D2EHDTPA evidently acts as a bidentate ligand. However, it is thought that complexes that are solvated with molecules of free D2EHDTPA can also be extracted in small quantities. Such complexes are less mobile and are separated from the main component on silica gel.[123]

In the IR spectrum of free DPDTPA there is an absorption band from the P=S group at 665 cm^{-1}; in the case of the potassium salt of DPDTPA the absorption band from this group appears at 690 cm^{-1}. The absorption bands from the P=S group in diphenyldithiophosphates of Ag(I), Cd, Hg(II), Bi, Pb, and Ni, are shifted to longer wavelength by 5—15 cm^{-1} compared to the frequency of vibrations from this group in the free acid and by 15—60 cm^{-1} compared to the potassium salt. The vibration frequency of the P—O—C group at 1160 and 1025 cm^{-1} remains unchanged.[139] Shishkov and Busev[139] attribute this to the formation of a chelate with a four-membered ring.

Dialkyldithiophosphates are mainly extracted as monomeric compounds, but some of them are associated in the organic phase. The degree of association of gold when it is extracted with solutions of D2EHDTPA in heptane is 3, while mercury(II) dibutyldithiophosphate is extracted from sulphuric acid solutions into carbon tetrachloride as its tetramer.[89] Association also occurs

in the organic phase when large quantities of copper(II) are extracted with D2EHDTPA solution.[97] Ammonium dialkyldithiophosphate is highly associated in an inert solvent.[104] As a rule, unsaturated coordinate complexes are associated in the organic phase.[89,97,102]

Extraction from acidic aqueous solution that takes into account association is given by the following equation

$$mM^{n+} + \frac{m}{x}(n+s)(HR)_x + my\,H_2O \rightleftarrows (MR_n \cdot s\,HR \cdot y\,H_2O)_m + mn\,H^+.$$

The extraction constants are given in Table 6.

For some metals the extraction constants are very large and they cannot be calculated by the standard method based on the functions $\log D - \log[HA]_{org}$ or $\log D - \log[H^+]_{aq}$ because of the impossibility of determining very low concentrations of metal ($10^{-8}-10^{-7}$ M) in the aqueous phase after distribution.[140] Although dialkyldithiophosphoric acids are classed as strong acids and extract metals from acid media, there are results that indicate that dithiophosphates can also be extracted from weakly alkaline media. This relates to those that are most soluble in water (DMDTPA, DEDTPA, DPrDTPA, DBDTPA). Thus, DMDTPA extracts nickel from aqueous solution in the region of pH > 4:[66,81]

$$Ni^{2+}_{(aq)} + 2A^-_{(aq)} \rightleftarrows NiA_{2(org)}.$$

Uranyl ions are extracted with these acids in a similar manner. Extraction from alkaline media is particularly characteristic of metals that do not form very stable dithiophosphates (Zn, Co, Ni). Extraction of metal dithiophosphates in the presence of amines or donor-active added components is confirmation of the formation of complexes in aqueous solution in an alkaline medium.

Dithiophosphates of the transition metals Mn(II), Fe(II), and Co(II) in the presence of 2,2′-dipyridyl (Dipy) or 1,10-phenanthroline (Phen) are extracted in weakly alkaline media as mixed ligand complexes. The maximum degree of extraction of Mn(II), Fe(II), and Co(II) complexes is reached at pH 6–7 while for Ni(II) the maximum occurs at pH < 2. The pH region for extraction is very narrow as at pH 1–3 ligand exchange can occur because of the low stability of the dithiophosphates. At pH < 7 all of the amine is in the aqueous phase and at pH < 2.5 it is completely protonated. On the other hand, dialkyldithiophosphate ions are protonated at H < 2.7 and the acid concentration in the organic phase increases sharply. In the pH region 6–7 dialkyldithiophosphoric acids (HA) and the amine exist completely in the aqueous phase and the ratio of Dipy : HA that is conducive to extraction of Fe(II) is 3 : 2. The formation of complexes with HA and amine occurs in the aqueous phase and can be represented by the following scheme:

$$Fe(Dipy)^{2+}_3 + 2A^- \rightleftarrows [Fe(Dipy)_3A_2]_{(org)}.$$

In the absence of amine or dithiophosphate ion there is no extraction of Fe(II) complexes. Only the combined presence of both ligands leads to a considerable synergistic effect.[41]

3. Effect of substituents on the extraction of dialkyldithiophosphates

Interesting observations have been made in comparing the extractive capacity of different dialkyldithiophosphoric acids. It should be noted first of all that replacement of oxygen atoms by sulphur increases the extractive capacity of dialkyldithiophosphoric acids compared to dialkylphosphoric acids. Thus, for example, the extraction constant of bismuth with a solution of D2EHDTPA is 10^{16} times higher than the extraction constant of bismuth with di-2-ethylhexylphosphoric acid (D2EHPA);[113] the extraction constant of silver with D2EHDTPA is 2.1×10^{41}, while its extraction constant with D2EHPA is 1.4×10^{-2}. A similar phenomenon occurs in the extraction of indium.[105]

Bode and Arnswald,[9,11] who had studied the extraction of metals with only DEDTPA, proposed that the RO group on the phosphorus atom has little effect on the properties of the extractant. However, it was shown[5] that replacement of ethyl groups by n-butyl groups leads to an increase in the degree of extraction of elements. Moreover, the use of acids with a larger number of carbon atoms in the alkyl group of the acid increases the range of extractable elements. Thus, in contrast to DEDTPA, the dibutyl analogue completely extracts Zn, Tl(III), and Ni, and partially extracts Co(II) and Cr(III); Au(III) is extracted without reduction to elemental gold. Mercury and zinc are extracted more effectively with D2EHDTPA than with DBDTPA. Out of those studied, D2EHDTPA is the most effective extractant.[5] The effect of subsituents on the extractive capacity of dithio acids is noticeable in the case of the extraction of uranyl ions;[81] on increasing the carbon chain in dialkyldithiophosphoric acids the distribution coefficients of the complexes decrease in the series $2\text{-}(C_2H_5)C_6H_{12} > n\text{-}C_4H_9 > C_3H_7 \gg C_2H_5$.

It is interesting to monitor the effect of substituents on the phosphorus atom in the case of the extraction of certain dialkyldithiophosphates.[71,141] Extraction can be quantitatively characterised by the two-phase stability constant of extracted complex ($K_{D,2}\beta_n$). A variation in substituents substantially changes the two-phase stability constant of dialkyldithiophosphate. As the number of carbon atoms in the substituents increases, there is a trend towards an increase in $K_{D,2}\beta_n$ (Table 7),[141] which may be due to the effect of substituents on the distribution constants of the complexes and their stability constants.[142]

Table 7. Characteristics of the extraction of dialkyldithiophosphates with different solvents.[141]

Alkyl	Nickel in		Zinc in C_7H_{16}	Calcium in $C_6H_5CH_3$	Lead in CCl_4
	$CHCl_3$	C_6H_6			
Ethyl-	4.45	4.06	2.70	5.22	8.84
Propyl-	7.11 (2.3)	6.87 (2.9)	5.13 (1.7)	7.55 (3.8)	11.62 (7.6)
Isopropyl-	7.98 (2.6)	7.43 (3.0)	5.44 (1.5)	7.95 (3.7)	11.78 (6.9)
Butyl-	9.97 (2.7)	9.41 (3.0)	7.72 (1.8)	10.32 (4.1)	14.37 (7.4)
Isobutyl-	9.32 (2.2)	9.07 (2.8)	7.49 (1.6)	10.03 (4.0)	13.83 (6.9)
sec-Butyl-	10.89 (2.9)	10.52 (3.4)	8.29 (1.6)	11.78 (3.5)	14.52 (6.8)
t-Butyl-	11.99 (2.5)	11.49 (3.1)		12.83 (4.1)	16.36 (7.2)
Amyl-	12.59 (2.8)	12.02 (3.0)	10.37 (1.9)	12.48 (4.3)	17.17 (7.4)
Isoamyl-	12.01 (2.7)	11.69 (3.3)	10.04 (2.0)	12.48 (4.3)	16.69 (7.9)
Hexyl-	15.07 (2.7)	14.63 (3.2)		15.58 (4.3)	

Note. $\log(K_{D,2}\beta_2)$ values are listed (those in brackets are $\log K_{ex}$ values).

The stability of the complexes increases with the introduction of a more electron-donating group into the ligand molecule, so complexes with dithiophosphinic acid derivatives are the most stable.[143] But an increase in stability of dialkyldithiophosphates is also due to the steric effects of substituents on phosphorus. A

linear correlation exists between the logarithms of the stability constants of the complexes and the sum of the steric constants of substituents on the phosphorus atom (E_s^0). However, in order to derive correlation equations it is also necessary to take into account the hydrophobic effects of the substituents, which affect the distribution constants of the complexes. In order to determine the two-phase stability constants of dialkyldithiophosphates, two-parameter equations that include the steric and hydrophobic effects of the substituents on the phosphorus atom have been propounded. Taft constants E_s^0 are used to determine the steric effect and the number of carbon atoms are used to determine the hydrophobic effect. Correlation equations for the determination of two-phase stability constants of nickel have been derived for the systems water–toluene, water–heptane, and water–carbon tetrachloride.[71]

The two-phase stability constants of the dithiophosphates of Zn, Cd, Pb, and Ni also rise with the increase in steric and hydrophobic effects of substituents on the phosphorus atom (Table 7).[71,141]

4. Effect of diluents on the extraction of dialkyldithiophosphates

This effect can be closely followed in the case of complexes of metals with D2EHDTPA. In the majority of studies unreactive organic diluents are used (Table 8).

Table 8. Extraction constants of bivalent elements ($\log K_{ex}$) with D2EHDTPA solutions in different diluents (μ = 5).[144]

Element	Octane	CCl_4	$CHCl_3$	MIBK	Octanol
Hg	40.18	39.02	38.62	39.62	35.12
Pt	24.11	33.00	22.60	20.85	19.05
Pd	20.10	18.94	18.54	16.54	15.04
Cu	12.06 (12.30)	11.50 (11.40)	10.50	8.80 (8.80)	7.00
Pb	8.55 (8.09)	7.39	6.99	5.29	3.49
Sn	7.55 (7.79)	6.39	5.99	4.29	2.49
Cd	7.55 (7.04)	6.39	5.99	4.29	2.49
Ni	3.09 (3.14)	1.87	1.37	−0.23	−2.03
Zn	2.02 (2.25)	0.86	0.46	−1.24	−3.04
Co	0.02	−1.14	−1.54	−3.24	−5.04
Fe	−3.00	−4.10	−4.56	−6.26	−8.06
Mn	−6.02	−7.17	−7.57	−9.27	−11.07

Note. Calculated values of $\log K_{ex}$ are listed (those in brackets are the experimental figures).

The extraction constants of tin(II) from solutions of HCl and HBr differ almost by a factor of 10, which is attributed[119] to a discrepancy in the data on the stability of chloride and bromide complexes of tin. The extraction constants from sulphuric acid solutions are less than from solutions of HCl and HBr. It was not possible to make a comparative determination of the extraction constants of tin with D2EHDTPA from perchloric acid solution because of the instability of tin(II) solutions in perchloric acid.

The extraction constants of bivalent metals with D2EHDTPA in different diluents as determined by calculation are in good agreement with the exeperimental values (Table 8).[144] By using the principle of strong and mild acids and bases (SMAB) as a basis for determining K_{ex} it is possible to calculate these values from three experimental quantities.

A comparison of the extraction constants of the di-2-ethylhexyldithiophosphates of silver,[102] tin(II),[119] and bismuth[113] in different diluents shows that inert diluents have little effect on the extraction of dialkylphosphorodithioates. Oxygenated solvents, such as tributyl phosphate (TBP) and trioctylphosphine oxide (TOPO), have a marked effect on extraction. Decane, benzene, CCl_4, and chloroform have little effect on the extraction constant of arsenic(III) with D2EHDTPA ($\log K_{ex}$ = 10.8), but methyl hexyl ketone, dibutyl ether, and dichloroethane decrease it by a factor of 100–1000.[111] On dilution with kerosene, the phases separate out slowly when these elements are re-extracted.[121]

Diluents affect the extraction of zinc and mercury(II) in quite different ways. The most complete extraction of zinc occurs when the extractant DBDTPA is diluted with n-heptane or carbon tetrachloride; amyl alcohol and amyl acetate cause extraction to be reduced. On the other hand, the distribution coefficients of mercury(II) when using oxygentaed solvents such as ethyl acetate and isopropyl ether are higher than when n-heptane, xylene, and toluene are used, particularly at a low acidity of the aqueous solution (0.1 M HCl).[5]

Table 9. Extraction constants of indium ($\log K_{ex}$) with D2EHDTPA solutions in different diluents (μ = 5).[105]

Diluent	$HClO_4$	H_2SO_4
Decane	(10.6)	(10.3)
CCl_4	9.6 (9.8)	9.3
Benzene	9.4 (9.5)	9.1
Chloroform	8.6 (8.2)	8.5 (8.3)
Dibutyl ether	7.1 (6.7)	6.8 (6.3)
Methyl hexyl ketone	6.6 (8.7)	6.3
TBP	5.1 (10.1)	4.8 (7.4)
Octanol	4.9	4.6 (7.4)

Note. Calculated values of $\log K_{ex}$ are listed (those in brackets are the experimental figures).

The experimental and calculated extraction constants of indium only coincide for solvents with low polarity (Table 9).[105] TBP can exert both an antagonistic effect and a synergistic effect depending on the concentration. The distribution coefficient of indium in extraction with a solution of D2EHDTPA in TBP initially decreases as the proportion of the latter increases and then, when the concentration of TBP is above 0.5 M, increases sharply, in all probability because a TBP molecule is being incorporated into the extracted compound.[105]

Diluents have a substantial effect on the distribution coefficients of thallium(I)[109] and relative to this factor are arranged in the series: alcohols > aromatic hydrocarbons > halogen derivatives > ethers > saturated hydrocarbons and cyclic hydrocarbons. The distribution coefficients are at a maximum when TBP is used as the diluent, but the solution of extractant changes its properties substantially on standing in this diluent. Thus, a freshly prepared 0.1 M solution of D2EHDTPA in TBP extracts thallium(I) from 0.1 M H_2SO_4 with a distribution coefficient of about 190, but on standing for two weeks this value decreases to 3. Such phenomena do not occur when other diluents are used.[107]

Oxygenated solvents have the strongest but an unequal effect on the extraction of low-stability complexes of cobalt and nickel (Table 10).[121] When TBP or 2-ethylhexanol are used, the distribution coefficients of cobalt are higher, while the distribution coefficients of nickel are lower, than when saturated hydrocarbons are used. For example, TBP and TOPO reduce the rate of extraction of nickel by a factor of 20.[145] According to the results of one study,[117] added quantities of 2-ethylhexanol and TBP increase the rate of extraction of nickel with a 1 M solution of D2EHDTPA in hexane from solutions of H_3PO_4, and instead of 12 h required for extracting nickel without donor-active components (DAC), in the presence of 20 vol. % 2-ethylhexanol nickel is completely extracted in 2 min. It has been proposed that the extraction of nickel is limited by surface reactions with a single rate-limiting stage. The kinetic functions in the extraction system nickel-D2EHDTPA are determined by the limiting role of chelate formation in the adsorbed layer on the phase interface. This process is represented hypothetically by the equations

$$[Ni(H_2O)_6^{2+}]_{(aq)} + R^-_{(s)} \rightleftarrows [Ni(H_2O)_{6-n}R]^+_{(s)} + nH_2O,$$
$$[Ni(H_2O)_{6-n}R]^+_{(s)} + R^-_{(s)} \rightarrow [NiR_2]_{(s)} + (6-n)H_2O,$$
$$[NiR_2]_{(s)} \rightleftarrows [NiR_2]_{(org)},$$

where the index s corresponds to the state of sorption at the phase interface.[146]

Table 10. Effect of diluents on the distribution coefficients of complexes of cobalt and nickel with D2EHDTPA.[121]

Diluent	Cobalt (0.25 M HA, 0.25 M $HClO_4$)	Nickel (0.1 M HA, 2.0 M $HClO_4$)
2-Ethylhexanol	12.0	0.81
Tributyl phosphate	8.7	1.72
Cyclohexane	4.3	2.12
Decane	3.5	14.2
Dibutyl ether	3.4	0.28
Carbon tetrachloride	1.5	3.66
Benzene	1.4	0.427
Chlorobenzene	0.96	0.56
Chloroform	0.4	0.66

Cobalt is oxidised during extraction with solutions of D2EHDTPA. The compound of cobalt(II) with D2EHDTPA that is extracted into the organic phase changes colour from blue at the start of extraction to dark brown on prolonged agitation. The Co(II) compound is rapidly extracted and then Co(II) in the organic phase is slowly oxidised to Co(III). This process is determined by an equilibrium that is slowly reached.[147] The time taken to establish equilibrium in the extraction of cobalt with a solution of D2EHDTPA in decane depends on the concentration of cobalt in the organic phase. At relatively high concentrations the equilibrium is established after 10 h. At a low concentration (less than 3×10^{-4} M), agitation is required for 45 h. If the concentration of cobalt(II) in the organic phase exceeds 1×10^{-3} M it is almost completely oxidised.[148] Added quantities of TBP and TOPO increase the rate of extraction of Co(II) and considerably reduce its rate of oxidation.[145] The latter phenomenon is due to formation of a mixed ligand complex Co–DAC–HA which is not oxidised in the organic phase.[145]

In general the effect of DAC on the extraction of cobalt and nickel is very complex and it depends on their concentration and nature (some added components inhibit extraction while others accelerate it) and also on the nature of the extracted complex. A reduction in time of phase contact, the introduction of DAC, and a lowering of the partial pressure enable cobalt and nickel to be separated.[145,149,150]

In the extraction of uranyl ions with solutions of diethyl-, di-n-propyl-, and di-n-butyl-dithiophosphoric acids in n-butanol, the distribution coefficients are higher than in benzene. It is thought[151] that n-butanol is incorporated into the extracted compound. The extraction constants of uranyl ions with solutions of 2DEHDTPA in different diluents are also dissimilar.[81] The values of $\log K_{ex}$ for different diluents are: benzene 0.37; chloroform 0.79; carbon tetrachloride 0.92; and cyclohexanol 0.28.[152]

IV. The use of dithio phosphorus acids for the separation of elements

There is virtually no information about the use of thio phosphorus acids for the separation of elements. It is only known that a solution of DBTPA in CCl_4 has been used for the extractive separation of the following element pairs in nitric acid solutions: Te(IV)–Se(IV), Au(III)–Tl(I), Pt(IV)–Pd(II), As(V)–In(III), As(V)–Sb(V), In(III)–Ga(III), and Bi(III)–As(V).[133] Apart from that, Te, Se, Bi, In, Zn, and Cu ions have been isolated from 0.3 M HNO_3 using a 0.3 M solution of DBTPA for their determination in pure silver.[153]

We will therefore examine below the separation of elements with dithio phosphorus acids, amongst which the main position is occupied by D2EHDTPA. In studying the extractive properties of this reagent, three groups of metal cations can be distinguished. The first is made up by elements that are effectively extracted from strongly acidic solutions — Ag(I), Au(I), Cu(I) and Cu(II), Hg(I) and Hg(II), Bi(III), Sb(III), As(III), Sn(II) and Sn(IV), Pb(II), and platinum metals. In the second group are elements that can only be slightly extracted (extracted at low concentrations of HCl or H_2SO_4) — Tl(I), Cd(II), In(III), Fe(III), Zn(II), Ni(II), and Co(II). The third group consists of unextractable elements: alkali metals, alkaline earth metals, Al, Ti(IV), Ga, Ga, Mn(II), Fe(II), Zr(IV), and Cr(III) and Cr(VI).[114,126] Different schemes for the separation of complex systems and methods for isolating elements using D2EHDTPA have been put forward.

1. Isolation of copper

Copper is isolated from unextractable elements and those of low extractability using D2EHDTPA solutions in inert diluents from solutions with a high concentration of H_2SO_4.[114] Ag, Au, Hg(II), In, Sb(III), and Bi are extracted together with copper. In, Sb(III) and Bi ions are re-extracted with conc. HCl[97] (copper is not re-extracted with solutions of acids, alkalis, or ammonia). Copper is slowly re-extracted only with solutions of oxidising agents that decompose the extractant[114] [in the re-extraction of copper(II) with an 85% solution of thiourea in 0.5 M H_2SO_4, 20–40% of D2EHDTPA is oxidised depending on the time of agitation[97]]. Because of the slow re-extraction of copper, it is possible to separate it from bismuth at this stage.

A number of ions remain in the aqueous phase when a metal dialkyldithiophosphate is used as the extractant, having an

extraction constant which is less than for copper but higher than for the remaining metals. Cadmium di-2-ethylhexyldithiophosphate is suitable for such a purpose (log K_{ex} = 10.67). In the extraction of copper(II) with a saturated solution of this extractant in a saturated hydrocarbon, Zn, Tl(I), Tl(III), Co, Ni, Sn(II) and (partly) In remain in aqueous solution.[97] Copper(II) is extracted almost completely from 1–6 M solutions of HCl with 0.05 M D2EHDTPA in heptane over a period of 2 min.[98] Under these conditions Pd(II), Sn(II), and Sn(IV) have very low distribution coefficients ($D < 0.1$). The small quantities of palladium which pass into the organic phase in the extraction of copper(II) do not interfere with a photometric determination of copper at 420 nm as the molar absorption coefficient of the palladium complex at this wavelength is a hundred times lower in magnitude. A 0.05 M solution of D2EHDTPA completely extracts palladium ($D > 5 \times 10^3$) from ammonium chloride solutions with a concentration of 0.5–6 M NH_3. In the presence of EDTA the distribution coefficient of copper is markedly reduced. In extraction from a 0.5–1 M solution of NH_3 containing 0.05 M EDTA, the partition coefficient of the Pd–Cu pair is 10^5, in other words, by adding EDTA to the ammonia solution it is possible to re-extract copper selectively.[98]

2. Isolation of mercury(II)

The use of a 0.05 M solution of D2EHDTPA in octane for extraction permits the complete extraction of 5×10^{-3} M Hg(II) from solutions containing 0.1–8.7 M $HClO_4$, 0.5–9 M H_2SO_4, 0.1–7 M HCl, or 0.1–2 M HBr ($D > 500$).[154] An increase in the concentration of hydrohalic acids sharply reduces the distribution coefficient of mercury, the reduction being more significant in extraction from HBr solutions than from HCl solutions. Mercury is effectively re-extracted with concentrated acid solutions of thiourea and NH_4SCN and concentrated solutions of HCl or HBr. The presence of a more than tenfold excess of tin(II) in the aqueous phase inhibits the extraction of mercury. The negative effect from the presence of tin can be eliminated by the addition of 1–2 ml of a 1% solution of NH_4F. Mercury is separated during extraction from elements of low extractability — Al, Ga, Ti(IV), Zr, Cr(III), Mn(II). In order to isolate it from the co-extracted elements — Zn, Cd, Sn, Pb, Tl(I), Ni, and As(III) — it is possible to use bismuth di-2-ethylhexyldithiophosphate. Mercury(II) is extracted with a 0.006–0.01 M solution of bismuth di-2-ethylhexyldithiophosphate in octane from 0.1–3 N mineral acids. Mercury is isolated from zinc and cadmium by extraction with a solution of DEDTPA in heptane; 2 M HCl or H_2SO_4 must be present in the medium. Cadmium is then separated from Hg(II) by re-extraction with a 1 M solution of HCl or it is directly determined with 1-(2-pyridylazo)-2-naphthol in the extract.[155]

3. Isolation of thallium(I)

Thallium(I) is separated from elements of low extractability by extraction with a solution of 1 M D2EHDTPA in 2-ethylhexanol from 1.5–2 M solutions of H_2SO_4.[108] Cu, Ag, Zn, As(III), Hg, Fe, Ni, and Sb(III) are extracted together with Tl(I). It is isolated from these elements by washing the organic phase with different complexing agents. Washing the extract with a 40% solution of diethylamine in 30% $(NH_4)_2SO_4$ leads to the re-extraction of Zn and Ni. A second component — pyro-2-ethylhexylphosphoric acid — is added to the organic phase in order to isolate Tl(I) from Sb and Fe. On shaking the mixed organic phase with an oxidising agent (8 M HNO_3), D2EHDTPA is decomposed and Tl(I) passes into the aqueous phase while Sb and Fe remain in the organic phase as the second component is not oxidised.

Ag and Hg(II) ions are not separated from Tl(I) on washing the organic phase with solutions of acids and bases or amines. But the oxidation product of D2EHDTPA — most probably bis(alkyldithiophosphoryl) disulphide — extracts silver and mercury with high distribution coefficients. Therefore, when D2EHDTPA is decomposed with a solution of HNO_3, Tl(I) passes into the aqueous phase while Ag and Hg remain in the organic phase.

Since the distribution coefficients of copper when it is extracted with D2EHDTPA are substantially higher than for Tl(I), copper readily displaces thallium from the organic phase.[108]

4. Isolation of tin(II)

Tin(II) is isolated from co-extracted metals by re-extraction with 3–5 M H_2SO_4 or 1–2 M HCl.[120] However, it is not possible to remove all the co-extracted elements in this manner but only Zn, Ni, Co, Fe(III), Sb(III), Mo(VI), and Tl(I). Cu, Ag, As, Bi, and Hg(II) are not separated even when the organic phase is washed with conc. H_2SO_4 or $HClO_4$, but Sn(II) is readily isolated by re-extraction with an 8 M solution of HCl. Bi and Sb(III) ions are re-extracted with HCl solutions of higher concentration, but As(III), Cu, and Hg are not re-extracted even with conc. HCl.[120]

5. Isolation of arsenic(III)

It is possible to separate As(III) from elements of low extractability — Mg, Mn, Cr, Ti, Zr, Al, rare earth elements — during extraction from acid solutions.[110] The separation of arsenic from metals that form anionic chloride complexes occurs when it is extracted from solutions with a high HCl content or after washing the extract with HCl. Solutions of the oxidising agents HNO_3, H_2O_2 + HCl, Tl(III), and Br_2, the most suitable of which is bromine,[156] can be used for the re-extraction of arsenic.

Arsenic can be extracted from sulphuric acid and hydrochloric acid solutions with nickel diethyldithiophosphate by means of exchange reactions. The exchange process between arsenic and nickel

$$3NiA_{2(org)} + 2As^{3+}_{(aq)} \rightleftarrows 2AsA_{3(org)} + 3Ni^{2+}_{(aq)}$$

is quite slow (about 2 h) and is very dependent on the pH of the solution. By using nickel diethyldithiophosphate it is possible to remove arsenic from a nickel electrolyte to a sufficient degree in two stages.[121]

6. Isolation of bismuth

In order to separate bismuth from elements of low extractability, it is extracted with a 0.01 M solution of D2EHDTPA in octane from 0.1–4 M $HClO_4$, H_2SO_4, HCl, or HBr and the organic phase is washed once with a 1.5–3 M solution of H_2SO_4.[157] Cu(II), Zn, Cd, In, Tl(I), Sn(II), Pb, As(III), Sb(III), Fe(III), Co, and Ni are extracted together with bismuth.[114] Bismuth is extracted almost quantitatively at any concentration of these elements and in addition it displaces them on extraction. Bismuth is separated from cobalt by extraction from 2.5 M H_2SO_4. Bismuth can be determined in the presence of the following elements (their admissible excess quantity relative to Bi is given in brackets): Zn, Cd (600); Ni (60); Sn(II) (8); Sb(III) (3). The adverse effect of Sn(II) is eliminated by washing the organic phase with 3–4 M HCl, since Sn(II) is re-extracted considerably less with concentrated HCl solutions than is bismuth.

Ag, Au, Hg, and Bi ions form strong thiourea complexes, but the latter do not interfere with the extraction of bismuth, so it can

be isolated from these elements. The product from oxidation of D2EHDTPA with nitric acid extracts Ag, Au, and Hg, but not Bi, with high distribution coefficients. Therefore, when the extract is washed with 6 M HNO_3, Ag, Au, and Hg ions remain in the organic phase while bismuth passes into the aqueous phase, where it can be determined using KI. Determination of bismuth is possible in the presence of a 20-fold excess of Ag and Au, and 10-fold excess of Hg.[157]

7. Separation of platinum metals

The scheme for separation of the platinum metals, Au, and Ag is based on a difference in the conditions for forming extractable di-2-ethylhexyldithiophosphates.[123,126] Ag, Au, and Pd and some of the class *a* metals are extracted under normal conditions without heating the aqueous solution in the presence of the reagent and acetone. After addition of 0.1 M $SnCl_2$ to the aqueous solution and allowing it to stand for 1 h, platinum and rhodium are extracted, the aqueous solution is then heated and iridium is extracted. Thus, D2EHDTPA can be used for the group concentration of platinum metals and for separations of the pairs palladium–platinum and rhodium–iridium.[123] Cu(I), Hg(I), As(III), Bi(III), and Sb(III) are extracted together with iridium. All of the metals apart from Cu(I) can be separated from iridium by re-extraction with a 10 M solution of HCl.

—o0o—

It should be pointed out in conclusion that there are no quantitative characteristics for determining the efficiency of the extraction processes involving dialkyldithiophosphates. A possible exception to this is D2EHDTPA, for which the extraction constants of metal cations are known. Nevertheless even for this the stability constants of the complexes are still unknown. In fact, a determination of extraction, stability, and distribution constants of complexes and also the two-phase stability constants provides material that serves as a basis for using dithio acids in analytical chemistry and therefore it is worthy of close attention.

References

1. A I Busev *Dokl. Akad. Nauk SSSR*, 1949, **66**(6) 1093
2. A I Busev *Zh. Anal. Khim.*, 1949, **4**(4) 234
3. T H Handley *Talanta*, 1965, **12**(10) 893
4. A I Busev, M I Ivanyutin *Tr. Komis. po Anal. Khim. Akad. Nauk SSSR*, 1960, **11** 172
5. T H Handley, J A Dean *Anal. Chem.*, 1962, **34**(10) 1312
6. T H Handley *Nucl. Sci. Eng.*, 1963, **16** 440
7. T H Handley, R H Zucal, J A Dean *Anal. Chem.*, 1963, **35**(9) 1163
8. T H Handley *Anal. Chem.*, 1965, **37**(2) 311
9. H Bode, W Arnswald *Fresenius' Z. Anal. Chem.*, 1962, **185**(3) 179
10. U Khudaibergenov, A G Ganiev *Aktivatsionnyi Analiz Blagorodnykh Metallov* (Activation Analysis of Noble Metals), Izd. Filial Akad. Nauk, Tashkent, 1970, p. 73
11. H Bode, W Arnswald *Fresenius' Z. Anal. Chem.*, 1962, **185**(2) 99
12. N A Ulakhovich, G K Budnikov, N K Shakurova *Zh. Anal. Khim.*, 1980, **35**(6) 1081
13. A I Busev, M I Ivanyutin, E M Feigina *Zavod. Lab.*, 1958, **24**(3) 265
14. A I Busev, T V Rodionova *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1968, (5) 63
15. A I Busev, T V Rodionova *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1969, (5) 77
16. A I Busev, T V Rodionova *Zh. Neorg. Khim.*, 1969, **14**(5) 1283 [English translation in *Russ. J. Inorg. Chem.*, 1969(5)]
17. A I Busev, T V Rodionova *Anal. Lett.*, 1969, **2**(1) 9
18. A I Busev, T V Rodionova, A Alvarez-Escartin *Zh. Neorg. Khim.*, 1970, **15**(6) 1624 [English translation in *Russ. J. Inorg. Chem.*, 1970(6)]
19. A I Busev, T V Rodionova, A Alvarez-Escartin, A N Shishkov *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1971, **12**(5) 590
20. A I Busev, T V Rodionova, A Alvarez-Escartin, Y A Albitsky *Anal. Lett.*, 1971, **4**(4) 231
21. A I Busev, T V Rodionova, A Alvarez-Escartin *Zh. Anal. Khim.*, 1972, **27**(8) 1508
22. A I Busev, T V Rodionova, A N Batalin, N J Verbitskaya *Anal. Lett.*, 1970, **3**(5) 243
23. A I Busev, T V Rodionova, N I Verbitskaya *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1972, **13**(5) 556
24. A I Busev, T V Rodionova, N J Verbitskaya *Anal. Lett.*, 1972, **5**(4) 237
25. A I Busev, T V Rodionova, P Nenning *Wiss. Z. Karl-Marx Univ. Leipzig. Math-Naturwiss. R.*, 1975, **24**(4) 439
26. V M Ivanov, T V Rodionova, G F Bel'skaya, S V Makarova *Zh. Neorg. Khim.*, 1986, **31**(9) 2330 [English translation in *Russ. J. Inorg. Chem.*, 1986(9)]
27. T V Rodionova, V M Ivanov *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1986, **27**(5) 493
28. T H Handley *Anal. Chem.*, 1964, **36**(3) 2467
29. I V Seryakova, G A Vorob'eva, G F Bebikh, Yu A Zolotov *Zh. Anal. Khim.*, 1976, **31**(5) 845
30. A I Busev, A N Shishkov, N K Nikolov *Zh. Anal. Khim.*, 1975, **30**(1) 136
31. A I Busev, M I Ivanyutin *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1957, (5) 157
32. A I Busev, A N Shishkov *Zh. Anal. Khim.*, 1968, **23**(2) 181
33. L K Kobanova, S V Usova, P M Solozhenkin *Izv. Akad. Nauk Tadzh. SSR, Otd. Fiz-Mat. i Geol-Khim. Nauk*, 1971, (1) 47
34. M I Ivanyutin, A I Busev *Nauchn. Dokl. Vyssh. Shkol. Khimiya i Khim. Tekhnol.*, 1958, (1) 73
35. A I Busev, M I Ivanyutin *Zh. Anal. Khim.*, 1958, **13**(1) 18
36. A I Busev, A N Shishkov *Zh. Anal. Khim.*, 1968, **23**(11) 1675
37. V F Toropova, G K Budnikov, N A Ulakhovich *Talanta*, 1978, **25** 263
38. G K Budnikov, N K Shakurova, N A Ulakhovich, et al. *Zh. Anal. Khim.*, 1977, **32**(7) 1326
39. V F Toropova, M G Gabdullin, A R Garifzyanov, R A Cherkasov *Zh. Anal. Khim.*, 1984, **39**(2) 267
40. N A Ulakhovich, G K Budnikov, L G Fomina, T N Kolesnikova *Izv. Vuzov: Khimiya i Khim. Tekhnol.*, 1979, **22**(12) 1449
41. N A Ulakhovich, I V Postnova, G K Budnikov *Zh. Anal. Khim.*, 1985, **40**(8) 1502
42. N A Ulakhovich, G K Budnikov, N K Shakurova *Zavod. Lab.*, 1978, **44**(3) 270

43. N A Ulakhovich, I V Postnova, G K Budnikov *Zh. Obshch. Khim.*, 1983, **53**(4) 736
44. N A Ulakhovich, I V Postnova, G K Budnikov *Zh. Obshch. Khim.*, 1985, **55**(12) 2696
45. G K Budnikov, N A Ulakhovich *Usp. Khim.*, 1980, **49**(1) 147 [English translation in *Russ. Chem. Rev.*, 1980(1)]
46. A D Beloglazova, V K Krupnov *Zavod. Lab.*, 1969, **35**(4) 451
47. T V Rodionova, V M Ivanov, M S Sheikh, G V Kozyreva *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1985, **26**(4) 398
48. H Berndt, J Messerschmidt *Fresenius' Z. Anal. Chem.*, 1981, **308**(2) 104
49. T V Rodionova, V M Ivanov *Zh. Anal. Khim.*, 1986, **41**(12) 2181
50. T V Rodionova, L N Simonova, M S Sheikh *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1985, **26**(1) 70
51. T A Bol'shova, E N Shapovalova, G A Okuneva, et al. *Zh. Anal. Khim.*, 1989, **44**(2) 284
52. R H Zucal, J A Dean, T H Handley *Anal. Chem.*, 1963, **35**(8) 988
53. M I Kabachnik, S T Ioffe, T A Mastryukova *Zh. Obshch. Khim.*, 1955, **25**(4) 684
54. A I Busev, M I Ivanyutin, M F Turchinskii *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1957, (2) 177
55. V F Toropova, M K Saikina, R Sh. Aleshov *Zh. Obshch. Khim.*, 1967, **37**(3) 725
56. J P Chupp, P E Nevallis *J. Org. Chem.*, 1962, **27**(11) 3832
57. M I Kabachnik, T A Mastrukova, A E Shipov, T A Melentjeva *Tetrahedron*, 1960, **9**(1) 10
58. V F Toropova, R A Cherkasov, N I Savel'eva, A N Pudovik *Zh. Obshch. Khim.*, 1970, **40**(5) 1043
59. M G Gabdullin, A R Garifzyanov, V F Toropova *Zh. Neorg. Khim.*, 1984, **29**(9) 2420 [English translation in *Russ. J. Inorg. Chem.*, 1984(9)]
60. T A Mastryukova, L L Spivak, A A Grigor'eva, et al. *Zh. Obshch. Khim.*, 1971, **41**(9) 1938
61. V F Toropova, M K Saikina, N I Guseva, et al. *Zh. Obshch. Khim.*, 1968, **38**(9) 2088
62. A K De, S M Khopkar, R A Chalmers *Solvent Extraction of Metals*, Van Nostrand–Reinhold, New York, 1970, p. 19
63. R A Cherkasov, F M Batyrshina, E M Petrova, N V Kashina *XII Nauchnaya Sessiya po Khimii i Khimicheskoi Tekhnologii Organicheskikh Soedinenii Sery i Sernistykh Neftei: Tezisy Dokladov* (Abstracts of Reports at the XIIth Scientific Session on the Chemistry and Chemical Technology of Organic Sulphur Compounds and Sulphur-containing Oils), Riga, 1971, p. 19
64. V F Toropova, R A Cherkasov, N I Savel'eva, E I Petrova *Zh. Obshch. Khim.*, 1974, **44**(3) 531
65. S Wingefors *Acta Chem. Scand., Ser. A*, 1980, **34**(4) 301
66. M Curtui, G Marcu, I Haiduc *Stud. Univ. Babes-Bolyai, Chem.*, 1976, **21** 74
67. S Wingefors *Acta Chem. Scand., Ser. A*, 1980, **34**(4) 327
68. H Bode *Fresenius' Z. Anal. Chem.*, 1954, **142** 414
69. A N Shishkov *Nauchn. Tr. Ped. Inst. Plovdiv*, 1971, **9**(1) 101
70. T F Rodina, V I Varentsova, A N Kolyshev, I S Levin *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1973, (6) No. 14 14
71. V F Toropova, A R Garifzyanov, I E Panfilova, et al. *Zh. Obshch. Khim.*, 1984, **54**(10) 2200
72. S Wingefors *Acta Chem. Scand., Ser. A*, 1980, **34**(4) 289
73. J Stary, Ed. *The Solvent Extraction of Metal Chelates*, Pergamon Press, New York, 1964 (Translated into Russian), Izd. Mir, Moscow, 1966, p. 252
74. E M Popov, M I Kabachnik, L S Mayants *Usp. Khim.*, 1961, **30**(7) 846 [English translation in *Russ. Chem. Rev.*, 1961(7)]
75. A Menefee, D Alford, C B Scott *J. Chem. Phys.*, 1956, **25**(2) 370
76. S Wingefors *Acta Chem. Scand., Ser. A*, 1980, **34**(4) 297
77. M I Kabachnik, T A Mastryukova *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1953, (1) 121
78. I A Kakovskii, B A Stepanov, O F Ryazantseva, N V Serebryakova *Zh. Fiz. Khim.*, 1959, **33**(8) 1830 [English translation in *Russ. J. Phys. Chem.*, 1959(8)]
79. J H Fletcher, J C Hamilton, I Hechenbleikner, E I Hoegberg, et al. *J. Am. Chem. Soc.*, 1961, **72**(12) 2461
80. R F Makens, H-H Vaughan, R R Chelberg *Anal. Chem.*, 1955, **27**(7) 1062
81. M Curtui, I Haiduc, G Marcu *J. Radioanal. Chem.*, 1978, **44**(1) 109
82. N Abdusalyamov, A Ganiev, P Kh Nishanov, A I Busev *Zh. Anal. Khim.*, 1969, **24**(1) 69
83. K Hayashi, Y Sasaki, S Tagashira, et al. *Bunseki Kagaku*, 1984, **33**(5) 247
84. N Abdusalyamov, A G Ganiev, K Yuldasheva *Uzb. Khim. Zh.*, 1968, **12**(1) 20
85. U Khudaibergenov, K T Yuldasheva, A G Ganiev *Dokl. Akad. Nauk Uzb. SSR*, 1978, (11) 28
86. N Abdusalyamov, O G Murtazin, M M Usmanova *Radioaktivatsionnye Metody Analiza Ob"ektov Prirodnogo Proiskhozhdeniya* (Radioactivation Methods for the Analysis of Samples of Natural Origin), Izd. Filial Akad. Nauk Tashkent, 1980, p. 79
87. A G Ganiev, K T Yuldasheva, R N Gafurova, Kh R Rakhimov *Dokl. Akad. Nauk Uzb. SSR*, 1983, (2) 21
88. N Abdusalyamov, K T Yuldasheva, A G Ganiev, A I Busev *Zh. Anal. Khim.*, 1968, **23**(5) 716
89. T V Rodionova, V M Ivanov, L V Karavaeva, N A Chernova *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1988, **29**(2) 199
90. V I Severin, E E Rakovskii, Tr. TsNIGRI, 1973, (107) 135
91. W A Forster, P Brazenall, J Bridge *Analyst (London)*, 1961, 86(1023) 407
92. A Shishkov, D Atanosova *Nauchn. Tr. Vyssh. Ped. Inst. Plovdiv.*, 1975, **13**(3) 209
93. S Wingefors, J Rydberg *Acta Chem. Scand., Ser. A*, 1980, **34**(5) 313
94. T H Handley, R H Zucal, J A Dean *Anal. Chem.*, 1962, **34**(10) 1312
95. T V Rodionova, V M Ivanov, Dada Assefa *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1986, **27**(2) 205
96. Yu A Zolotov, G E Vlasova, E V Rybakova, et al. *Tsvet. Metally*, 1978, (1) 14
97. I S Levin, N A Balakireva, L A Novosel'tseva, V G Ponomareva *Zh. Anal. Khim.*, 1975, **30**(7) 1296
98. T A Udalova, Yu M Yukhin, O V Tarasova *Zavod. Lab.*, 1984, **50**(12) 1
99. I S Levin, N A Balakireva *Zh. Neorg. Khim.*, 1978, **23**(7) 1888 [English translation in *Russ. J. Inorg. Chem.*, 1978(7)]
100. V I Kuz'min, O A Logutenko, A I Khol'kin, A Yu Erastov *Zh. Neorg. Khim.*, 1986, **31**(10) 2613 [English translation in *Russ. J. Inorg. Chem.*, 1986(10)]

101. Yu A Zolotov, G E Vlasov, E V Rybakova *Zh. Prikl. Khim. (Leningrad)*, 1976, **49**(8) 1703
102. Yu M Yukhin, N E Kozlova, L A Novosel'tseva, I S Levin *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1974(3) No. 7 64
103. N A Balakireva, L A Novosel'tseva, I S Levin *Zh. Anal. Khim.*, 1975, **30**(4) 684
104. Yu M Samoilov, Yu M Yukhin, S S Shatskaya *Zh. Neorg. Khim.*, 1985, **30**(8) 2053 [English translation in *Russ. J. Inorg. Chem.*, 1985(8)]
105. I S Levin, O M Frid, T F Rodina *Zh. Neorg. Khim.*, 1977, **22**(10) 2816 [English translation in *Russ. J. Inorg. Chem.*, 1977(10)]
106. O M Talapova, I S Levin *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1981(2) No. 4 60
107. I S Levin, V I Varentsova, T F Rodina *Izv. Sib. Otd. Akad. SSSR, Ser. Khim. Nauk*, 1973,(3), No. 7 132
108. V I Varentsova, T F Rodina, I S Levin *Zh. Anal. Khim.*, 1973, **28**(6) 1086
109. V I Varentsova, T F Rodina, I S Levin, et al. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1974(4) No. 9 147
110. I S Levin, V V Sergeeva, L I Tishchenko *Zh. Anal. Khim.*, 1973, **28**(5) 962
111. I S Levin, V V Sergeeva, I A Vorsina *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1975(2) No. 4 107
112. Yu M Yukhin, I S Levin, G A Marinkina, A P Korzhov *Zh. Anal. Khim.*, 1979, **34**(1) 142
113. I S Levin, Yu M Yukhin, I A Bykhovskaya, et al. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1973(5), No. 12 83
114. I S Levin, V V Sergeeva, V A Tarasova, et al. *Zh. Neorg. Khim.*, 1973, **18**(6) 1643 [English translation in *Russ. J. Inorg. Chem.*, 1973(6)]
115. Yu M Samoilov, I S Levin *Zh. Neorg. Khim.*, 1979, **24**(9) 1993 [English translation in *Russ. J. Inorg. Chem.*, 1979(9)]
116. L Ya Shubov, I B Zalesnik, S I Mitrofanov, et al. *Tsvet. Metally*, 1975, (11) 84
117. A I Potapova, M K Zhekeev, A I Dzhurumbaev *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.*, 1986, (3) 10
118. A N Turanov, I N Kremenskaya *Zh. Neorg. Khim.*, 1978, **23**(9) 2481 [English translation in *Russ. J. Inorg. Chem.*, 1978(9)]
119. V A Tarasova, I S Levin *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1974(3), No. 7 59
120. I S Levin, V A Tarasova *Zh. Anal. Khim.*, 1973, **28**(7) 1341
121. I S Levin, V L Kheifets, L M Gindin *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk*, 1973(5), No. 12 117
122. L M Gindin, L M Kuznetsova, A I Khol'kin *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk*, 1972(6), No. 14 126
123. N A Borshch, O M Petrukhin, Yu A Zolotov *Zh. Anal. Khim.*, 1978, **33**(6) 1120
124. T A Udalova, Yu M Yukhin, S S Shatskaya *Zh. Anal. Khim.*, 1984, **39**(4) 659
125. I S Levin, V V Sergeeva *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk*, 1974(3), No. 7 53
126. O M Petrukhin, G I Malofeeva *Teoriya i Praktika Ekstraktsionnykh Metodov* (The Theory and Practice of Extraction Methods), Izd. Nauka, Moscow, 1985, p.246
127. A N Shishkov *Nauchn. Tr. Vyssh. Ped. Inst. Plovdiv*, 1969, **7**(1) 129
128. A I Busev, A N Shishkov *Nature (Plovdiv)* 1970, **3**(1) 71
129. A N Shishkov, D Atanasova, A Georgieva *Nauchn. Tr. Vyssh. Ped. Inst. Plovdiv*, 1975(1976), **13**(3) 199
130. A I Busev, A N Shishkov, N K Nikolov *Nature (Plovdiv)*, 1968, **2**(1) 55
131. G E Vlasova, E V Rybakova, A R Garifzyanov, et al. *Zh. Neorg. Khim.*, 1981, **26**(8) 2204 [English translation in *Russ. J. Inorg. Chem.*, 1981(8)]
132. T H Handley *Anal. Chem.*, 1963, **35**(8) 991
133. P I Artyukhin, E A Startseva, I L Kotlyarevskii, Z M Bobrova *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk*, 1971(4), No. 9 131
134. USSR P. 699 804; *Byull. Izobret.*, 1980(37), 316
135. A G Pilipenko, A L Rozenfel'd *Ukr. Khim. Zh (Russ. Ed.)*, 1970, **36**(11) 1151
136. L M Kuznetsova, L M Gindin, A I Khol'kin *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk*, 1973(1), No. 2 42
137. L M Kuznetsova, L M Gindin, A I Khol'kin, et al. *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk*, 1973(6), No. 14 29
138. C K Jörgensen *Inorganic Complexes*, Acad. Press, New York–London, 1963, p. 133
139. A N Shishkov, A I Busev *Nature (Plovdiv)*, 1970, **3**(1) 77
140. I S Levin, V V Sergeeva, T F Rodina, et al. *Gidrometallurgiya. Avtoklavnoe Vyshchelachivanie, Sorbtsiya, Ekstraktsiya* (Hydrometallurgy: Autoclave Leaching, Sorption, and Extraction), Izd. Nauka, Moscow, 1976, p. 211
141. V F Toropova, A R Garifzyanov, I E Panfilova, R A Cherkasov *Zh. Obshch. Khim.*, 1985, **55**(11) 2547
142. V F Toropova, A R Garifzyanov, V V Ovchinnikov *XIV Vsesoyuznoe Chugaevskoe Soveshchanie po Khimii Kompleksnykh Soedinenii: Tezisy Dokladov* (Abstracts of Reports at the XIVth All-Union Chugaev Conference on the Chemistry of Complex Compounds), Ivanovo, 1981, Part 2, p. 474
143. V F Toropova, R A Cherkasov, N I Savel'eva, et al. *Zh. Obshch. Khim.*, 1971, **41**(8) 1673
144. O M Petrukhin, N A Borshch *Koord. Khim.*, 1982, **81**(1) 22
145. Yu B Kletenik, S A Sedova *Zh. Prikl. Khim. (Leningrad)*, 1983, **56**(7) 1510
146. S A Sedova, Yu B Kletenik *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk*, 1976(5), No. 12 73
147. G N Dolenko, A I Khol'kin, A S Chernobrov, et al. *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk*, 1979(1), No. 2 32
148. A I Khol'kin, A S Chernobrov, L M Gindin, et al. *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk*, 1976(5), No. 12 68
149. USSR P. 699 806; *Byull. Izobret.*, 1980(37)
150. S A Sedova, V A Navrotskaya, Yu B Kletenik *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk*, 1984(6), No. 17 98
151. G Marcu, M Curtui, I Haiduc *J. Inorg. Nucl. Chem.*, 1977, **39**(8) 1415
152. M Curtui, I Haiduc *J. Radioanal. Nucl. Chem. Lett.*, 1984, **16**(5) 281
153. V P Khrapai, E A Startseva, L E Zhuravleva, N M Popova *Zh. Anal. Khim.*, 1974, **29**(11) 2137
154. Yu M Yukhin, I S Levin, B Sh Litvinova *Zh. Anal. Khim.*, 1975, **30**(6) 1091
155. T V Rodionova, V M Ivanov, L V Karavaeva, I P Efimov *Zh. Anal. Khim.*, 1989, **44**(6)
156. V V Sergeeva, I S Levin, L I Tishchenko, V S Dan'kova *Zh. Anal. Khim.*, 1973, **28**(11) 2188
157. Yu M Yukhin, I S Levin, N M Meshkova *Zh. Anal. Khim.*, 1975, **30**(1) 99