184. G. O. Schenck, Naturwiss., 35, 28 (1948).
185. G. O. Schenck and K. G. Kinkel, Naturwiss., 38, 355, 503 (1951).
186. G. O. Schenck, Naturwiss., 40, 205, 229 (1953).
187. G. O. Schenck and E. Koch, Z. Elektrochem., 64, 170 (1960).
188. G. O. Schenck, Z. Elektrochem., 64, 997 (1960).
189. E. J. Bowen and D. W. Tanner, Trans. Faraday Soc., 51, 475 (1955).
190. E. J. Bowen, "The Photochemistry of Aromatic Hydrocarbon Solutions", in "Advances in Photochemistry", Vol. I, Interscience, New York, 1963, p. 23.
191. G. O. Schenck, H. Eggert, and W. Denk, Annalen, 584, 177 (1953).
192. G. O. Schenck, German P. 933 925 (1943); Chem. Zentr., 3998 (1956).
193. G. O. Schenck, K. Gollnick, and O. A. Neumüller, Annalen, 603, 46 (1957).
194. G. O. Schenck, O. A. Neumüller, and W. Eisfeld, Annalen, 618, 202 (1958).
195. G. O. Schenck and O. A. Neumüller, Annalen, 618, 194 (1958).
196. G. O. Schenck and K. H. Schulte-Elte, Annalen, 618, 185 (1958).
197. G. O. Schenck, S. Schroeter, and G. Ohloff, Chem. and Ind., 459 (1962).
198. G. O. Schenck, K. Gollnick, G. Buchwald, G. Ohloff, G. Schade, and S. Schroeter, Angew. Chem., 76, 582 (1964).
199. G. O. Schenck, K. Gollnick, G. Buchwald, S. Schroeter, and G. Ohloff, Annalen, 674, 93 (1964).
200. K. Gollnick and G. O. Schenck, Pure Appl. Chem., 9, 507 (1964).
201. A. Nickon and J. F. Bagli, J. Amer. Chem. Soc., 81, 6330 (1959); 83, 1498 (1961).
202. R. L. Kenney and G. S. Fischer, J. Amer. Chem. Soc., 81, 4288 (1959).
203. R. L. Kenney and G. S. Fischer, J. Org. Chem., 28, 3509 (1963).
204. H. Kautsky and H. de Bruijn, Naturwiss., 19, 1043 (1931).
205. H. Kautsky, H. de Bruijn, R. Neuwirth, and W. Baumeister, Ber., 66, 1588 (1933).
206. H. Kautsky, Biochem. Z., 291, 271 (1937).
207. J. L. Rosenberg and D. J. Shombert, J. Amer. Chem. Soc., 82, 3257 (1960).
208. J. Corey and W. C. Taylor, J. Amer. Chem. Soc., 86, 3881 (1964).
209. C. S. Foote and S. Wexler, J. Amer. Chem. Soc., 86, 3880 (1964).
210. S. N. Foner and R. L. Hudson, J. Chem. Phys., 25, 601 (1956).
211. G. Bernhardt and F. Korte, Angew. Chem., 77, 133 (1965).
212. Chem. Eng. News, 43, No. 16, 41 (1965).

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THE EXTRACTION OF HETEROPOLY-COMPOUNDS AND ITS APPLICATION IN INORGANIC ANALYSIS

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CONTENTS

I. Introduction 574
II. Brief historical review 575
III. General characteristics of the extraction of heteropoly-compounds 575
IV. Mechanism of the extraction of heteropoly-compounds 576
V. Chief factors influencing the extraction of heteropoly-compounds 577
VI. Analytical application of the extraction of heteropoly-compounds 580

I. INTRODUCTION

In recent years, in the analytical determination of silicon, phosphorus, and arsenic, small quantities of which are most reliably determined by photometric measurements on their heteropoly-acids, increasing use has been made of the extraction of these heteropoly-acids by organic solvents.

The increasing introduction of the extraction method in the field of heteropoly-compounds cannot be attributed entirely to the general and nowadays widely known advantages of this method. Certain particular advantages of the extraction method are shown to a greater extent by heteropoly-compounds than by any other types of compounds. In this connection it is sufficient to mention two features.

A serious disadvantage of all analytical methods based on photometric measurements on molybdenum heteropoly-compounds (particularly their reduced blue forms) is the superposition of the light absorption of the reagent itself — molybdate; the use of extraction makes possible the ready and reliable elimination of the influence of molybdate, since isopolymolybdate, unlike heteropolymolybdates, is generally not extracted by organic solvents.

Another frequent obstacle to the analytical application of heteropoly-compounds is the instability of the light absorption of the solutions taken for the photometric measurements. This is due to the existence of complex equilibria in aqueous solutions of the heteropoly-compounds, which are extremely sensitive to very small changes in the conditions. The solutions obtained as a result of extraction of the heteropoly-compound by organic solvents are much more stable than the aqueous solutions.

The study of the extraction behaviour of heteropoly-compounds, apart from its analytical value[1-4], is also of undoubted interest from other viewpoints.

The most important method for the preparation of the heteropoly-acids of most elements is the ether method, based on separation of the heteropoly-acids from acidified solutions of their salts by means of diethyl ether[4].

Extraction may provide a valuable method for studying the physicochemical properties of heteropoly-compounds, for which reliable experimental methods are still urgently required[5].

The combination of the most varied properties in a single chemical individual, so characteristic of heteropoly-compounds, is a favourable factor in obtaining useful and concentrated information on the theory of extraction when these compounds are chosen as objects for study (models).

II. BRIEF HISTORICAL REVIEW

The first information on the behaviour of heteropoly-compounds towards organic solvents appeared in papers by Marignac[6], Parmentier[7], and Sobolev[8], who studied various physicochemical properties of tungstosilicic, molybdophosphoric, and tungstophosphoric acids, including their solubility in diethyl ether.

Drechsel[9] was the first to make use of the solubility of heteropoly-acids in diethyl ether for their isolation in the free state. The ethereal extraction method for the preparation of heteropoly-acids became a classical method, and was later studied in detail by Scroggie[10], who showed the possibility of replacing diethyl ether by other oxygen-containing organic solvents.

The first views on the mechanism of the extraction of heteropoly-acids by diethyl ether were put forward by Rosenheim[11], and the composition of the compound extracted (for the case of molybdophosphoric acid) was first studied by Copaux[12]. A detailed study of the quaternary system molybdophosphoric acid–sulphuric acid–water–diethyl ether was made by Souchay[13]. Extensive studies of equilibria in the systems formed by saturated heteropoly-acids with organic solvents were made by Nikitina and her coworkers; the results of these studies are described in a recently published monograph[4].

The analytical application of the extraction of heteropoly-acids by organic solvents was begun in work by Denigès[14], who pointed out the possibility of making use of the extraction of the reduced forms of molybdophosphoric and molybdoarsenic acids by diethyl ether or pentanol for the qualitative detection of phosphorus and arsenic†. The extraction of heteropoly-acids was first used for quantitative analysis by Copaux[12], who determined the concentration of phosphorus in native phosphates by measuring the volume of an ethereal extract of molybdophosphoric acid. The first extraction–colorimetric method of analysis using heteropoly-compounds was developed by Shneerson[16] for the determination of phosphorus in steels: the method involves the extraction of reduced molybdophosphoric acid by diethyl ether, followed by colorimetric measurements on the extract using a standard series. The use of extraction for the quantitative separation of elements as the heteropoly-acids was first carried out by Alekseev[17] in the analysis of phosphate–arsenate–silicate mixtures. Of considerable importance for the development of extraction methods for the separation and determination of elements as their heteropoly-compounds were the ideas of Keggin[18], and also the work of Berenblum and Chain[19], Allen[20], Proctor and Hood[21], and Wadelin and Mellon[22].

Bibliographies on the extraction of heteropoly-compounds and its use in chemical analysis are to be found in monographs[4,23] and reviews[3,24-29] on the chemistry of heteropoly-compounds, in a monograph[2] and reviews[1,30-42] on the extraction of inorganic compounds, in textbooks on the photometric determination of elements[43-46], in reviews of the analytical chemistry of phosphorus[47-51] and silicon[52-54], and also in a number of original papers[22,55-62].

As far as we are aware, the present review is the first attempt to systematise the available published material.

† Earlier, Jacobs[15] had made use of the extraction of molybdophosphoric acid by pentanol to remove this acid from the mother-liquor after the precipitation of tungstophosphates, but this work was preparative rather than analytical.

III. GENERAL CHARACTERISTICS OF THE EXTRACTION OF HETEROPOLY-COMPOUNDS

Heteropoly-acids and their salts are extracted from acidified aqueous solutions by oxygen-containing organic solvents (alcohols, ethers, esters, ketones, and aldehydes)[2-4,10,17,18,22-29,49,53,62-73]. They are not extracted by solvents containing no oxygen (hydrocarbons, halogenohydrocarbons, carbon disulphide, petroleum ether), but solutions of nitrogen-containing compounds (amines) in non-polar solvents (benzene or chloroform) are excellent extracting agents for heteropoly-compounds[57,74,75]. Thus the effective extraction of heteropoly-compounds requires the presence of a basic oxygen or nitrogen atom in the molecule of the organic extractant.

Of the binary heteropoly-acids of molybdenum, the most readily extracted is molybdophosphoric acid; the ease of extraction of the heteropoly-acids studied decreases in general in the order: molybdophosphoric > molybdoarsenic > molybdosilicic > molybdogermanic. It is difficult as yet to say anything definite about the extraction behaviour of other known heteropoly-acids of molybdenum, since they have been little studied in this connection (there are only a few data on the extraction of molybdoceric[76,77], molybdotitanic[78], and molybdozirconic[78] acids).

The behaviour of binary heteropoly-acids of tungsten towards organic solvents is in general similar to that of their molybdenum analogues. This is indicated by the scant but fairly convincing experimental data on the extraction of tungstophosphoric (diethyl ether[8,15,79,80] and pentanol[15,79]), tungstosilicic (diethyl ether[6,9,10], ethyl acetate, etc.[10]), and tungstogermanic (diethyl ether[81], butanol[82], ethyl acetate[82]) acids.

The appearance of a third element in the structure of the heteropoly-complex (in addition to the two necessary elements other than oxygen and hydrogen) also produces no fundamental change in the behaviour of the heteropoly-complex towards organic solvents. The available published data on the extraction of molybdovanadophosphoric[83-93], tungstovanadophosphoric[71,94,95], tungstoarsenophosphoric[96], molybdovanadogermanic[81,82,97], tungstovanadogermanic[81,82], molybdotitanophosphoric[73,98,99], and molybdoniobophosphoric[100,101] acids indicate that ternary heteropoly-compounds are in general readily extracted by oxygen-containing solvents, but are not extracted by solvents containing no oxygen. The ternary heteropoly-acids, for example molybdoniobophosphoric[100], molybdotitanophosphoric[73], and telluromolybdophosphoric[102] acids, however, are not extracted by certain oxygen-containing solvents, in particular butyl acetate. The extraction behaviour of ternary heteropoly-acids possibly depends on whether the third component is the central atom in the structure of the complex or is present in the ligand part of the complex.

The extraction behaviour of reduced heteropoly-compounds, judging from the few data relating to this field[57,69,70,72,75], does not differ in principle from that of the unreduced heteropoly-compounds. This is a further indication that the structures of the reduced (blue) and unreduced (yellow) forms of the heteropoly-compounds are identical[103].

The extraction of heteropoly-compounds, like any process, depends to a marked extent on the conditions, and is influenced by various factors, of which the most important — the nature of the compound being extracted, the nature of the solvent, the acidity of the aqueous phase, the con-

centration of the compound being extracted in the aqueous phase, the presence of neutral salts, and the temperature — are of considerable significance for the utilisation of the extraction of heteropoly-compounds in chemical analysis, and will be examined in more detail below.

The physicochemical properties of extracts of heteropoly-compounds have been little studied: only a few data relating to their optical characteristics are available. The extracts of both reduced and unreduced heteropoly-compounds retain the colour characteristic of their aqueous solutions (blue and yellow respectively). The general appearance of the absorption spectra of the extracts remains unchanged in both cases[21,22,58,59,67,72,82,104-116], but the light-absorption maxima for the heteropoly-compounds in organic solvents are generally displaced slightly towards shorter wavelengths compared with the maxima of the same heteropoly-compounds in aqueous solutions. For example, unreduced molybdophosphoric acid in aqueous solution shows a light-absorption maximum at 345 mμm[49], and the reduced form shows maxima at 630 and 735 mμm[49]; the corresponding maxima for the same acid in organic solvents lie at 310 mμm[22,59,109,110], or 625 and 725 mμm[21,104,109,111]. Unreduced molybdosilicic acid in aqueous solution has an absorption maximum at 350–355 mμm[53], and the reduced form a maximum at 800–820 mμm[53]; the corresponding maxima for the same acid in organic solvents lie at 330 mμm[22,58], or 630 and 720 mμm[112].

The composition of the forms in which the heteropoly-acids are extracted (the extractable forms) has not been specially studied. Fairly convincing experimental data indicate, however, that at a comparatively low acidity ($< 2\ N$), when the possibility of the extraction of isopoly-molybdate is excluded, the stoichiometric composition of molybdophosphate in ethyl acetate[117], butyl acetate[59], and butanol–chloroform[118] extracts corresponds to a constant P : Mo ratio of 1 : 12; this ratio remains unchanged even for the extraction of molybdophosphoric acid with insufficient molybdate[117]. These data indicate that the molybdophosphate complex enters the organic phase in the form of the dodecamolybdophosphoric acid or its salt. An interesting feature is that sodium is extracted into ethyl acetate together with phosphorus and molybdenum in the proportions Na : P : Mo = 2.1 : 1 : 11.9 and 0.7 : 1 : 11.19, depending on the acidity[177]; it is possible that in this case an acid sodium salt of molybdophosphoric acid is extracted.

The increase in the distribution coefficient, for molybdophosphoric and molybdosilicic acids between aqueous solution and butanol, with dilution of the aqueous heteropoly-acid solutions indicates indirectly that the monomeric form of the heteropoly-acids enters the organic solvent during extraction[119,120], since dilution of aqueous solutions of the heteropoly-acids leads to depolymerisation of these acids to forms of low molecular weight. The increase in the extractability of molybdophosphoric and molybdosilicic acids with increase in the hydrogen-ion concentration in the aqueous phase may indicate the preferential extraction of these acids in the undissociated (molecular) form in accordance with the equilibrium[119]

$$\begin{array}{l}(H_nA)_m \rightleftarrows mH_nA \rightleftarrows nH^+ + A^{n-} \text{ (in water)},\\ \quad\downarrow\uparrow\\ \quad H_nA \qquad\qquad \text{(in butanol)}.\end{array} \qquad (1)$$

The results of experiments on light-scattering by solutions of tungstophosphoric acid in various organic solvents[121] are of interest in this connection. The molecular weight of tungstophosphoric acid in ethanol and allyl alcohol, determined by the light-scattering method, was found to have the values 2600 and 2900 respectively, showing good agreement with the formula weight for $H_3PW_{12}O_{40}$ (2880) and indicating that tungstophosphoric acid is monomeric in these solvents.

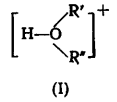
It is quite probable that the formation of a true (molecular) solution as a result of the extraction of heteropoly-compounds by organic solvents is one of the reasons for the greater stability of the organic extracts of heteropoly-compounds (particularly the reduced forms) compared with their aqueous solutions, which, according to some authors[115,122,123], are colloidal solutions and thus have a tendency to undergo gradual decomposition on standing (particularly at high concentrations).

IV. MECHANISM OF THE EXTRACTION OF HETEROPOLY-COMPOUNDS

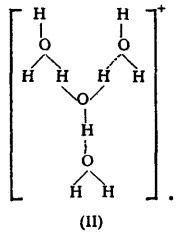
Various suggestions have been made regarding the mechanism of the extraction of heteropoly-compounds by organic solvents, but none has been confirmed by special experimental studies.

The earliest suggestion was that oxygen-containing organic solvents (in particular diethyl ether) extract heteropoly-compounds from acidic solutions with the formation of alkyl-substituted oxonium salts (etherates)[11]. If the acidity is not too high, or the solvent present in large excess, only part of the oxygen-containing solvent enters the oxonium salt and the latter dissolves in the excess of solvent, to which it is structurally similar. This mechanism, known as the oxonium mechanism, accounts well for the most important necessary conditions for the extraction of heteropoly-compounds — the presence of an acid medium and of an oxygen-containing solvent.

The oxonium-mechanism theory, previously used to explain many other examples of extraction[30], has recently been subjected to serious criticism. The main assumption in this theory, that the proton of the acid is attached directly to the oxygen atom of the organic solvent with the formation of an oxonium (solvonium) cation (I) is unjustified in a number of cases. Experimental data which have accumulated in recent years on the extraction of strong acids suggest that the main reaction in this case is attachment of the proton of the acid to the oxygen atom of water, with the formation of a hydroxonium cation, which in turn is hydrated by several water molecules (II); the organic solvent is attached to the water molecules polarised in the field of the hydroxonium ion. This extraction mechanism, which has been called the hydrate–solvate mechanism[124,125], has unfortunately not yet been verified for heteropoly-compounds.



(I)



(II)

According to another suggestion, the extraction of heteropoly-compounds with oxygen-containing solvents is

accompanied by formation of a coordination compound between a molecule of the organic solvent (as electron donor) and the anion of the heteropoly-acid (as electron acceptor)[65]; the compound formed in this way is covalent, and dissolves more readily in the organic solvent than in water. In the formation of coordination compounds of this type, a direct part is apparently played by the electronegative oxygen atom of the organic solvent and a molybdenum atom of the heteropoly-anion, which in this case shows a coordination number of 8. This mechanism readily explains cases of the extraction of heteropoly-compounds by non-polar solvents (chloroform or benzene) using amines and other compounds with marked basic (electron-donating) properties[74].

Both of these suggestions regarding the mechanism of the extraction of heteropoly-compounds are based on the assumption that a donor–acceptor interaction takes place between the heteropoly-compound and the extracting agent; the difference lies in which part (cationic or anionic) of the heteropoly-compound reacts with the extracting agent.

Another suggestion is based on the assumption that the extraction of heteropoly-compounds involves physical distribution, in which the heteropoly-compounds are distributed between the aqueous phase (in ionised form) and the organic phase (in molecular form) as a result of the difference in their solubilities in water and the organic solvent, without the formation of saltlike compounds with the latter[30]. This mechanism explains fairly simply certain regular features observed in the extraction of heteropoly--compounds, for example the salting-out action of salts.

Finally, it is also possible that the extraction of heteropoly-compounds involves a so-called colloid-chemical mechanism, in which the compound being extracted is transferred from the aqueous phase to the organic phase in the form of highly dispersed colloidal particles[126].

The data at present available on the mechanism of the extraction of heteropoly-compounds do not make it possible to give preference to any of the above mechanisms. Most of the experimental facts relating to the extraction of heteropoly-compounds are explained equally satisfactorily on the basis of any of these mechanisms; at the same time there are a number of facts which are explained by none of them. For example, the extractability of heteropoly-compounds by amines of high molecular weight dissolved in inert solvents can be interpreted in terms of any of the above mechanisms, but it can also be understood without recourse to them, simply on the basis of the generally accepted anion-exchange mechanism of extraction with amines[127].

V. CHIEF FACTORS INFLUENCING THE EXTRACTION OF HETEROPOLY-COMPOUNDS

1. Nature of the Compound Being Extracted

The extractability of binary heteropoly-compounds (of molybdenum and tungsten) depends to a considerable extent on the nature of the central atom (phosphorus, arsenic, silicon, germanium, etc.). The difference in the extraction behaviour of heteropoly-compounds is revealed as a difference in the percentage extraction for the same solvent and differences in the number of solvents suitable for the extraction.

Heteropoly-acids having quinquevalent elements (phosphorus and arsenic) as central atoms are extracted much more readily than those with quadrivalent elements (silicon, germanium, cerium, etc.). For example, the degree of extraction of molybdophosphoric acid by organic solvents from aqueous solutions of pH 1, is 100% for pentyl acetate, 70% for dibutyl ether, 54% for hexyl butyrate, 50% for diethyl ether, 8% for isopentyl acetate, and 5% for ethyl acetate, n-propyl acetate, isopropyl acetate, n-butyl acetate, and isobutyl acetate; molybdosilicic acid undergoes almost no extraction by any of these solvents under the same conditions[68].

Comparison of the extractability of molybdophosphoric and molybdoarsenic acids (Table 1) shows clearly that the former acid is more readily extracted.

Comparison of the molybdenum heteropoly-acids of quadrivalent elements, for example with respect to their behaviour towards diethyl ether, reveals a clearly defined order: silicon > germanium > titanium > zirconium > > cerium > thorium[78]. The heteropoly-acids of the first three elements are prepared by the ether method: i.e. they are extracted by diethyl ether. But the heteropoly-compounds of the last three elements cannot be prepared by the ether method, since they are not extracted by diethyl ether. The poor extractability of molybdoceric acid (compared with molybdosilicic and molybdogermanic acids) has also been demonstrated for other solvents[76,77].

It is difficult on the basis of data at present available to follow the difference in extraction behaviour between binary heteropoly-acids of tungsten and molybdenum. In the case of the ternary heteropoly-acids, however, it can be definitely stated that the introduction of a third component into the molecule of the heteropoly-acid generally leads to a decrease in the ability of the acid to undergo extraction by organic solvents. Even with molybdovanadophosphoric and tungstovanadophosphoric acids, the range of solvents is slightly restricted (compared with that for the binary acids of phosphorus), and acids such as molybdoniobophosphoric[100], molybdotitanophosphoric[73], and telluromolybdophosphoric[102] acids are not extracted at all, for example, by butyl acetate or isobutyl acetate. Here, of course, a significant feature is the part played by the newly introduced third component, i.e. whether it is the central atom or part of a ligand.

The regular features of the influence of the nature of the central atom have also been observed for reduced heteropoly-acids[69]. The reduced heteropoly-compounds are apparently extracted slightly more readily than their unreduced analogues[69,70,72]. In this case an important part is undoubtedly played by the nature of the reducing

TABLE 1. Extraction of molybdophosphoric and molybdoarsenic acids by various solvents[62].

Solvent	Percentage extraction	
	P–Mo	As–Mo
Ethyl acetoacetate	100.00	96.67
Butanol + chloroform (1 : 4)	94.97	4.74
Ethyl acetate	79.92	29.46
Butyl acetate	73.58	8.49
Isobutanol + benzene (1 : 1)	72.63	36.76
Isobutanol	67.21	86.05
Butanol	60.63	87.91
Octanol	29.86	14.39
Chloroform	00.00	00.00
Benzene	00.00	00.00

agent; recent data[128] suggest that organic solvents are extremely sensitive to the slightest changes in the process of heteropoly-compound reduction and to the reduction products.

The extractability of heteropoly-acids (reduced and unreduced) increases sharply when basic substances (for example amines) are introduced into the system[57,74,75], i.e. when conditions are created for the formation and extraction of the salts of the heteropoly-acids with organic bases (sometimes called "addition products"). As noted above, in this case inert solvents of the benzene and chloroform type may act as extractants for heteropoly--compounds.

2. Nature of the Solvent–Extractant

According to Alekseev[17], organic solvents can be divided into two groups — light (sp. gr. < 1) oxygen-containing solvents (alcohols and ethers), and heavy (sp. gr. > 1) solvents containing no oxygen (chloroform and carbon tetrachloride) — according to their behaviour towards heteropoly-compounds. Such compounds dissolve much more readily in solvents of the first group than in water, and are therefore readily extracted by these solvents from aqueous solutions; heteropoly-acids are almost insoluble in solvents of the second group. The extracting power of solvents of the first group decreases when solvents of the second group are added; the decrease is proportional to the quantity of inert solvent added, and is different for different heteropoly-acids.

The results of a large number of studies[17,22,55,60-73,114] show that, for heteropoly-compounds, alcohols are the most effective extractants and ethers the most selective. Of the aliphatic alcohols, the best extracting properties are shown by those containing 4–8 carbon atoms: lower alcohols do not extract heteropoly-compounds quantitatively from aqueous solutions, and higher alcohols from stable emulsions, which are difficult to remove, at the phase boundary.

The addition of a second solvent (usually inert) to the main solvent (usually containing oxygen), in addition to changing the solvent power of the main solvent, sometimes ensures a distinct boundary of separation between the phases, decreases the mutual solubility of the solvents in the extraction system, improves certain operating parameters of the extracting agent, etc. These advantages of mixed solvents are of course not specific for heteropoly--compounds, but are nevertheless of considerable interest for the application of the extraction of heteropoly-compounds in chemical analysis, and they will be examined in more detail below.

3. Acidity of the Aqueous Phase

The extraction of heteropoly-compounds is sensitive to change in the acidity of the aqueous phase (Table 2). At low acidities, heteropoly-compounds are extracted only to a slight extent or not at all; their solubility in organic solvents generally increases with increase in the acidity of the aqueous phase. The upper limit of acidity is determined by the stability of the given heteropoly-complex at high acidities, although the optimum range of acidity for extraction does not always overlap the optimum range of acidity for stability of the heteropoly-complex, and is usually wider.

TABLE 2. Influence of acidity on the extraction of molybdoarsenic acid by butanol[129].

10 M HCl added, ml	Optical density of extract (400 μg As) at 370 mμm		
	for test soln. (D_1)	for blank soln. (D_0)	true ($D_1 - D_0$)
0.25	0.735	0.401	0.334
0.50	0.556	0.146	0.410
0.75	0.536	0.031	0.505
1.00	0.559	0.027	0.532
1.33	0.569	0.029	0.540
1.50	0.573	0.029	0.544
1.67	0.574	0.032	0.542
2.00	0.570	0.025	0.545
2.50	0.139	0.015	0.124
5.00	0.031	0.011	0.020

The optimum acidity for the extraction of heteropoly--acids by different solvents varies considerably for the different cases studied: the range corresponds to 0.01–2.0 N with respect to a strong acid in the aqueous phase for molybdophosphoric acid[16,19,58,59,66,67,106,109,117,118,130-133], pH 1.0–1.3 for molybdoarsenic acid[130,134], 0.25–6.0 N for molybdosilicic acid[58,67,74,108,112,114,135], 0.8–3.0 N for molybdogermanic acid[107], 0.4–1.6 N for molybdovanadophosphoric acid[89,90], 0.3–0.8 N for tungstovanadophosphoric acid[95], 0.5–1.0 N for tungstovanadosilicic acid[136], and 3.6–5.4 N for molybdovanadogermanic acid[97].

If it is assumed that the organic solvent extracts the monomeric form of the heteropoly-acid, and that the heteropoly-acid dissociates to form ions only in aqueous solution, it is possible to examine theoretically the dependence of the distribution coefficient for the heteropoly-acid on the hydrogen-ion concentration in the aqueous phase[60].

If we denote the heteropoly-acid by H_nA, its dissociation constant by K_i, and the distribution constant by P, we obtain

$$K_i = \frac{[H^+][H_{n-i}A^{i-}]}{[H_{n-i+1}A^{-i+1}]} \qquad (1)$$

and

$$P = \frac{[H_nA]_{org}}{[H_nA]_{aq}}. \qquad (2)$$

The distribution coefficient is

$$D = \frac{[H_nA]_{org}}{\sum_{i=0}^{n} [H_{n-i}A^{i-}]_{aq}}. \qquad (3)$$

Putting $i = p$ in Eqn. (1) and making use of (2), we find that

$$[H_{n-p}A^{-p}]_{aq} = \frac{1}{P} \times \frac{\prod_{i=1}^{p} K_i}{[H^+]^p_{org}} \times [H_nA]_{org}. \qquad (4)$$

Substitution of (4) in (3) gives finally

$$D = \frac{P}{1 + \sum_{p=1}^{n} \frac{\prod_{i=1}^{p} K_i}{[H^+]^p}}. \qquad (5)$$

When the values of K_i and P are fixed (for a given heteropoly-acid), D is thus a function of $[H^+]$: i.e.

$$\log D = f(pH). \qquad (6)$$

Despite the fact that in the derivation of formula (5) no allowance was made for the influence of ionic strength, the mutual solubility of the solvents, temperatures, polymerisation, and other factors, the observed extraction

behaviour of molybdophosphoric and molybdosilicic acids conforms to the relationships predicted on the basis of this formula[60].

The nature of the acid used has no significant influence on the extraction of molybdophosphoric[117] and molybdoarsenic[137] acids, but in the case of molybdosilicic acid[135] the optimum range of acidity for extraction is different with hydrochloric, nitric, and sulphuric acids. The dependence of the extraction on the nature of the acid is even more marked with ternary heteropoly-acids; for example, tungstovanadophosphoric acid is extracted quantitatively by ethyl methyl ketone from hydrochloric and sulphuric acids, but is incompletely extracted from nitric acid, and is not extracted at all from perchloric acid medium[95].

4. Concentration of Compound Being Extracted

In the extraction of heteropoly-acids by organic solvents from relatively dilute aqueous solutions, the distribution coefficient at first increases, and then decreases, with increase in the concentration of the heteropoly-acid in the aqueous phase[119,120]. These observations can be explained on the assumption that the organic solvents extract the undissociated monomeric forms of the heteropoly-acids. The initial increase in the distribution coefficient is apparently due to the gradual suppression of the dissociation of the heteropoly-acid with increase in its concentration in the aqueous phase, and the subsequent decrease in the distribution coefficient is due to the increase in the polymerisation of the acid.

At a comparatively high concentration of heteropoly-acid, e.g. molybdophosphoric acid, in the aqueous phase, the extraction (for instance by diethyl ether) gives a heavy oily liquid (a saturated solution of the heteropoly-acid in ether), which is usually present in a three-layer system in equilibrium with the pure organic solvent (ether) and water (or aqueous mineral acid solution)[6,7,14,15]. The addition of crystalline heteropoly-acid to this three-layer system leads to the gradual disappearance of the liquid ethereal phase; further addition of the solid heteropoly-acid leads to mixing of the aqueous and etherate phases, with the formation of a single liquid phase in equilibrium with the solid heteropoly-acid, which separates in the form of a hydrate with 14 molecules of water[13].

5. Presence of Neutral Salts (Electrolytes)

Neutral salts (NaCl, $NaNO_3$, Na_2SO_4, etc.) in low concentrations (1–3%) have no significant influence on the extraction of heteropoly-compounds[138]. The distribution coefficients of molybdosilicic and molybdophosphoric acids decrease at moderate concentrations (< 1 M) of NaCl[60] or $NaNO_3$.[120]

At high concentrations, neutral salts increase the distribution ratios of heteropoly-acids, apparently as a result of a salting-out effect[119,120]. The salt effect depends on the pH of the aqueous phase[60,139], but is apparently independent of the nature of the heteropoly-acid. This last feature often leads to a levelling of the extraction of different heteropoly-acids in the presence of large quantities of salts; for example, the ratio of the distribution coefficients for molybdophosphoric and molybdosilicic acids (the separation factor) is quite favourable for their separation by butanol in the absence of salts ($10^2 : 10^{-2}$ at pH 2.5), but decreases considerably when neutral salts are added[139].

In a number of cases, the mechanism of the influence of neutral salts on the extraction of heteropoly-compounds is not quite clear. In this connection it may be noted again that, in the extraction of molybdophosphoric acid by ethyl acetate in the presence of NaCl, partial extraction of sodium together with the heteropoly-acid takes place[117]. Since sodium undergoes almost no extraction with molybdate in the absence of phosphate (or with phosphate in the absence of molybdate)[117], this can be regarded as an example of coextraction[140].

Of particular importance in the examination of the extraction of molybdenum heteropoly-compounds is the question of the influence of an excess of molybdate (sodium or ammonium) on the extraction. The results of special studies[60,120] indicate that the extraction of molybdosilicic or molybdophosphoric acid by butanol begins to decrease even at a low concentration (> 0.1 M) of molybdate in the aqueous solution. This cannot be attributed entirely to the influence of the presence of molybdate on the acidity of the aqueous phase and hence on the extraction; the influence of molybdate (sodium or ammonium) as a neutral salt evidently plays some part.

6. Temperature

Slight changes in temperature have no appreciable influence on the extraction of heteropoly-compounds[21,60,70,89,141]. In the examination of the influence of temperature, however, allowance must be made for the fact that the equilibria in aqueous solutions of heteropoly-compounds may show a marked dependence on temperature (and on pH). With molybdophosphoric acid, for example, certain authors[142–145] assume that in aqueous solution an equilibrium is established between the colourless and yellow forms of the acid. This equilibrium depends to a marked extent on temperature: at low temperature the colourless form predominates, and at high temperature the yellow form[144,145]. Recent studies have shown that organic solvents (isopentyl acetate) extract only the yellow form of molybdophosphoric acid[146]; thus at low temperatures ($< 9°$) — in the range of stability of colourless molybdophosphoric acid — extraction takes place extremely slowly, whereas at high temperatures ($> 50°$) the extraction is almost instantaneous, as a result of rapid formation of the yellow form.

Analogous equilibria exist in aqueous solutions of other heteropoly-acids. The very interesting equilibrium between the α and β forms of molybdosilicic acid, which also depends on temperature[147,148], has unfortunately not been studied from the extraction viewpoint; there are merely reports of the possibility of stabilisation of the β form of molybdosilicic acid by extraction with a solution of tridecylamine in toluene[74].

Equilibria are known to be established in the reduction of heteropoly-acids. It may be noted, for the case of molybdosilicic acid, that the different products of the reduction of a given heteropoly-acid are extremely sensitive and specific in their behaviour towards organic solvents[128], Since the equilibrium involving these reduction products is usually markedly temperature-dependent, even slight changes in temperature in this case may lead to marked changes in extraction.

VI. ANALYTICAL APPLICATION OF THE EXTRACTION OF HETEROPOLY-COMPOUNDS

1. Separation of Elements by Extraction

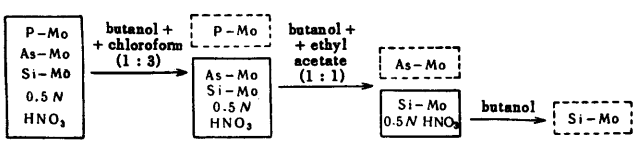
The extraction of heteropoly-compounds by organic solvents provides a valuable method for the separation of mixtures containing phosphorus, arsenic, silicon, and germanium. Such separations are possible in principle for all elements forming heteropoly-compounds.

The separation of elements by extraction as their heteropoly-compounds is based on the creation of conditions for selective behaviour of these compounds towards the organic solvents. This is achieved by changing the acidity of the aqueous phase, by selecting the solvents and combinations of solvents, by using complex-forming reagents, etc. All these cases are well illustrated by three typical examples of the separation of mixtures: scheme *1* for P + As + Si,[17] scheme *2* for P + Si + As,[138] and scheme *3* for P + As + Si + Ge [106] (in these separation schemes the full lines denote aqueous phases, and the broken lines organic phases).

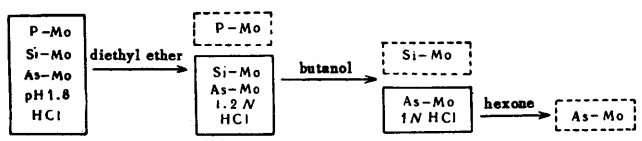
The extraction of molybdophosphoric acid has been used by various workers for the separation of phosphorus from silicon (isobutanol[67,108], diethyl ether[69,138], ethyl acetate[68,130,149,150], butyl acetate[151], isopentyl acetate[68,105], butanol + chloroform[17,58,120], butanol + benzene[60,139], and isobutanol + chloroform[106]), phosphorus from arsenic (pentanol[66,152], diethyl ether[138], ethyl acetate[150], isopentyl acetate[105], butanol + chloroform[17,62,129,137,153,154], isobutanol + chloroform[106], and ethyl acetate + butyl acetate[155]), phosphorus from vanadium (ethyl acetate[117] and ethyl acetate + butyl acetate[155]), phosphorus from calcium and magnesium (butanol + chloroform[156]), molybdophosphate from molybdate (isobutanol + diethyl ether[132]), and molybdophosphate from molybdotitanophosphate (butyl acetate[73,98,99]). Thanks to the ease of extraction of molybdophosphoric acid, it is not difficult to choose an effective and at the same time selective solvent for this compound; from the practical viewpoint, however, it is more convenient in this case to use a mixture of butanol with chloroform or benzene.

The extraction of molybdoarsenic acid has proved suitable for the separation of quinquevalent arsenic from tervalent arsenic (isobutanol[134]), arsenic from silicon (isopentyl acetate + ethanol[105], butanol + ethyl acetate[17], and butanol + ethyl acetate + chloroform[106]), and arsenic from germanium (butanol + ethyl acetate + chloroform[106]); the extraction of molybdosilicic acid for the separation of silicon from arsenic (butanol[138], butanol + chloroform[153], and butanol + ethyl acetate[153]), silicon from phosphorus (isobutanol[67,108]), and molybdosilicate from molybdate (pentanol + diethyl ether[136]); the extraction of molybdogermanic acid for the separation of germanium from arsenic (isopentanol[82,107] and butanol + ethyl acetate[82,107]); the extraction of molybdoniobophosphoric acid for the separation of niobium from titanium and tantalum (butanol[101]); and the extraction of molybdotitanophosphoric acid for the separation of titanium from chromium, copper, nickel, cobalt, manganese, iron, aluminium, lead, tantalum, and hafnium (pentanol + cyclohexanol[73]).

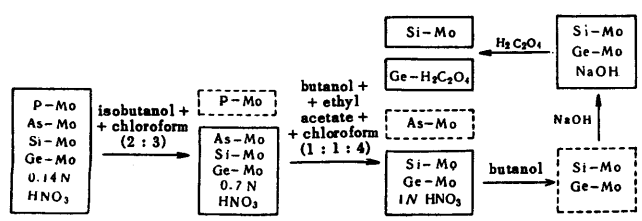
SCHEME *1*



SCHEME *2*



SCHEME *3*



2. Extraction–Photometric Determination of Elements

The extraction–photometric method has been used to determine phosphorus, silicon, arsenic, vanadium, and germanium as the reduced or unreduced heteropoly-compounds; it is also possible to determine molybdenum, titanium, cerium, thorium, zirconium, niobium, etc. The chief advantages of the extraction method over other methods are in this case high sensitivity and selectivity and the ease of prevention of interference.

High sensitivity in the extraction–photometric determination of elements as heteropoly-compounds is achieved not only as a result of the usual factors associated with extraction, but also by certain characteristic methods. One such method is the use for the photometric measurements of the decomposition products of the heteropoly--compounds, since these exhibit intense light absorption in the ultraviolet range of the spectrum; the preliminary separation of the heteropoly-compounds from the excess of analytical reagent, identical with the decomposition products, is achieved by extraction. The sensitivity of the determination in this way of, for example, phosphorus[132] and silicon[136] is characterised by molar absorption coefficients of 57 400 and 59 000 respectively.

Direct photometric measurements on the actual heteropoly-compound are avoided also in another original method: after separation of the heteropoly-complex from the excess of reagent by extraction, photometric measurements are made on one of its components, for which sensitive analytical reactions are available. For example, the sensitivity of the determination of phosphorus by photometric determination of the molybdenum from molybdophosphoric acid based on the thiocyanate reaction is characterised by a molar absorption coefficient of 185 000 (calculated as phosphate)[118].

An exceptionally high sensitivity is achieved in the determination of elements by photometric measurements on salts of the corresponding heteropoly-acids with organic bases, which are extractable even by inert solvents of the benzene and chloroform type. Silicon, for example, is

determined with a sensitivity reaching 1 μg litre^{-1} (calculated as SiO_2) in the form of the blue polyoxyethyldodecylammonium molybdosilicate, extracted by chloroform[57,75]; the sensitivity of the extraction–photometric determination of phosphorus as the molybdophosphate of safranine[157] is characterised by a molar absorption coefficient of 190 000.

An extremely important feature in the extraction–photometric determination of elements as heteropoly-compounds is the ease of eliminating the interfering influence of an excess of the reagent, e.g. of molybdate when molybdenum heteropoly-acids are used. The non-extractability of unreduced isopolymolybdate under the conditions of the analytical application of heteropoly-compounds is well known and has been convincingly demonstrated in many experiments. Data on the extractability of reduced isopolymolybdate are contradictory, but there is no doubt that by altering the conditions it is possible to achieve complete suppression of the extraction of this form of molybdate also. For well-known reasons, separation from the excess of molybdate helps considerably the attainment of reliable and reproducible results in the determination, since it decreases the size of the blank specimen and opens up new possibilities for increasing the sensitivity of the analysis.

The process of extraction in the photometric determination of elements as heteropoly-compounds has interesting possibilities in connection with the stabilisation of the necessary analytical forms. For example, the main difficulties and errors in the determination of silicon as β-molybdosilicic acid are associated with the instability of this form of molybdosilicic acid in aqueous solution and its gradual conversion into the more stable α form; the extraction of β-molybdosilicic acid by organic solvents contributes appreciably to the solution of this problem, since the β form is stabilised in the organic solvent[74].

In the extraction–photometric determination of phosphorus, n-butanol or isobutanol is most frequently used as solvent. The use of butanol for the extraction of phosphorus as molybdophosphoric acid, with subsequent reduction and photometric determination of the latter in the organic phase, has been used successfully to determine phosphorus in biological materials[19,56,132,158-161], natural waters[21,61,162-167], plant materials[104,141], steels[109,168], aluminium alloys[169,170], vanadium[171], technical products[108], iron ores[168], petrol[172], and artificial mixtures[67]; photometric measurements on a butanol extract of molybdophosphoric acid without preliminary reduction can be used for the determination of phosphorus in biological materials[173].

The use of other alcohols instead of butanol gives no fundamental advantages, although some authors note increased sensitivity in the determination of phosphorus on extraction with isopentanol[174,175] or n-hexanol[176], better separation of the layers when pentanol is used[66], a lower degree of extraction of isopolymolybdate with n-octanol[64] and isopentanol[115], and also the greater availability of isopentyl alcohol[177] compared with butanol.

Extraction properties much better than those of butanol are shown by mixtures of n-butanol with chloroform[17,22,58,110,118,120,154,178-180], isobutanol with chloroform[106,181], and, more particularly, isobutanol with benzene[60,63,133,139,182-186]. This last mixture always has a component ratio of 1 : 1; the composition of the mixtures of butanol with chloroform, used in different cases, varies considerably (from 1 : 1 to 1 : 10), but most authors consider that the optimum butanol : chloroform ratio is ~1 : 3.

Other solvents suitable for the extraction of molybdophosphoric acid in the photometric determination of phosphorus include diethyl ether[55,138,187-197], ethyl acetate[117,130,149], butyl acetate[59,198], isopropyl acetate[199], isopentyl acetate[146,200,201], isobutyl methyl ketone[111], and mixtures of butanol with diethyl ether (1 : 1)[202] and of ethyl acetate with butyl acetate (7 : 3)[203,204].

Butanol is also the solvent most frequently used for the extraction of molybdoarsenic and molybdosilicic acids in the photometric determination of arsenic[129,134,137,153] and silicon[17,58,67,106,108,117,138,179]. The best extractants, however (particularly as regards selectivity), are — for molybdoarsenic acid, isobutyl methyl ketone (hexone)[113,138] and mixtures of butanol with ethyl acetate (1 : 1)[17,107,154,171,179], isopentyl acetate with ethanol (5 : 1)[105], and butanol with ethyl acetate and chloroform (1 : 1 : 4)[106]; and for molybdosilicic acid, n-pentanol[205,206], isopentyl alcohol[135,207], and isobutyl methyl ketone[112].

Butanol[106], isopentyl alcohol[82,107], and a mixture of butanol with ethyl acetate (1 : 1)[82,107] are suitable for the extraction–photometric determination of germanium as molybdogermanic acid.

Extraction of the reduced forms of heteropoly-acids is little used in photometric analysis. The only determinations described are those of phosphorus by extraction as the reduced molybdophosphoric acid (n-butanol[56,208], isobutanol[20,209], isopentanol[115], diethyl ether[16,69,210], isobutyl methyl ketone[211], acetophenone[70], and a mixture of isopentanol with diethyl ether[175]), the determination of arsenic by extraction as reduced molybdoarsenic acid (isopentanol[212-214] and a mixture of isopentanol with diethyl ether[215]), and the determination of silicon by extraction as reduced molybdosilicic acid (isopentanol[207,216]).

The extraction of ternary heteropoly-acids has recently been used successfully for the photometric determination of various elements, Thus for example, the extraction of molybdovanadophosphoric, tungstovanadophosphoric, molybdotitanophosphoric, molybdoniobophosphoric, and molybdovanadogermanic acids has been used for the determination respectively of phosphorus[84,86-93], vanadium[71,94,95], titanium[73,98,99], niobium[101], and germanium[97].

3. Other Examples of the Use of the Extraction of Heteropoly-Compounds

The extraction of heteropoly-compounds can be used not only in photometric methods but also in combination with other methods — gravimetric[150], titrimetric[155], spectroscopic[217], and radiometric[62,218,219].

For the determination of comparatively large quantities of phosphorus[12,65,220,221] and arsenic[222], some workers have used a method based on measurement of the volume of the oily layer obtained on extraction of the heteropoly-acid with diethyl ether. The extraction of heteropoly-acids also forms the basis of highly sensitive and selective methods for the detection of phosphate[14,223], arsenate[14,223,224], germanate[224], vanadium[225], and molybdenum[225].

In conclusion, brief mention may be made of other applications of the extraction of heteropoly-acids (other than analytical). The preparative importance of the extraction of heteropoly-compounds is well known: the use of extraction for the preparation of heteropoly-acids has been described in a monograph on heteropoly-compounds[4].

The extraction method is being used successfully to investigate the formation and reduction of heteropoly-complexes [110,128,142,146], and to study their composition [72,96], redox properties [226], etc. [177,189,212,227].

The further study of the extraction behaviour of heteropoly-compounds will undoubtedly facilitate investigation of the structure and nature of the bonding in the molecules of heteropoly-complexes, and will also extend the range of their practical application.

1. R. M. Diamond and D. G. Tuck, "The Liquid–Liquid Extraction of Inorganic Compounds" [Translated into Russian from Progr. Inorg. Chem., 2, 109 (1960)], Gosatomizdat, Moscow, 1960, p. 80.
2. G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry" [Translated into Russian from Analyt. Chem., 32, 37R (1960)], Goskhimizdat, Leningrad, 1960, p. 148.
3. M. G. Mellon, Proc. Symposium on Heteropolyanions (New York, 1956), New York, 1956, p. 35.
4. E. A. Nikitina, "Geteropolisoedineniya" (Heteropoly--Compounds), Goskhimizdat, Moscow, 1962.
5. I. Lindqvist, Proc. Symposium on Heteropolyanions (New York, 1956), New York, 1956, p. 20.
6. C. Marignac, Ann. Chim. Phys., 3, 5 (1864).
7. F. Parmentier, Compt. rend., 104, 686 (1887).
8. M. N. Sobolev, Zhur. Russ. Fiz.-Khim. Obshch., 28, 186 (1896); Z. anorg. Chem., 12, 16 (1896).
9. E. Drechsel, Ber., 20, 1452 (1887).
10. A. G. Scroggie, J. Amer. Chem. Soc., 51, 1057 (1929).
11. A. Rosenheim and J. Jaenicke, Z. anorg. Chem., 100, 304 (1917).
12. H. Copaux, Compt. rend., 173, 656 (1921).
13. P. Souchay, J. Chim. phys., 42, 61 (1945).
14. G. Denigès, Compt. rend., 171, 802 (1920).
15. W. A. Jacobs, J. Biol. Chem., 12, 429 (1912).
16. S. B. Shneerson, Zavod. Lab., 3, 21 (1934).
17. R. I. Alekseev, Zavod. Lab., 11, 122 (1945).
18. J. F. Keggin, Proc. Roy. Soc., A144, 75 (1934).
19. I. Berenblum and E. Chain, Biochem. J., 32, 295 (1938).
20. R. J. L. Allen, Biochem. J., 34, 858 (1940).
21. C. M. Proctor and D. W. Hood, Analyt. Chem., 24, 2016 (1952); J. Marine Res. (Sears Found. Marine Res.), 13, 122 (1954).
22. C. Wadelin and M. G. Mellon, Analyt. Chem., 25, 1668 (1953).
23. P. Souchay, "Polyanions et Polycations", Gauthier-Villars, Paris, 1963.
24. M. Jean, Chim. analyt., 37, 125, 163 (1955).
25. L. C. W. Baker, Climax Molybdenum Co., Bulletin Cdb–12, New York, 1956.
26. L. Malaprade, in P. Pascal, "Nouveau Traité de Chimie minérale", Vol. 14, Masson, Paris, 1959, p. 903.
27. H. B. Jonassen and S. Kirschner, in J. C. Bailar and D. H. Busch (Editors), "The Chemistry of the Coordination Compounds" (Translated into Russian), Inostr. Lit., Moscow, 1960, p. 399.
28. J. R. van Wazer, "Phosphorus and Its Compounds" (Translated into Russian), Part 1, Inostr. Lit., Moscow, 1962, p. 427.
29. M. Jean, Chim. analyt., 44, 195, 243 (1962).
30. V. I. Kuznetsov, Uspekhi Khim., 23, 654 (1954).
31. F. G. Zharovskii, Trudy Nauch.-Tekh. Obshch. Chernoi Metallurgii, 4, 138 (1965).
32. T. S. West, Metallurgia, 53, 103 (1956).
33. I. P. Alimarin and V. N. Polyanskii, Sbornik Trudov. Moskov. Vechern. Metallurg. Inst., No. 2, 187 (1957); Nauch. Trudy Moskov. Ped. Inst., Nos. 5–6, 229 (1957).
34. G. H. Morrison and H. Freiser, Analyt. Chem., 30, 632 (1958).
35. A. K. Babko and F. G. Zharovskii, Zavod. Lab., 25, 42 (1959).
36. W. E. Clarke, J. Res. Develop. B. C. I. R. A., 7, 813 (1959).
37. G. H. Morrison and H. Freiser, Analyt. Chem., 32, 37 (1960).
38. G. H. Morrison and H. Freiser, Analyt. Chem., 34, 64 (1962).
39. A. K. Babko and F. G. Zharovskii, Zavod. Lab., 28, 1287 (1962).
40. T. Ishimori and K. Kimura, Japan Analyst, 11, 85 (1962).
41. A. K. Babko and F. G. Zharovskii, Trudy Kom. Anal. Khim. Akad. Nauk SSSR, 14, 218 (1963).
42. V. A. Nazarenko, Trudy Kom. Anal. Khim. Akad. Nauk SSSR, 14, 3 (1963).
43. A. K. Babko and A. T. Pilipenko, "Kolorimetricheskii Analiz" (Colorimetric Analysis), Goskhimizdat, Moscow–Leningrad, 1951, p. 247.
44. B. Lange, "Kolorimetrische Analyse", Verlag Chemie, Weinheim, 1956, pp. 302, 308.
45. F. D. Snell, C. T. Snell, and C. A. Snell, "Colorimetric Methods of Analysis", Vol. 2A, Van Nostrand, New York, 1959, pp. 548, 570.
46. G. Charlot, "Dosages colorimétriques des Éléments minéraux", Masson, Paris, 1961, pp. 289, 317.
47. R. Klement, "Handbuch der analytischen Chemie", Vol. 5, Part 3, Springer, Berlin, 1953, p. 1.
48. A. M. G. Macdonald, Ind. Chemist, 36, 88, 134 (1960).
49. W. Rieman and J. Beukenkamp, in "Treatise on Analytical Chemistry", Vol. 5, Part 2, Interscience, New York, 1962, p. 315.
50. P. Maggi, Corriere farmac., 17, 584 (1962).
51. D. F. Boltz and C. H. Lueck, in D. F. Boltz (Editor), "The Colorimetric Determination of Non-Metals" (Translated into Russian), Inostr. Lit., Moscow, 1963, p. 9.
52. I. Iwasaki, Japan Analyst., 9, 184 (1960).
53. H. R. Shell, in "Treatise on Analytical Chemistry", Vol. 2. Part 2, Interscience, New York, 1962, p. 107.
54. G. V. Potter, in D. F. Boltz (Editor), "The Colorimetric Determination of Non-Metals" (Translated into Russian), Inostr. Lit., Moscow, 1963, p. 34.
55. B. A. Generozov and M. A. Gramolina, Zavod. Lab., 17, 1043 (1951).
56. J. L. Delsal and H. Manhouri, Bull. Soc. Chim. biol., 37, 1041 (1955).
57. W. Sonnenschein, Z. analyt. Chem., 168, 18 (1959).
58. M. Lheureux and J. Cornil, Ind. chim. belge, 24, 634 (1959).
59. M. Ishibashi and M. Tabushi, Japan Analyst., 8, 588 (1959).
60. L. H. Andersson, Acta Chem. Scand., 13, 1743 (1959).
61. V. G. Datsko and A. D. Semenov, Gidrokhim. Mat., 29, 219 (1959).
62. H. H. Ross and R. B. Hahn, Talanta, 7, 276 (1961).
63. J. B. Martin and D. M. Doty, Analyt. Chem., 21, 965 (1949).
64. F. L. Schaffer, J. Fong, and P. L. Kirk, Analyt. Chem., 25, 343 (1953).
65. H. Saint-Chamant and R. Vigier, Bull. Soc. chim. France, [5], 20, 344 (1953).
66. H. Goto and Y. Kakita, Sci. Reports Res. Inst. Tôhoku Univ., A7, 294 (1955).
67. E. Ruf, Z. analyt. Chem., 151, 169 (1956).
68. J. Paul and W. F. R. Pover, Analyt. Chim. Acta, 22, 185 (1960).
69. J. Paul, Analyt. Chim. Acta, 23, 178 (1960).
70. M. Miyamoto, Japan Analyst, 12, 32 (1963).
71. D. G. Biechler, D. E. Jordan, and W. D. Leslie, Analyt. Chem., 35, 1685 (1963).
72. N. Yoza and S. Ohashi, Bull. Chem. Soc. Japan, 37, 33 (1964).
73. Yu. F. Shkaravskii, Zhur. Anal. Khim., 19, 320 (1964).
74. H. N. Wilson and J. M. Skinner, Rec. Trav. chim., 79, 574 (1960).

75. K. Sono, H. Watanabe, and Y. Mitsukami, Japan Analyst, 12, 352 (1963).
76. S. A. Gavrilova, Candidate's Thesis, Moscow State University, Moscow, 1958.
77. Yu. F. Shkaravskii, Ukrain. Khim. Zhur., 29, 356 (1963).
78. E. N. Semenovskaya, Candidate's Thesis, Moscow State University, Moscow, 1963.
79. H. Wu, J. Biol. Chem., 43, 189 (1920).
80. W. Fischer, W. Dietz, K. Brünger, and H. Grieneisen, Angew. Chem., 49, 719 (1936).
81. R. K. Motorkina, Candidate's Thesis, Moscow State University, Moscow, 1955.
82. Z. F. Shakhova and R. K. Motorkina, Trudy Kom. Anal. Khim. Akad. Nauk SSSR, 8, 100 (1958).
83. N. V. Maksimova and M. T. Kozlovskii, Zhur. Anal. Khim., 2, 353 (1947).
84. J. Kinnunen and B. Wennerstrand, Chem. Analyst., 40, 33 (1951).
85. F. G. Zharovskii, Ukrain. Khim. Zhur., 18, 553 (1952).
86. U. T. Hill, Analyt. Chem., 26, 425 (1954).
87. L. Berak, Hutnické Listy, 9, 672 (1954).
88. W. T. Elwell and H. N. Wilson, Mikrochim. Acta, Nos. 5—6, 1097 (1955); Analyt. Chem., 28, 140 (1956); Analyst, 81, 136 (1956).
89. H. Kitagawa and N. Shibata, J. Japan Inst. Metals (Sendai), 23, 215 (1959).
90. H. Kitagawa and N. Shibata, Japan Analyst, 8, 302 (1959).
91. E. Booth, At. Energy Res. Estab. (G. Brit.), Rept., No. AM7 (1959).
92. E. Booth and A. Parker, At. Energy Res. Estab. (G. Brit.), Rept., No. AM4 (1959).
93. T. Fujunuki, Japan Analyst, 11, 124 (1962).
94. V. G. Shcherbakov and R. M. Veitsman, Zavod. Lab., 20, 663 (1954).
95. H. Kitagawa and N. Shibata, Japan Analyst, 7, 624 (1958).
96. E. Vandalen and M. G. Mellon, Analyt. Chem., 36, 1068 (1964).
97. Z. F. Shakhova and R. K. Motorkina, Zhur. Anal. Khim., 11, 698 (1956).
98. Yu. F. Shkaravskii, Zavod. Lab., 28, 265 (1962).
99. Yu. F. Shkaravskii, Zhur. Anal. Khim., 19, 514 (1964).
100. A. K. Babko and Yu. F. Shkaravskii, Zhur. Neorg. Khim., 7, 1565 (1962) [Russ. J. Inorg. Chem., 809 (1962)].
101. Yu. F. Shkaravskii, Zhur. Anal. Khim., 18, 196 (1963).
102. Tsan Lung K'u, F. P. Sudakov, and Z. F. Shakhova, Zhur. Anal. Khim., 19, 968 (1964).
103. I. P. Alimarin, Z. F. Shakhova, and R. K. Motorkina, Dokl. Akad. Nauk SSSR, 106, 61 (1956).
104. W. A. Pons and J. D. Guthrie, Ind. Eng. Chem., Analyt., 18, 184 (1946).
105. M. A. DeSesa and L. B. Rogers, Analyt. Chem., 26, 1381 (1954).
106. T. Kiba and M. Ura, J. Chem. Soc. Japan, 76, 520 (1955).
107. Z. F. Shakhova and R. K. Motorkina, in "Metody Analiza Redkikh i Tsvetnykh Metallov" (Methods for the Analysis of Rare and Non-Ferrous Metals), Izd. Moskov. Gos. Univ., Moscow, 1956, p. 47.
108. E. Ruf, Z. analyt. Chem., 161, 1 (1958).
109. C. H. Lueck and D. F. Boltz, Analyt. Chem., 28, 1168 (1956).
110. R. P. A. Sims, Analyst, 86, 584 (1961).
111. D. Ishii and T. Takeuchi, Japan Analyst, 10, 1391 (1961).
112. D. Ishii and T. Takeuchi, Japan Analyst, 10, 1394 (1961).
113. D. Ishii and T. Takeuchi, Japan Analyst, 11, 118 (1962).
114. F. H. Harrison, Metallurgia, 66, 300 (1962).
115. J. T. McAloren and G. F. Reynolds, Talanta, 10, 145 (1963).
116. "Tables of Spectrophotometric Absorption Date of Compounds Used for the Colorimetric Determination of Elements", Butterworth, London, 1963.
117. W. Fischer, R. Paul, and H. J. Abendroth, Analyt. Chim. Acta, 13, 38 (1955).
118. K. Sugawara and S. Kanamori, Bull. Chem. Soc. Japan, 34, 258 (1961).
119. A. K. Babko and Yu. F. Shkaravskii, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 2, 157 (1959).
120. A. K. Babko and Yu. F. Shkaravskii, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 3, 370 (1961).
121. M. Kerker, D. Lee, and A. Chou, J. Amer. Chem. Soc., 80, 1539 (1958).
122. J. B. Mullin and J. P. Riley, Analyt. Chim. Acta, 12, 162 (1955).
123. N. V. Sidgwick, "Chemical Elements and Their Compounds", Vol. 2, Oxford Univ. Press, 1950, p. 1046.
124. Yu. A. Zolotov and I. P. Alimarin, Dokl. Akad. Nauk SSSR, 136, 603 (1960).
125. Yu. A. Zolotov, Uspekhi Khim., 32, 220 (1963) [Russ. Chem. Rev., 107 (1963)].
126. K. V. Troitskii, Uspekhi Khim., 32, 239 (1963) [Russ. Chem. Rev., 116 (1963)].
127. F. L. Moore, "Liquid–Liquid Extraction with High-Molecular-Weight Amines", NAS-NS 3101, Office of Technical Services, Washington, 1960.
128. P. Souchay and R. Massart, Compt. rend., 253, 1699 (1961).
129. C. Wadelin and M. G. Mellon, Analyst, 46, 708 (1952).
130. J. Hurê and T. Ortis, Bull. Soc. chim. France, 16, 834 (1949).
131. N. S. Ging, Analyt. Chem., 28, 1330 (1956).
132. C. H. Lueck and D. F. Boltz, Analyt. Chem., 30, 183 (1958).
133. E. Q. Laws and D. J. Webley, Analyst, 86, 249 (1961).
134. M. Daniels, Analyst, 82, 133 (1957).
135. M. Miyamoto, Japan Analyst, 10, 433 (1961).
136. L. Trudell and D. F. Boltz, Analyt. Chem., 35, 2122 (1963).
137. J. Kinnunen and B. Merikanto, Chem. Analyst., 42, 88 (1953).
138. W. S. Clabaugh and A. Jackson, J. Res. Nat. Bur. Stand., 62, 201 (1959); Chem. Rundschau (Solothurn), 12, 479 (1959).
139. L. H. Andersson, Arkiv Kemi., 19, 257 (1962).
140. I. P. Alimarin, Yu. A. Zolotov, and N. V. Shakhova, Trudy Kom. Anal. Khim. Akad. Nauk SSSR, 14, 24 (1963).
141. C. P. Sideris, Ind. Eng. Chem., Analyt., 14, 762 (1942).
142. I. Berenblum and E. Chain, Biochem. J., 32, 286 (1938).
143. I. P. Alimarin and V. S. Zverev, Trudy. Inst. Prikl. Miner., No. 63 (1934); Mikrochem., 22, 89 (1937).
144. C. Ferrari, Gazzetta, 81, 795 (1951).
145. C. Ferrari, Mikrochim. Acta, Nos. 1—3, 551 (1956).
146. W. J. Kirsten and M. E. Carlson, Microchem. J., 4, 3 (1960).
147. J. D. H. Strickland, J. Amer. Chem. Soc., 74, 862 (1952).
148. I. R. Morrison and A. L. Wilson, Analyst, 88, 88 (1963).
149. K. Stoll, Z. analyt. Chem., 112, 81 (1938).
150. B. Wurzschmitt and W. Schuhknecht, Angew. Chem., 52, 711 (1939).
151. T. Kato, Y. Okinaka, and K. Oizumi, Technol. Reports Tôhoku Univ., 15, 70 (1950).
152. A. Tominaga and S. Watanabe, Japan Analyst, 5, 495 (1956).
153. D. J. Lisk, J. Agric. Food Chem., 8, 121 (1960).
154. S. Yokosuka, Japan Analyst, 5, 395 (1956).
155. K. Aiba, Japan Analyst, 8, 436 (1959).
156. R. E. Collier, Chem. Analyst, 43, 41 (1954).
157. L. Ducret and M. Drouillas, Analyt. Chim. Acta, 21, 86 (1959).
158. P. L. Kirk and M. Danielson, Analyt. Chim. Acta, 20, 1122 (1948).
159. A. H. Ennor and L. A. Stocken, Austral. J. Exp. Biol. Med. Sci., 28, 647 (1950).
160. J. L. Peel and B. C. Loughman, Biochem. J., 65, 709 (1957).
161. L. T. Pietra and M. T. Cuzzoni, Farmaco (Pavia), Ed. Prat., 17, 338 (1962).

162. V. G. Datsko and A. D. Semenov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 357 (1958).
163. J. Heron, Limnol. Oceanog., 6, 338 (1961).
164. A. D. Semenov, I. M. Semenova, and V. G. Datsko, in Collected Papers, "Sovremennye Metody Analiza Prirodnykh Vod" (Modern Methods for the Analysis of Natural Waters), Izd. Akad. Nauk SSSR, Moscow, 1962, p. 110.
165. V. G. Datsko and A. D. Semenov, *ibid.*, p. 112.
166. P. G. W. Jones and C. P. Spencer, J. Marine Biol. Assoc., 43, 251 (1963).
167. A. Henriksen, Analyst, 88, 898 (1963).
168. G. Picasso, Metallurgia Ital., 52, 358 (1960).
169. Z. Večeřa and B. Bieber, Hutnické Listy, 14, 56 (1959).
170. M. L. Davey, Metallurgia, 65, 151 (1962).
171. V. V. Stepin, A. M. Pliss, and E. V. Silaeva, Byull. Nauch.-Tekh. Inform. Ural'sk. Nauch.-Issled. Inst. Chernoi Metallurgii, No. 4, 103 (1958).
172. E. R. Fett and G. Matsuyama, Chem. Analyst, 47, 32 (1958).
173. J. L. Delsal and H. Manhouri, Bull. Soc. Chim. biol., 40, 1169 (1958).
174. N. Ya. Tarasov, T. G. Bogdanov, and F. G. Slyusareva, Trudy Nauch.-Tekh. Obshch. Chernoi Metallurgii, 4, 104 (1956).
175. S. Komatsu and Y. Iwakuma, J. Chem. Soc. Japan, 80, 881 (1959).
176. I. Heron, Limnol. Oceanog., 7, 316 (1962).
177. C. Rainbow, Nature, 157, 268 (1946).
178. R. V. Mervel', Zavod. Lab., 11, 135 (1945).
179. N. A. Filippova and L. I. Kuznetsova, Zavod. Lab., 16, 536 (1950).
180. F. G. Zharovskii and A. P. Kostyshina, Ukrain. Khim. Zhur., 19, 201 (1953).
181. M. Ura, Japan Analyst, 7, 420 (1958).
182. H. Weil-Malherbe, Biochem. J., 55, 741 (1953).
183. K. Field and E. Q. Laws, Analyst, 82, 667 (1957).
184. E. Q. Laws and D. J. Webley, Analyst, 84, 28 (1959).
185. D. Caverly and P. S. Hall, Analyst, 86, 478 (1961).
186. K. K. Tewari and P. S. Krishnan, Analyt. Chim. Acta, 27, 111 (1960).
187. I. F. Drozd, Novosti Tekhniki, No. 44, 28 (1936).
188. L. D. Raskin, Zavod. Lab., 5, 267 (1936).
189. L. D. Raskin, D. T. Miroshnichenko, and M. M. Bondarenko, Zavod. Lab., 7, 860 (1938).
190. N. D. Ivanova and S. I. Malov, Zavod. Lab., 12, 246 (1946).
191. K. A. Matveeva, Zavod. Lab., 13, 1136 (1947).
192. E. F. Pen'kova, A. M. Dmitrieva, and P. Ya. Yakovlev, Zavod. Lab., 16, 744 (1950).
193. N. Ya. Tarasov and P. V. Moshkovskii, Trudy Nauch.-Tekh. Obshch. Chenoi Metallurgii, 4, 98 (1956).
194. V. G. Goryushina and E. Ya. Biryukova-Gailis, Zavod. Lab., 24, 402 (1958).
195. A. A. Fedorov, Sbornik Tsentr. Nauch.-Issled. Inst. Chernoi Metallurgii, No. 19, 22 (1960).
196. A. A. Fedorov and F. V. Linkova, Zavod. Lab., 26, 535 (1960).
197. L. A. Soldatova and L. B. Kristaleva, Trudy Tomsk. Univ., 157, 279 (1963).
198. A. Yoda, J. Chem. Soc. Japan, 80, 488 (1959).
199. B. E. Wahler and A. Wollenberger, Biochem. Z., 329, 508 (1958).
200. W. J. Kirsten, Z. analyt. Chem., 181, 1 (1961).
201. E. Debal, Chim. analyt., 45, 66 (1963).
202. B. M. Dobkina and A. L. Khersonskaya, Zavod. Lab., 20, 914 (1954).
203. S. Yasutomi, M. Ihida, and Y. Takano, J. Iron Steel Inst. (Japan), 46, 1071 (1960).
204. S. Gregorczyk, Hutnik, 29, 369 (1962).
205. S. Yokosuka, Japan Analyst, 5, 285 (1956).
206. J. Minczewski and J. Chwastowska, Chem. Analit., 6, 715 (1961).
207. V. A. Nazarenko and G. V. Flyantikova, Zavod. Lab., 24, 663 (1958).
208. H. Namiki, Japan Analyst, 10, 945 (1961).
209. K. Stephens, Limnol. Oceanog., 8, 361 (1963).
210. F. K. Gerke and Z. I. Kardakova, Zavod. Lab., 4, 1343 (1935).
211. D. N. Rhodes, Nature, 176, 215 (1955).
212. V. A. Nazarenko and G. I. Byk, Ukrain. Khim. Zhur., 22, 234 (1956).
213. V. A. Nazarenko, G. V. Flyantikova, and N. V. Lebedeva, Zavod. Lab., 23, 891 (1957).
214. L. A. Maksai and A. A. Silaeva, Sbornik Trudov. Vses. Nauch.-Issled. Gornometallurg. Inst. Tsvent. Metallov, No. 7, 345 (1962).
215. L. B. Kristaleva and P. V. Kristalev, Trudy Kom. Anal. Khim. Akad. Nauk SSSR, 14, 279 (1963).
216. L. Sassi, Arch. Inst. Pasteur Tunis, 32, 283 (1955).
217. J. Orsag and Pichery, Congr. Group Avan. Methodes Anal. Spectrog. Prod. Met., 19, 85 (1956) (published 1958).
218. V. G. Shcherbakov, Yu. N. Yurkevich, and G. G. Besproskurnov, Sbornik Trudov Vses. Nauch.-Issled. Inst. Tverdykh Splavov, No. 3, 44 (1960).
219. W. B. Silker, Analyt. Chem., 28, 1782 (1956).
220. J. Daric, Bull. Soc. chim. France, 35, 409 (1924).
221. C. Bănăteanu, A. Serbănescu, and E. Vrăbiescu, Lucrarile Inst. Petrol Gaze Bucuresti, 3, 345 (1957).
222. M. Poussiques, Ann. Chim. analyt., 5, 263 (1923).
223. A. Dyfverman and R. Bonnichsen, Analyt. Chim. Acta, 23, 491 (1960).
224. G. Tölg, Z. analyt. Chem., 190, 161 (1962).
225. F. G. Zharovskii, Ukrain. Khim. Zhur., 18, 553 (1952).
226. Z. F. Shakhova and R. K. Motorkina, Zhur. Obshch. Khim., 26, 2663 (1956).
227. V. I. Kuznetsov and P. D. Titov, Dokl. Akad. Nauk SSSR, 131, 840 (1960).

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THE STRUCTURE AND EXTRACTIVE POWER OF AMINES AND THEIR SALTS

V. S. Shmidt and E. A. Mezhov

I. Introduction 585

II. Brief information on the mechanism of extraction of acids and metal salts by amine salts 585

III. The effect of the structure of amine salts on the stability of the compounds extracted by different extraction mechanisms 586

IV. Principal structural factors of amines determining the structure of their salts 587

V. The effect of the structure of amines on the extractive power of their salts with extraction by an addition mechanism 593

VI. The effect of the structure of amines on the extractive power of their salts with extraction by an anion-exchange mechanism 594