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Extraction of Heteropolycompounds and Its Application in Inorganic Analysis

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Data on the extraction of heteropolycompounds published in the period 1965 - 1977 have been reviewed. The principal directions of study and recent achievements in establishing the regular features of extraction and investigating the mechanism of extraction have been examined. Data on the use of extraction to separate and determine elements in inorganic analysis have been given. The bibliography contains 211 references.

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I. INTRODUCTION

The extraction of heteropolycompounds is recognised as a reliable method for separating a number of elements and for determining trace quantities in various materials. Up to 1965, a comparatively large amount of experimental material had been published on the optimum conditions for the extraction of molybdenum and, to a smaller extent, tungsten heteropolycompounds (this work has been reviewed[1]). In the last ten years, workers engaged in the extraction of heteropolycompounds have carried out theoretical studies devoted to the establishment of the regular features of the process and the mechanism of extraction, and also applied studies, which have lead to success in the development of methods for separating and determining a number of elements. The development of ideas in the extraction of heteropolycompounds is related to the latest achievements in the chemistry of heteropolycompounds[2-4]. A partial bibliography on problems of extraction can be found in Refs. 5–8. An important contribution to the development of the theory and practice of the extraction of heteropolycompounds has been made by combined schools of research workers[8-126]. The behaviour of heteropolycompounds in non-aqueous and mixed media has been described[28,88,98,127,128,129,130-132]. Methods have been developed for determining traces of elements in highly pure materials[14,25,35,101,117,122,123,133-156].

Until the nineteen-sixties, most studies of the extraction of heteropolycompounds were of an applied nature, and included the results of the empirical selection of the optimum conditions for the extraction of a given heteropolycomplex. In recent years there has been an increase in the number of papers devoted to the systematic study of the influence of various factors on extraction equilibrium, the determination of quantitative relationships, and the calculation of extraction constants. Attention is being paid to the composition of the compounds extracted, the nature of the chemical bonding in these compounds, the stoichiometry of extraction, and processes in the organic phase. Amines of high molecular weight, and other extracting agents, are being introduced in place of the traditional oxygen-containing solvents. A number of papers have been devoted to the extraction of ionic associates of heteropolyacids with dyes of various classes.

In analytical chemistry it is possible to distinguish a trend associated with the development of indirect methods for determining elements. These are based on the extraction of a heteropolycompound and the determination of the element from the concentration of the ligand after re-extraction and decomposition of the complex. A characteristic feature of studies in recent years is the introduction of physicochemical and physical methods in the study of extraction (infrared and NMR spectroscopy, radiometry, and polarography). Many analytical procedures recommend a combination of different methods. Extraction has been combined with chromatographic, luminescent, polarographic, atomic-absorption, and neutron-activation methods to determine and separate elements as heteropolycompounds.

II. FACTORS INFLUENCING THE EXTRACTION OF HETEROPOLYCOMPOUNDS

The extraction equilibrium in a system formed by a heteropolycompound and an organic solvent is determined by many factors operating simultaneously. The principal factors are the nature of the extracting agent, the nature and concentration of the heteropolycomplex being extracted, the nature and concentration of mineral acid in the aqueous phase, the presence of neutral salts, and temperature. The extraction equilibrium is reversible, so that the regular features of the extraction and re-extraction are the same. A universal characteristic of extraction is the equilibrium constant. Unfortunately, there are few experimental data on the determination of extraction constants and distribution coefficients. A number of papers give distribution coefficients (or extraction factors) for a definite acidity of the aqueous phase, and this makes it difficult to compare the data of different authors.

1. Nature of the Extracting Agent

Comparison of the properties and extracting power of more than forty solvents of different classes shows that extraction is influenced to a considerable extent by their

basic strength and dielectric constant, and also by their structure and miscibility with water. Attempts to obtain the dependence of the extraction properties of a solvent on any single factor lead to lack of agreement between the theoretical and experimental extraction series. If only the basic strength of the solvent is taken into account, the theoretical order is: nitrobenzene > methyl isobutyl ketone = methyl ethyl ketone > ethyl acetate > pentyl acetate, whereas the experimental order is: pentyl acetate < nitrobenzene < ethyl acetate < methyl isobutyl ketone < methyl ethyl ketone < isopentyl alcohol < octanol < butanol[77].

The extracting power of a solvent shows a correlation with the solubility of heteropolycompounds in it and the dielectric constant of the solvent. Murata and Kiba[107] divided solvents into three groups: those in which heteropolyacids are sparingly soluble (ϵ = 2–4), soluble (ϵ = 3–8), and highly soluble (ϵ = 5–18).

The relationship between the extracting power and solubility of heteropolycompounds has also been studied by other workers[76] (Table 1). Among oxygen-containing solvents, alcohols have the highest extracting power. They extract all known heteropolyacids, in both oxidised and reduced forms. Alcohols are also the best reagents for the extraction of ionic associates of heteropolyacids with dyes of different classes[17,30]. Cyclic alcohols are better extracting agents than aliphatic alcohols[8]. The action of esters and ketones is more selective. Increase in the length and degree of branching of the carbon chain leads to a decrease in extraction[8,10,90,104,157] (Table 2). The distribution coefficients of reduced molybdophosphoric acid in 1.5 M sulphuric acid solutions for extraction by isomeric alcohols and esters are given below[104]:

butanol	pentanol	butyl acetate	isobutyl alcohol	isopentyl alcohol	isobutyl acetate
279.0	259.3	0.42	70.1	85.1	0.28

Table 1. Distribution coefficients of tungstophosphoric acid between aqueous and organic phases (28 ± 1°C, initial concentration 6.1×10^{-3} M).[76]

Solvent	D	Basic strength*	Solubility, M	ϵ
o-Dichlorobenzene	$4.1 \cdot 10^{-5}$	—	—	—
Chloroform	$2.0 \cdot 10^{-5}$	—	—	4.8
Carbon tetrachloride	$2.0 \cdot 10^{-5}$	—	—	2.2
Benzene	$2.2 \cdot 10^{-5}$	—	—	2.3
Pentyl acetate	$1.1 \cdot 10^{-2}$	90	0.023	4.8
Nitrobenzene	$3.1 \cdot 10^{-2}$	28	0.0146	34.8
Ethyl acetate	$3.2 \cdot 10^{-2}$	84	0.031	6.0
Methyl ethyl ketone	1.5	77	0.171	—
Methyl isobutyl ketone	0.11	77	0.043	13.1
Octanol	2.2	—	0.073	—
Butanol	2.4	—	0.88	17.1

* The basic strength was measured from the displacement of the CH_3OD band in the infrared spectra.

The addition of an inert solvent to the extraction system decreases the extraction[1,90,94]. The use of solvent mixtures is convenient in practice, since in this case the separation of the phases is more rapid (because of the decrease in the miscibility with water), and the organic phase becomes heavier. In the selection of solvent in analysis, account is taken of the miscibility with water, the absorption of light in a given range of the spectrum, the selectivity, and the possible extraction of the ligand. Sometimes, in addition to the principal extracting agent, a solvent having a high solubility in water is added (acetone, propanediol carbonate[45]) to eliminate emulsified water from the extract. Amines, tributyl phosphate, and dimethyl sulphoxide are used only in mixtures with a diluent, polar or non-polar.

Table 2. Influence of the length of the carbon chain on the extraction ($\lg K_{ex}$) of heteropolyacids by alcohols (pH 1, $HClO_4$).[10]

Alcohol	Mo-P	Mo-Si
Propanol	3.29	—
Butanol	1.85	6.29
Pentanol	1.95	6.29
Hexanol	1.66	6.04
Octanol	0.63	5.64

2. Nature of the Compound Being Extracted

The extraction of heteropolycompounds depends on the nature of the central atom and, to a lesser extent, on the nature of the ligand. The decisive factors are the valency of the central atom (which is related to the charge of the anion) and its size. Extraction decreases with decrease in the valency of the complex-forming atom, that is with increase in the charge of the heteropolyanion (Table 3)[8,10,68,77]. In a series of heteropolycompounds of elements of identical valency, the extraction decreases with increase in the ionic radius of the element. The distribution coefficients of molybdophosphoric and molybdoarsenic acids under identical conditions[67] are given below:

	HCl, M	for Mo-As	for Mo-P
Butyl acetate	1.2	$10^{-2} \times 4.4$	100
Butanol + chloroform	0.35	$10^{-3} \times 1.4$	30

The distribution coefficients and extraction constants for molybdenum and tungsten heteropolyacids having the same central atom are of the same order of magnitude in all solvents studied[67,68,77,78] (Table 3).

Table 3. Distribution coefficients of molybdenum and tungsten heteropolyacids of silicon and phosphorus[77].

Solvent	Mo—P	W—P	Mo-Si	W—Si
Pentyl acetate	$1.9 \cdot 10^{-2}$	$1.1 \cdot 10^{-2}$	$2.26 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$
Nitrobenzene	0.21	$3.1 \cdot 10^{-2}$	$4.2 \cdot 10^{-3}$	$3.08 \cdot 10^{-3}$
Ethyl acetate	0.23	$3.2 \cdot 10^{-2}$	$8.5 \cdot 10^{-4}$	$3.9 \cdot 10^{-4}$
Methyl isobutyl ketone	1.08	0.11	$1.1 \cdot 10^{-2}$	$7.0 \cdot 10^{-3}$
Methyl ethyl ketone	1.58	1.5	0.42	0.18
Isopentyl alcohol	3.7	1.8	$1.1 \cdot 10^{-2}$	$1.06 \cdot 10^{-2}$
Octanol	9.6	2.2	$2.5 \cdot 10^{-3}$	$1.04 \cdot 10^{-3}$
Butanol	9.2	2.4	4.28	1.32

Comparison of the distribution coefficients calculated by different workers for specific conditions casts doubt on the above relationships. Under real conditions, however,

the distribution coefficient is influenced by many factors (the stability of the given heteropolycomplex, the nature of the mineral acid, the concentration of the ligand, and temperature), so that the breakdown of the relationships is only apparent (Table 4).

Table 4. Optimum concentration of hydrochloric acid for the extraction of molybdenum heteropolyacids, and their distribution coefficients[6].

Extracting agent	v/v₀	HCl, M	D	v/v₀	HCl, M	D
	Molybdophosphoric acid			Molybdosilicic acid		
Diethyl ether	1.7	1.0—1.3	1.65	1.0	0.1—4.0	0.01
Diethyl ether–pentanol (5:1)	4.2	0.1—1.5	410	4.2	1.5—4.0	410
Butyl acetate	0.3	0.1—1.0	620	1.0	3.0	0.6
Methyl isobutyl ketone	0.3	0.1—1.5	620	7.1	0.1—4.0	710
Chloroform–butanol (4:1)	1.0	0.5—1.5	1.2	1.0	0.1—2.0	0.01
	Molybdoarsenic acid			Molybdogermanic acid		
Diethyl ether	1.0	0.5	1.1	1.0	2.0	0.06
Diethyl ether–pentanol (5:1)	4.2	0.1—1.5	1.1	4.2	1.0—1.4	100
Butyl acetate	1.0	2.0	0.07	1.0	2.0	0.08
Methyl isobutyl ketone	0.3	0.1—1.5	620	1.0	0.1—2.0	620
Chloroform–butanol (4:1)	1.0	0.1—2.0	0.01	1.0	0.1—2.0	0.01

The composition of the heteropolyanion remains unchanged on transfer to the organic phase. This is indicated by the fact that the absorption spectra of aqueous solutions and re-extracts of the heteropolycompounds are identical[76], and is confirmed by chemical analysis of the organic phases[7,76,77], by the isomolar-series method[11], by radiometric measurements[158], and by other methods. The fact that the composition of the heteropolycomplex remains unchanged on extraction has made it possible to detect unsaturated complexes of molybdophosphoric acid, formed under certain conditions. At pH 1, complexes having a ratio Mo : P < 12 (even at a ratio Mo : P = 42 in the aqueous phase), extracted quantitatively by butyl acetate and heptanol, are formed[105]. Solutions of phosphate and molybdenum contain highly coordinated forms (Mo : P ≥ 18), extracted by a mixture of butanol and chloroform[13]. The preferential extraction of unsaturated complexes of phosphorus, silicon, and germanium by butanol, and of complexes having a higher molybdenum content by a mixture of butanol and chloroform, has been confirmed[83,85,87]. In some cases, decomposition of the mixed complexes on extraction and the transfer of the binary compounds to the organic phase have been observed[103,159].

Special comparative studies of the extraction of the α- and β-isomers of heteropolycompounds have not been carried out. It has been reported that there are no significant differences in the extraction of the isomers of molybdosilicic acid by dioctylamine[74] and isobutyl alcohol[129].

3. Nature and Concentration of Mineral Acid

In spite of lack of agreement in published data on the pH at which extraction starts, it can readily be seen that the greater the extracting power of a solvent and the ability of the heteropolycompound to be extracted, the lower the acidity of the aqueous phase at which extraction of the complex begins. It is for this reason that in most studies, the comparative extracting power is estimated from the pH corresponding to the start or completion of the extraction of the heteropolycompound. The dependence of the extraction on the acidity of the aqueous phase is represented in the form of distribution curves obtained by plotting the distribution coefficient D (or the percentage extraction, optical density of the organic phase, etc.) against pH, and also in the form of distribution diagrams obtained by plotting lg D against pH (Figs. 1 and 2). The distribution curve has three sections: in the first section, the extraction increases with increase in the acidity, the second section is the range of optimum extraction (D = const), and in the third section the extraction decreases with increase in the acidity. Published papers do not always give all sections of the distribution curve; most frequently, only the first two are given.

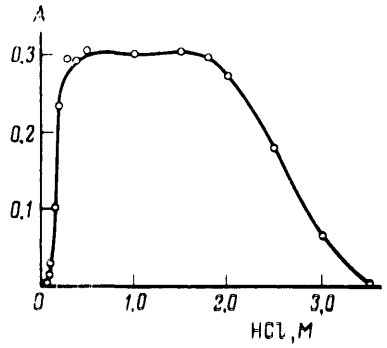


Figure 1. Dependence of the extraction of molybdoarsenic acid by butanol on the concentration of hydrochloric acid in the aqueous phase[67].

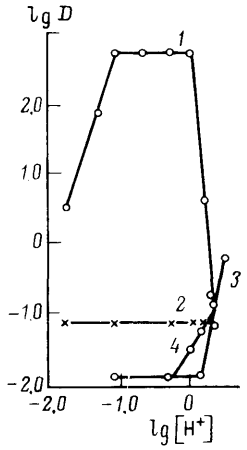


Figure 2. Distribution of molybdenum heteropolyacids between the aqueous phase and butyl acetate[6]: *1*) Mo–P, *2*) Mo–As, *3*) Mo–Si, *4*) Mo–Ge.

The functional pH dependence of the distribution constant on the first section of the curve has the form[1]:

$$\lg D = n \lg [H^+] + \text{const} .$$

Using this relationship, some authors attempt to determine the degree of participation of hydrogen ions in the reaction involved in extraction (Table 5). The results are contradictory, and this casts doubt on the justification of determining the number of hydrogen ions by this method. In fact, a priori assumption that the distribution constant remains constant is not completely correct in such a complex system as the heteropolycompound–acid–ligand–solvent system. Simon and Boltz[6] suggest that a correlation cannot be drawn between the slope of the $\lg D$–pH curves and the number of hydrogen ions. This method, which gives good results in the study of the extraction of hydrogen halogenometallates, cannot be used in systems in which, in the opinion of the authors cited[6], the solvent plays a definite role in the formation of the compound being extracted.

Table 5. Experimentally determined numbers of hydrogen ions n taking part in the extraction of heteropolyacids.

Extracting agent	Mineral acid	pH	n	References
Molybdophosphoric acid				
Butanol–kerosene	HCl	1.2—1.5	3	107
Propyl acetate	HNO_3	0.6—1.4	2	9
Propyl acetate	HNO_3	0—0.6	0	9
Butanol, alkyl acetates	$HClO_4$	1—2.5	1	10
Butyl acetate	HCl	1—2	3.3	6
Diethyl ether	HCl	0—1	2.6	6
Chloroform–butanol	HCl	0—1	2	6
Molybdosilicic acid				
Methyl ethyl ketone	HCl	0—2	2	77
Alcohols	$HClO_4$	0—1.5	2	9
Diethyl ether–pentanol	HCl	0—1	3.3	6
Molybdogermanic acid				
Diethyl ether–pentanol	HCl	0—1	3.3	6
Tungstophosphoric acid				
Methyl ethyl ketone	HCl	0—3	1	76
Ethyl acetate, methyl isobutyl ketone, isopentyl alcohol	HCl	0—3	2	76
Nitrobenzene	HCl	0—3	0.5	76

The nature of the anion of the mineral acid has little influence on the first section of the distribution curve, but has a considerable influence on the third section, that is in the range of acidity in which decomposition of the complex takes place. The decrease in the extraction takes place at a lower acidity in sulphuric acid than in nitric acid and other media. This phenomenon is not observed for the extraction of tungsten acids. The difference can be attributed to possible complex formation by molybdenyl ions with sulphate ions[67].

4. Presence of Neutral Salts and Ligand Ions

The influence of added electrolytes on the extraction equilibrium has not been studied systematically. The mechanism of the influence of electrolytes on extraction is not clear. In the opinion of some authors[6,68], the published quantitative characteristics of extraction are greatly distorted, since most measurements have been made at a high concentration of electrolytes, that is in the range in which the discrepancy between the concentration of the components and their activity is considerable. The impossibility of comparing the experimental data obtained by different workers is often due to the difference in the ionic strengths at which the experiments were carried out.

Data have been published on the influence of various ions on the degree of extraction of heteropolyacids in the analysis of specific materials for silicon, phosphorus, and arsenic[106,107,113–116,141,143,144,160]. The mechanism of the influence of neutral salts on the extraction equilibrium is apparently different in each case. Previously, the increase in the distribution coefficients of heteropolyacids at high salt concentrations was attributed to the salting-out effect[1], but recent data show that the influence of sodium, lithium, and caesium salts cannot be regarded as merely due to the change in the ionic strength[76,161–166]. Extracts of heteropolyacids of molybdenum and tungsten with silicon and phosphorus have been found to contain compounds in which the ratio of lithium to the heteropolyanion is 1 : 1.[76] The extraction of molybdophosphoric acid at pH 1–2 is more complete in the presence of sodium, potassium, and lithium chlorides than in their absence, because of the formation and extraction of sodium molybdophosphate having a ratio Na : P = 2.5.[166] Caesium can be extracted quantitatively from solutions of heteropolyacids as a consequence of exchange between caesium ions from the aqueous solution and hydrogen ions of the heteropolyacid from the organic phase[163].

The extraction of salts of molybdenum and tungsten is of particular interest, since all heteropolycompounds are formed and are stable in aqueous solutions only in a definite excess of the ligand ions. It is particularly important to take account of the possible extraction of the ligand in the development of indirect methods for determining an element via the ligand. Isopolymolybdates and isopolytungstates are extracted less effectively than the corresponding heteropolycompounds. Their extraction obeys the same regular features as the extraction of heteropolycompounds[8,105,110,167–169]. Isopolymolybdates are extracted most effectively by alcohols, and least effectively by esters and ketones[7,67,68]. Metatungstate is extracted only by butanol and methyl isobutyl ketone at a concentration of mineral acid $\geq$ 5 M.[68] The distribution of isopolymolybdate between the aqueous and organic phases depends on the nature of the mineral acid, because of complex formation by molybdenum(VI) ions with the anions of mineral acids.

Babko and coworkers[8] introduced the separation factor of molybdenum heteropolyacids and isopolymolybdates, equal to the ratio of their distribution coefficients, and calculated its values in the molybdophosphoric acid–sodium molybdate–solvent system. The greatest separation effect[8] is observed for extraction by esters ($\gamma > 1000$ for propyl acetate at pH 0.2), and the least effective differentiation is observed for alcohols ($\gamma < 50$ in butanol and pentanol). Isopolymolybdates are extracted effectively by solutions of amines of high molecular weight in various diluents[110,167].

5. Time and Temperature

It is considered that shaking a mixture of an aqueous solution of a heteropolycompound with an extracting agent for 1–2 min is sufficient for maximum extraction of the complex into the organic phase under given conditions[7,8,29,66]. It has been reported that equilibrium is established after shaking for 30 s [101] or even 20 s [105,170]. Other studies[66,67] have shown, however, that the percentage extraction of

molybdoarsenic and molybdophosphoric acids increases with increase in the duration of extraction to 30 min. When the extraction mixture is shaken for such long periods, separation of the phases into layers becomes unsatisfactory[170]. It is considered[104] that the time required for extraction equilibrium to be established depends on the initial concentration of the complex in solution. A study of the kinetics of the extraction of α-molybdosilicic acid by trioctylamine in toluene showed that the process is heterogeneous and involves several stages[42].

The influence of temperature on the extraction equilibrium has not been described. The choice of temperature has been determined only by the conditions of formation of the given heteropolycomplex[105].

III. EXTRACTION OF MIXED HETEROPOLYCOMPOUNDS

Considerable attention is being paid to the study of the extraction of mixed complexes, chiefly because of the possible extension of the range of elements whose determination is based on the formation of heteropolycompounds (particularly in the development of indirect methods of analysis), and also because extraction has proved to be an effective method for studying mixed complexes in solution. Mixed complexes are extracted less effectively than the corresponding binary compounds, although the regular features of extraction, noted above, are preserved. The best extracting agents are alcohols and methyl isobutyl ketone[90,104,106,159,171,172]; ethers and esters either do not extract mixed complexes at all or require a high acidity for extraction[31,159,173]. The process is sometimes accompanied by decomposition of the compound[103,159]. Mixtures of alcohols with esters or hydrocarbons extract a complex more effectively, the higher the concentration of alcohol. This is used in analysis to separate mixed complexes from binary complexes[15,47,56,58,60,82]. Trioctylamine extracts mixed molybdenum heteropolyacids quantitatively over a wide range of acidity[35,37].

Extraction depends on the nature and number of atoms replacing the ligand atoms in the coordination sphere. The greatest ability to be extracted is shown by mixed complexes of phosphorus with the maximum number of molybdenum atoms. When molybdenum(VI) is replaced by V(V), W(VI), Nb(V), Th(IV), Ti(IV), and Zr(IV), the ability to be extracted decreases. The extraction of molybdenum complexes of phosphorus decreases in the order Th(IV) > Ti(IV) > Zr(IV), and the form of the curves giving the dependence of the distribution coefficient on the ratio of chloroform and butanol in the extraction mixture is specific for each compound[15]. The greater the metal : molybdenum ratio, the less effective the extraction of the complex[90,159]. In the extraction of the compounds formed in the systems Ge(IV)–Mo(VI)–Cr(III) and P(V)–Mo(VI)–Cr(III), only compounds having a low chromium content are extracted into the organic phase[80,82].

The extraction of a number of mixed complexes of molybdenum and phosphorus has been studied, and the results have been used for the indirect determination of metals[56–58,60,61]. It is considered that the complexes have the compositions P : Nb : Mo = 1 : 1 : 11 for niobium, Ti : Mo = 2 : 11 for titanium, Ce : P = 2 : 1 for cerium, and Th : P = 2 : 1 for thorium. On extraction by alcohols and esters, the thorium and cerium complexes decompose[103], and molybdophosphoric acid passes into the organic phase. The extraction of vanadomolybdophosphoric acid having a ratio P : V : Mo = 1 : 1 : 11 has been most fully studied. The complex is extracted quantitatively by pentanol at pH 0,[48,50] by butanol at pH 1,[60] by methyl isobutyl ketone at pH 0.3,[106] by a mixture of pentanol and diethyl ether[49], and by trioctylamine in various diluents[35,37]. Methyl isobutyl ketone is used particularly frequently. The composition of the complex is preserved on extraction.

Phosphorus compounds are extracted much more effectively than compounds containing other central atoms[100,173].

IV. EXTRACTION OF REDUCED HETEROPOLYCOMPOUNDS

The structures of the yellow (oxidised) and blue (reduced) forms of heteropolycompounds are identical[2], so that it is to be expected that the principal regular features of extraction should be preserved after reduction of the complex.

Unfortunately, it is very difficult to compare published quantitative data, since the distribution data (distribution coefficients, percentage extraction) have been obtained under the optimum conditions for the extraction of the given complex, that is at definite concentrations of the ligand ions, mineral acid, and added electrolytes. This has led firstly to lack of agreement in the results obtained by different workers, and secondly to conclusions which are not fully justified, since the variations in the distribution data are small (under optimum conditions, extraction is practically quantitative) and can be attributed to experimental errors.

Alcohols are recognised as the most effective extracting agents for molybdosilicic acid blues. Isopentyl alcohol is usually employed. Although alcohols having a similar number of carbon atoms in the molecule have a greater extracting power, isopentyl alcohol is sparingly soluble in water, and this is a practical advantage. For molybdophosphoric acid, methyl isobutyl ketone is more frequently used[160,174], in spite of the fact that alcohols have a higher extracting power[7,175,176]. It has been reported that there is a decrease in the molar absorptivity with preservation of a high percentage extraction of acid blues by various oxygen-containing solvents, and that the stability of the complexes in the organic phase depends on the nature of the extracting agent[29,175]. Unfortunately, the works cited do not give the purity of the solvents used, or data on the extent of the oxidation of the heteropolyanion in the organic phase, so that there is some doubt as to whether the decrease in the value of $\bar{\epsilon}$ is due to the partial oxidation of the heteropolyanion blue by impurities in the solvents, particularly since data on the stability of reduced complexes in the organic phase do not always agree[7,176]. Thus the conclusion[175] that the properties of the compound formed in the organic phase depend on the nature of the extracting agent is not completely correct.

The transfer of reduced heteropolycompounds from an aqueous solution to an organic solvent is accompanied by a displacement of the absorption bands in the visible range of the spectrum. The displacement of the absorption maximum is generally hypsochromic (Table 6). In the extracts of heteropolycompound blues reduced by tin(II) salts, a second absorption maximum appears. The reduction products have been divided into two groups, according to their extraction behaviour[7,29]: a) those obtained by the action of "mild" reducing agents (ascorbic acid, 1-amino-2-naphthol-4-sulphonic acid, hydrazine sulphate, p-methylaminophenol sulphate), for which the spectrum of the extract gives one absorption maximum; and b) those obtained by the action of tin(II) salts, for which the spectra

of the extracts contain two absorption maxima. The position of the absorption band is independent of the extracting agent. It has been reported, however, that the absorption spectra of molybdophosphoric acid blues depend on the extracting agent[176]. The α- and β-isomers show different behaviour on extraction[29].

Table 6. Positions of the absorption maxima (nm) for reduced heteropolyacids in aqueous solutions and extracts after extraction by butanol.

Hetero-polyacid	Tin(II) salts		Ascorbic acid		1-Amino-2-naphthol-4-sulphonic acid		Hydrazine sulphate		Refs.
	water	butanol	water	butanol	water	butanol	water	butanol	
α-Mo—Si	740	630 and 720	720	720	—	—	790	720	32
β-Mo—Si	800	630 and 720	800	780	805	800	825	805	32
Mo—P	740	625 and 725	825	780	825	780	825	780	7
Mo—Nb—P	700	730	—	—	—	—	—	—	104

Amines of high molecular weight extract reduced heteropolyacids more effectively than oxygen-containing solvents[24,33]. Thus molybdosilicic acid blue is extracted quantitatively by trioctylamine at pH 1–1.6. The extraction is accompanied by a displacement of the absorption maximum; the magnitude of the displacement depends on the diluent and the nature of the heteropolyacid, but is independent of the nature of the amine[24,26]. Reduced mixed heteropolycompounds are extracted less effectively than the binary compounds.

In analysis, use is made of the extraction of heteropolyacids reduced in aqueous solution, and also of a heteropolycompound in the organic phase after its extraction in the non-reduced form[69,91-93,95,113,115,122-124,133,134,138,141,143,146,147,149,152-156,177-179]. Although the last procedure is more widely used, the process of reduction in organic solvents has been very little studied. The reduction of heteropolycompounds is more difficult in the organic phase than in aqueous solution. The use of tin(II) chloride, mixtures of iron(II) chloride[180] with ascorbic acid[137], and ferrocene[154] have been recommended.

In the reduction of the isomers of molybdosilicic acid, the formation of two-electron blues of β-molybdosilicic acid, and two- and four-electron blues of the α-isomer, has been observed in extracts obtained using dioctylamine in chloroform[73]. In the opinion of the authors cited[72], the four-electron β-isomer can exist only in aqueous solution, and not in the organic phase. Similar results were obtained in a study of the reduction of the isomers of molybdosilicic acid in oxygen-containing solvents[72]. The formation of intermediate products of the reduction of the α-isomer, containing tin(IV) as hetero-atom, is assumed[72].

The polarographic behaviour of heteropolycompounds in organic solvents has been studied in most detail. It is difficult to compare the results of polarographic studies by different workers, since the experiments have been carried out under different conditions (supporting electrolyte, nature of the electrodes, and solvent). The magnitude of the reduction potential and the intensity of the signal are influenced by many factors, but the mechanism of their action is not clear[53,69-73,91-96,99,111,112,122,123,179,181].

V. EXTRACTION OF HETEROPOLYCOMPOUNDS BY AMINES OF HIGH MOLECULAR WEIGHT

The extraction of heteropolycompounds by amines has been comparatively little studied[24,33-42,72-75,109-172,182-185]. The use of amines is extremely promising in analysis, since the presence, in the molecule of the extracting agent, of the nitrogen atom, which is more basic than the oxygen atom, ensures the quantitative extraction of the elements as the heteropolycompounds. It is true that this is accompanied by a decrease in the selectivity of extraction. The theoretical study of the extraction of heteropolyacids as ionic associates is of interest. Amines in which the hydrocarbon chain contains less than seven carbon atoms are not used, because of their ready miscibility with water. Primary amines extract heteropolyacids with the formation of precipitates, which float at the interface between the phases, particularly in non-polar diluents. The formation of precipitates is also observed in extraction by secondary and even tertiary amines at low concentrations. In the opinion of some authors[24], secondary amines are better extracting agents than tertiary amines.

Extraction by amines is carried out over a wide range of acidity, restricted only by the protonation of the amine and the stability of the heteropolyanion. The extraction of reduced forms begins at a higher acidity[24,33]. The extraction without acidification, reduction of the heteropolycomplex by trioctylamine is observed[39]. The reduction of molybdophosphoric acid by other amines in sulphuric, perchloric, and hydrochloric (but not nitric) acids has been observed by Ivanov[182]. In the extraction of heteropolyacids by insufficient quantities of an amine in diluents having a low polarity, extraction of the complex in quantities greater than that corresponding to the stoichiometry of the ionic associate formed is observed[34]. This effect, which is characteristic of all strong acids, is probably due to the extraction of additional molecules of the heteropolyacids by the compound extracted.

No significant differences are observed in the extraction of the isomers of molybdosilicic acid[35,74]. The composition of the coordination sphere of the heteropolycomplexes remains unchanged on extraction. In the extraction of molybdoarsenic acid from hydrochloric acid solution, however, the ratio of the number of central atoms to the number of ligand atoms is 1 : 11.[74] It was suggested[74] that two forms of complex are extracted: a saturated form having a ratio As : Mo = 1 : 12, and an unsaturated form having a ratio As : Mo = 1 : 9. At the interface between the phases, the colourless unsaturated complex is partly converted into the yellow saturated complex.

The compounds formed on extraction are ionic associates[34,109]. The compositions of the products extracted correspond to the complete replacement of the protons in the non-reduced forms[34,37,109,182]. Fractional amine : heteropolyacid ratios have been found[74], however (from saturation curves). This is attributed to the possible existence of different protonated forms of the complexes in the strongly acidic media in which the experiment was carried out.

The nature of the absorption spectra of the organic phase is independent of the nature of the amine. In the opinion of some authors[24], the position of the maximum in the spectra of extracts of reduced molybdophosphoric acid depends on the reducing agent and the solvent used to dilute the amine.

The mechanism of the extraction of heteropolycompounds as their associates with dyes and quinolinol is probably similar to that for extraction by amines. Heteropolyacids

react with basic organic compounds (generally containing a nitrogen atom in the molecule) to give products sparingly soluble in water. From the nature of the bonding, they can be regarded as ionic associates. In some cases, these compounds dissolve in organic solvents which are immiscible with water, that is it is possible to extract the heteropolycomplex as ionic associates with organic bases (various types of dye, 8-quinolinol). The use of dyes as extracting agents in analysis is promising, since most dyes have high molar absorptivities. The compounds of molybdophosphoric acid with a number of dyes (Crystal Violet, Methyl Violet, Malachite Green, Iodine Green, Safranine, Rhodamine, etc.) are extracted by hydrocarbons, alcohols, and ketones[17,18,22,23,25,59]. The compounds of molybdosilicic acid with dyes of the triphenylmethane, xanthone, and antipyrine series are also soluble in alcohols and ketones, but are not extracted by hydrocarbons and nitrobenzene[30]. Molybdoarsenic acid reacts with dyes to form compounds which can be extracted by alcohols and ketones[16].

Alcohols and ketones, particularly the aromatic and cyclic compounds[17,30], and propyl acetate, are regarded as the best extracting agents for the ionic associates formed by heteropolyacids with dyes. Extraction is sometimes accompanied by flotation at the interface between the phases[30,18]. The extraction of ionic associates takes place in a definite range of acidity, which is broader than that for the extraction of heteropolycomplexes by oxygen-containing solvents. According to some authors[17], the ionic associates of molybdophosphoric acid are extracted at pH 1.3–1.5; according to others[59], the ionic associate of the same acid with Rhodamine B, $[RhB]_3^+[Mo\text{–}P]$, is extracted at the pH of formation of the complex without additional acidification. The same is observed in the extraction of the reduced molybdophosphoric acid by Safranine T.[25] As in the case of extraction by amines, the acidity range is apparently restricted by the stability of the heteropolycomplexes.

The compositions of the compounds formed by molybdosilicic acid with dyes depend on the nature of the dye: the molecule of the molybdosilicic heteropolyacid adds on four molecules of Rhodamine 6G and three molecules of Methyl Violet[30]. 8-Quinolinol also reacts with molybdophosphoric acid to form a compound which is sparingly soluble in water but soluble in oxygen-containing organic solvents[19]. The ability of the compound formed by 8-quinolinol with molybdophosphoric acid to pass into the organic phase decreases in the solvent order[79]: nitrobenzene > carbon tetrachloride > chloroform, that is the order coincides with the order of extraction of the heteropolycomplex in the absence of quinolinol[79]. It is suggested that the compound $[PMo_{12}O_{40}](HOx)_3$, where Ox = 8-quinolinol, is formed.

VI. MECHANISM OF THE EXTRACTION OF HETEROPOLYCOMPOUNDS

Various suggestions have been made regarding the mechanism of the extraction of heteropolycompounds, but the experimental material available up to the nineteen-sixties did not make it possible to give preference to any of these[1]. It is now possible to exclude from the number of hypotheses the suggestion that there is physical distribution of the heteropolycompound between the aqueous and organic phases. The solubilities of heteropolycompounds in water and organic solvents are commensurate, so that the distribution coefficient for a physical distribution mechanism should be ~1, which is not confirmed by experimental data. Experimental observations also do not confirm the hypothesis of an oxonium mechanism of extraction by oxygen-containing solvents, according to which heteropolycompounds are extracted as alkylsubstituted oxonium salts, the so-called etherates. In this case the extraction should take place in a strongly acidic medium, whereas the extraction of heteropolycompounds has been reported even at pH 3–1.

At the present time, two mechanism of extraction, based on the assumption that the heteropolycompound reacts with the extracting agent, are being discussed. According to the donor–acceptor mechanism, extraction is accompanied by the formation of a coordination compound between the molecule of the organic solvent (electron donor) and the heteropolyanion (electron acceptor). The formation of the coordination compound involves the oxygen, nitrogen, or phosphorus atoms of the organic solvent and an atom of the ligand of the heteropolycomplex, in particular molybdenum, which in this case has a coordination number equal to eight. According to the hydrate–solvate mechanism, the reaction of the solvent with the heteropolycompound involves its cationic part. For the extraction of heteropolycompounds by amines of high molecular weight and in the form of compounds with dyes, the ion associate mechanism and anion exchange are also being discussed.

The reaction between heteropolycompounds and the solvent is indicated by changes in the absorption spectra in the visible, ultraviolet, and infrared ranges, and in the PMR and NMR spectra. The spectra of extracts of molybdophosphoric acid show a maximum in the range 308–320 nm;[5,9,109] the same maximum is observed when molybdophosphate is formed in aqueous organic media[28,130]. In the spectra of extracts of tungsten heteropolyacids, the absorption maximum is displaced by 10–15 nm.[68,76,108] In the extraction of the reduced forms, a hypsochromic shift of the absorption maxima in the visible range is observed. The PMR spectra show the chemical shifts and the change in the width of the lines due to water, and also the chemical shifts of the signals of the proton-containing groups of the solvent[83,86,186].

The changes in the absorption spectra are not always interpreted correctly, however. In the opinion of some authors[24,25], the hypsochromic shift of the absorption maximum in the spectra of the extracts of reduced heteropolyacids is due to the donor–acceptor interaction of the molybdenum(VI) atom of the heteropolyanion with the oxygen atom of the solvent. The changes in the spectra might have been due to other factors, however. Thus a change in the oxidation state of the heteropolyanion leads to a change in the absorption spectrum. The products of the attachment of from one to six electrons to molybdosilicic acid differ in the positions and intensities of the absorption band maxima[187]. Differences are also observed in the absorption spectra of the products of the reduction of α-molybdosilicic acid by two and four equivalents of tin(II) chloride or oxalate[29,75].

Changes in the spectra may also be due to a change in the degree of protonation of the heteropolyanion, as shown by a number of workers[188]. The protonation of the sextuply-charged α-molybdosilicate blue leads to a bathochromic shift of the absorption maximum by 60–70 nm, whereas for β-molybdosilicate, a hypsochromic shift of 80–100 nm is observed. Moreover, tin(IV) evidently takes part in the formation of intermediate compounds in the reduction of heteropolycompounds by tin(II) salts. The stabilisation of intermediate mixed compounds may also lead to changes in the absorption spectra of extracts, compared with those of the aqueous solutions. The suggestion

that there is donor–acceptor interaction between the heteropolyanion and the oxygen atom of the solvent, based on the displacement of the bands in the infrared spectra in heteropolyacid–ketone systems[86], was found to be unjustified. It was later shown that the displacement of the bands is due to the formation of new compounds in the system, including alkyl derivatives of benzene[186].

In the opinion of Lebedeva and Vanchikova[83,84,87], evidence in support of the donor–acceptor mechanism of extraction of heteropolycompounds is provided by data obtained in the study of the solvation of molybdenum and tungsten heteropolycompounds of phosphorus, silicon, and germanium by NMR and PMR spectroscopy. According to their observations, the extraction of the heteropolyacids of silicon and phosphorus takes place by different mechanisms. In the presence of an organic solvent, the anionic part of the heteropolycomplex is solvated, whereas in an excess of the solvent, the cationic part is also solvated. The donor–acceptor mechanism has been used[83,84,87] to explain various regular features of the extraction of saturated and unsaturated molybdenum heteropolycomplexes, and also the differences in the extracting power of oxygen-containing solvents. Thus the greater extracting power of alcohols can be attributed to their greater solvating power, since they can act as both electron donor and proton donor; esters and ketones, however, exhibit only electron-donor properties.

Most of the regular features of the extraction of heteropolyacids can be described satisfactorily on the basis of the hydrate–solvate mechanism of extraction of strong acids. The participation of the functional groups of the organic solvents in hydrogen bond formation is indicated by the displacement of the bands due to the stretching vibrations of the OH bonds in butanol and the C = O bonds in propyl acetate towards lower wavenumbers (by 170 cm^{-1} and 40 cm^{-1} respectively) in the infrared spectra of the extracts[9]. In Ivashkovich's opinion[9], the increase in the extraction of molybdophosphoric acid with increase in the acidity of the aqueous phase, that is with suppression of the acidic dissociation of the complex acid, indicates the possible existence of a hydrogen bond between the hydrogen ions of the heteropolyacid and the oxygen atom of the solvent. This gives an associate which is extracted into the organic solvent by a hydrate–solvate mechanism. The formation of an ion pair between the triply-charged anion of molybdophosphoric acid and a solvated hydroxonium ion is assumed by a number of authors[76,77,107,159]. Simon and Boltz draw an analogy between extraction systems of the type iron(III)–hydrochloric acid–organic solvent and the heteropolyacid–organic solvent system; for molybdophosphoric acid, the equation for the reaction involved in extraction should be written in the form[6]:

$$3H(H_2O)\,(S)_x^+ \cdot Cl + [PMo_{12}O_4]^{3-} \rightleftarrows 3H(H_2O)\,(S)_x^+ \cdot [PMo_{12}O_{40}]^{3-},$$

where S represent the solvent.

For the description of the same process, with the assumption that a hydrated heteropolyanion is present in the aqueous solution, Ivashkovich[9] proposed the equation

$$[PMo_{12}O_{40}]^{n-} \cdot m\,H_2O\ (aq) + n\,H^+ \rightleftarrows H_n[PMo_{12}O_{40}]\,m\,H_2O\ (aq) + q\,S \rightleftarrows \rightleftarrows H_n[PMo_{12}O_{40}] \cdot m\,H_2O\,q\,S.$$

A similar equation for extraction has been put forward by other workers[10].

Using the equations for extraction and generally accepted techniques, various authors have tried to determine the solvation number, that is the number of molecules of the solvent taking part in the formation of the ion pair (Table 7). The results are contradictory, and this casts doubt on the justifiability of determining solvation numbers in this case by the usual methods. In fact, in extraction by mixtures of an extracting agent and inert diluents of different composition, the changes in the dielectric constant of the extracting agent are usually not taken into account. It has been shown[78] that the increase in ϵ with increase in the proportion of tributyl phosphate in its mixtures with chloroform leads to an increase in the dissociation of the ion pair in the organic phase, and in the final analysis to a value of the solvation number which is too high. This possibly explains the value of the solvation number, equal to six, found in a study of the tungstophosphoric acid–tributyl phosphate system[189].

Table 7. Experimentally determined solvation numbers m.

Solvent	Medium	m	References
	Molybdophosphoric acid		
Any solvent	HCl	6	91
Propyl acetate	pH 0.3; HNO_3	8	9
	pH 2.0; HNO_3	6	9
Alcohols	$HClO_4$	5	10
Tributyl phosphate		8–9	87
Esters, ketones		0.26–5.3	186
Tributyl phosphate		3	78
	Molybdosilicic acid		
Alcohols	$HClO_4$	8	10
Tributyl phosphate		3	78
		12	87
Dibutyl sulphoxide		6	190
	Tungstophosphoric acid		
Tributyl phosphate	HNO_3	6	189
»		3	78
	Tungstosilicic acid		
Tributyl phosphate		3	78

The values obtained for the solvation numbers, and also the numbers of hydrogen ions involved in the reaction (Table 5), have been used to calculate the extraction constants[10,77–79,97]. The values of the constants found by different authors naturally do not coincide. However, the extraction constants and distribution coefficients found under the same conditions can be used to estimate the comparative extracting power of solvents or the extraction of different heteropolycompounds, so that their determination is undoubtedly necessary.

Various reactions may take place in the organic phase containing extracted compounds, Lakshmanan[77] showed that ion pairs dissociate in nitrobenzene with the removal of the solvated proton. This provides evidence in support of a hydrate–solvate mechanism of extraction.

The differences in the extraction of heteropolyacids having different central atoms are readily explained by the hydrate–solvate theory: the greater the charge of the heteropolyanion, the less effectively it should be extracted. This is confirmed by experimental data (Table 3). The decrease in the extraction of mixed heteropolycompounds compared with the binary compounds can also be understood, in view of the increase in the charge of the heteropolyanion when the molybdenum(VI) atom is replaced by an atom of lower valency (vanadium(V), niobium(V), titanium(IV), etc.). The suggestion that the decrease in

extraction is due to steric hindrance[31] is apparently not fully justified, since the replacement of one atom by another in the coordination sphere has no significant influence on the size of the anion, and the structure of the complex remains unchanged.

Contradictory views have been put forward on the comparative extraction of reduced and non-reduced forms. From the hydrate–solvate mechanism of extraction, a decrease in extraction on reduction should be expected, since the charge of the heteropolyanion increases. According to some authors[19], molybdophosphoric acid blue is extracted more effectively than the yellow form, and this was attributed to a decrease in the acidic dissociation of the compound and a decrease in the hydration of the anion in the aqueous phase. As noted above, however, the conditions under which the extraction of the two forms was studied were not identical, so that in this case, conclusions cannot be reached regarding the comparative extraction of the complexes. The hydrate–solvate mechanism of extraction of heteropolycompounds is confirmed indirectly by the fact that the α- and β-isomers are extracted to practically the same extent (the charges of the two forms are identical).

The same ideas can be used to explain the low value of the extraction factor for isopolymolybdate ions, which carry a high charge (hepta- and octamolybdates). The complex dependence of the distribution coefficient of molybdenum(VI) on the concentration of hydrogen ions and molybdate in the aqueous phase agrees with the suggestion that molybdate solutions contain polymeric species, the composition and charge of which are determined by the concentration conditions and pH.

Extraction by amines can most probably be represented by the following scheme: protonation of the amine, formation of an ionic associate of the heteropolyacid and the mineral acid with the amine (neutralisation), extraction of ionic associates into the organic phase, ion exchange between the mineral acid and the heteropolyacid, and dissociation of the ionic associate in the organic phase. The first attempt to obtain the quantitative characteristics of the extraction equilibrium in a heteropolyacid–amine system was made by workers[109] who determined the composition of the compound extracted in the extraction of α-molybdosilicic acid by tri-iso-octylammonium nitrate in dichloroethane and suggested that the compound is dissociated in the organic phase. From a study of the distribution of the heteropolycomplex between the aqueous and organic phases, they proposed the following equation for the extraction:

$$H_4[SiMo_{12}O_{40}]\ (aq) + 4R_3NHNO_3\ (org) \rightleftarrows \{[SiMo_{12}O_{40}]\ (R_3NH)_{4-n}^{n-}\}\ (org) + n\,R_3NH^+\ (org) + 4NO_3^-\ (aq) + 4H^+\ (aq).$$

From the relationship between the equilibrium concentrations of the components and the stoichiometry of the compound extracted, other workers[109] obtained an equation which made it possible to determine the stoichiometry of the dissociation of the complex in the organic phase, and they calculated the conditional extraction equilibrium constant. According to their calculations, the ionic associate dissociates with the removal of one protonated amine particle; the equilibrium constant depends on the concentration of acid in the aqueous phase, because of the protonation of the heteropolyanion.

Suggestions[109] regarding the nature of the bonding, composition, and behaviour of the ionic associate in the organic phase were confirmed by studies of the extraction of molybdosilicic and vanadomolybdophosphoric acids by trioctylamine in various diluents[34,36,37,41]; infrared spectroscopy and isolation in solid form established that the compounds extracted are ionic. The dissociation of the associates was confirmed conductometrically[36,41].

The nature of the diluent plays an important part in extraction by amines. The extraction is influenced by the dielectric constant and solvating power of the solvent[37,38]. Solvation may involve the cationic part of the heteropolycomplex in the case of a diluent having nucleophilic properties (benzene, toluene), or the anionic part in the case of a diluent having electrophilic properties (dichloroethane). The extraction constant and the distribution coefficient should reflect the overall result of the electrostatic and solvating effects of the diluent and be determined by the contributions made by each. A specific feature of heteropolycompounds is that the charge density on the anion is very low (because of the large size of the anion), so that solvation of the anionic part of the complex has a low probability.

A method has been proposed[182] for calculating the overall constant for the extraction and formation of heteropolyacids by amines, based on published data on the polymerisation of molybdenum(VI) in solution:

$$H_3PO_4 + \frac{3}{2}\,H_4Mo_8O_{26} + 3BHNO_3 \rightleftarrows (BH)_3PMo_{12}O_{40} + 3HNO_3 + 3H_2O,$$

where B represents the amine. No allowance was made, however, for processes in the organic phase.

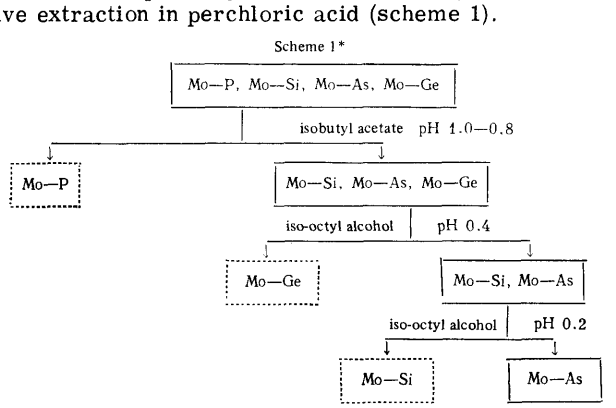
Thus the study of the mechanism of the extraction of heteropolycompounds raises many unresolved problems, and final conclusions regarding the mechanism of the transfer of heteropolycompounds to the organic phase can only be reached using a large amount of experimental material, including the results of kinetic studies of the process.

VII. ANALYTICAL APPLICATION OF THE EXTRACTION OF HETEROPOLYCOMPOUNDS

1. Separation of Elements by Extraction

The greatest number of schemes has been proposed for the separation of phosphorus, silicon, arsenic, and germanium. Methods have been developed for the successive separation of all four elements, the extraction of one of the heteropolyacids in the presence of the others, and the separation of combinations of two or three elements. The distribution diagrams for molybdenum heteropolyacids in oxygen-containing solvents and their mixtures[6] can be used to select conditions for the quantitative separation of many elements (Table 4). Paul[63] put forward a scheme for separating the same elements, based on selective extraction in perchloric acid (scheme 1).

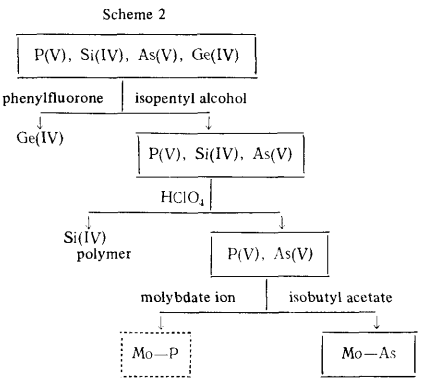
Scheme 1*



† The continuous lines denote aqueous phases, and the broken lines organic phases.

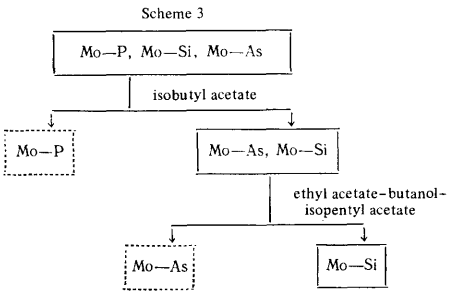
The separation schemes sometimes include reactions not associated with the formation of heteropolycompounds (polymerisation, complex formation by one or several elements, precipitation). Thus a scheme for separating germanium, phosphorus, silicon, and arsenic[64] proposes the separation of germanium as its complex with phenylfluorone, and the conversion of silicon into polymeric forms which do not give a complex with molybdate ions (scheme 2).

Scheme 2



The following scheme has been proposed for separating phosphorus, arsenic, and silicon by varying the extracting agents[191]:

Scheme 3



Amines of high molecular weight are less selective, but it is possible to separate the molybdosilicate complex from 2 M sulphuric acid solution and the molybdophosphate complex from 2 M perchloric acid solution using tri- and dioctylamine in chloroform, in the presence of arsenic and germanium[74].

Methods have been proposed for separating silicon from its mixtures with phosphorus and arsenic by the extraction of the molybdenum complex into methyl isobutyl ketone in the presence of citrate ions, which decompose the phosphorus and arsenic complexes[191], and for separating silicon from arsenic by extracting the molybdosilicate into iso-octyl alcohol[192]. A method has been proposed for separating phosphorus from the same mixture by extracting the compound of molybdophosphate with Crystal Violet into alkyl acetates at pH 0.2–0.5. The extraction is not affected by the presence of unlimited quantities of silicon, or by a tenfold excess of arsenic[8].

A method has been proposed for separating phosphorus from silicon and germanium by extracting the tungsten heteropolycomplex into butyl acetate or its mixtures with diethyl ether from 0.5–1 M sulphuric acid solution[68].

A method has been proposed[124] for separating the corresponding molybdenum heteropolyacids from a mixture of silicon, phosphorus, and arsenic by extracting into isobutyl alcohol at different acidities. Methods for separating pairs of elements (phosphorus and silicon, phosphorus and arsenic, phosphorus and germanium) are based on the ease of extraction of the heteropolycompounds of phosphorus[62,63,105,142,193]. Various methods for separating elements are based on a combination of extraction and the selective decomposition of the heteropolycomplexes in mineral acids[35].

2. Extraction Methods for Determining Elements

Extraction–photometric methods for determining elements are most widespread. This is natural, in view of the high molar absorptivity of heteropolycompounds, particularly the reduced forms (in the visible range) and the mixed complexes. Extraction extends considerably the possibilities provided by the photometric method for a number of reasons: firstly, the element is concentrated; secondly, the unstable isomers of heteropolycomplexes are stabilised; thirdly, the separation from the excess of molybdate or tungstate ions makes it possible to carry out measurements in the near ultraviolet range, where the absorption by the complexes is a maximum; and finally, extraction has provided extensive possibilities for developing indirect methods for the photometric determination of elements via the ligand.

The extraction of molybdosilicic acid by pentanol is used to determine down to 0.02% silicon in copper and brass[150], and by ethyl acetate to determine silicon in sea water[157]. In the extraction of reduced forms, butanol is used to determine down to 5×10^{-4}% silicon in titanium[101], isopentyl alcohol is used to determine silicon in a number of salts, alloys, and steels[113,120], and traces of silicon in antimony, thallium, gallium, and indium[133,134], and a mixture of chloroform and propane-1,2-diol carbonate is used to determine down to 0.2 $\mu g\ ml^{-1}$ silicon in solutions[45]. A number of methods for determining silicon are based on the extraction of the yellow forms of heteropolyacids with subsequent reduction in the organic phase. Extraction of molybdosilicic acid by pentanol with reduction by tin(II) chloride has been proposed for determining silicon in highly pure aluminium[149], extraction by butanol with reduction by a mixture of iron(II) sulphate and ascorbic acid for the determination of down to 2×10^{-3}% silicon in niobium and tantalum[137,138], extraction by methyl isobutyl ketone with reduction by tin(II) chloride for the determination of down to 2×10^{-3}% silicon in vanadium[140] and in solutions of hydrogen fluoride in the presence of tantalum[155], and extraction by isopentyl alcohol with reduction by tin(II) chloride for the determination of traces of silicon in copper and copper alloys[114].

Amines of high molecular weight are being widely used as extracting agents. Conditions have been recommended for the extraction of yellow molybdosilicic acid by a solution of tri-iso-octylammonium nitrate in dichloroethane for the determination of down to 10^{-4}% silicon in solutions[109], by a solution of trioctylamine in toluene for the determination of down to 10^{-3}% silicon in vanadium pentoxide[35], by solutions of di- and trioctylamine in chloroform for the determination of silicon in steels[74], and by a solution of diethylhexylamine in dichloroethane for the determination of down to 1 $\mu g\ ml^{-1}$ silicon in solutions[183]. The extraction of the reduced forms of molybdosilicic acid by amines has also been proposed: by a solution of dioctylamine in pentanol for the determination of down to 0.01 $\mu g\ ml^{-1}$ silicon in solutions[26]; by a solution of trioctylamine in toluene for the determination of silicon in plants and fertilisers[33]; and by a polyethoxylated amine in butanol for the determination of down to 10^{-7}% silicon in pure water[194].

Extraction by isopentyl alcohol of molybdoarsenic acid reduced by hydrazine sulphate is used for the extraction–photometric determination of down to 5×10^{-5}% arsenic in tin, antimony, aluminium, thallium, and indium[133,134,136]. A method involving reduction of the complex by tin(II) chloride after its extraction by a mixture of diethyl ether and butanol, having a detection limit of 10^{-4}% arsenic[148], and also a method for extracting the non-reduced complex by di- and trioctylamine (detection limit 10^{-4}%) and by a number of other amines for the determination of down to 0.04 μg ml^{-1}, [152,184] have been proposed. Arsenic and phosphorus can be determined in tungsten–rhenium alloys[156].

The extraction of molybdophosphoric acid by butyl acetate has been recommended for determining down to 4×10^{-6}% phosphorus in iron[177] and 0.35 μg ml^{-1} in solutions[195], extraction by isobutyl alcohol in mixtures with benzene and ethanol for the determination of phosphorus in solutions containing the products of the deprotonation of adenosine triphosphate[196], and extraction by di- and trioctylamine for determining phosphorus in steels[74]. Most extraction–photometric methods for determining phosphorus, however, used extraction of the mixed vanadomolybdophosphoric acid, and also reduction of the complex in the aqueous phase before extraction or in the organic phase after extraction. Extraction of the mixed heteropolycomplex by methyl isobutyl ketone is proposed for determining phosphorus in steels and alloys[105,144], in ferroniobium, ferrotitanium, and niobium ores[121], in ferrovanadium and ferrous alloys[120], extraction by butanol for the analysis of silicon tetrachloride (detection limit 5×10^{-7}% phosphorus)[133], by pentanol for the analysis of solutions containing down to 1.5 μg ml^{-1} phosphorus[50], and by trioctylamine in toluene for determining down to 10^{-3}% phosphorus in vanadium pentoxide[35].

Reduced forms of molybdophosphoric acid are extracted by mixtures of dioctylamine with pentanol and chloroform in the analysis of solutions with a detection limit of 0.01 μg ml^{-1} phosphorus[26], by isopentyl alcohol for determining down to 10^{-6}% phosphorus in tin[133] and down to 5×10^{-7}% phosphorus in methyltrichlorosilane[139], by methyl isobutyl ketone for the analysis of pure iron, and by butanol and isobutyl alcohol for the analysis of solutions containing down to 0.05 μg ml^{-1} phosphorus[175,176]. Many procedures recommend the extraction of the yellow molybdophosphate complex with subsequent reduction in the organic phase, most frequently using tin(II) chloride. The extraction is usually carried out by alkyl acetates; butyl acetate for determining traces of phosphorus in salts, metals, and alloys[115], and isobutyl acetate[63], ethyl acetate[62,180], and isopentyl acetate[178] for the analysis of iron and steels[147]. Various authors recommended diethyl ether[133], alcohols, and their mixtures with chloroform[141,143,146,177]. A method involving the reduction of the molybdophosphate complex by ascorbic acid in the re-extract after extraction by butanol has also been proposed for the analysis of alloy steels[151].

A number of methods for determining phosphorus in solution are based on the extraction of the ionic associates of molybdophosphate with dyes of different types[12,17,18,25,59].

In addition to traditional extraction–photometric methods, methods based on the reactions of heteropolycompounds in organic phases are now being developed. Titrimetric methods for determining phosphorus and silicon, based on the neutralisation of the heteropolyacids by strong bases in the organic phase with visual[20,21,197] and conductometric indication of the end-point of the titration[198], have been proposed. Phosphorus in natural waters has been determined by flame photometry in sodium molybdophosphate extracts[166] (detection limit 10^{-3} μg ml^{-1} phosphorus). A neutron-activation method has been proposed for determining phosphorus in steels, involving the extraction of molybdophosphoric acid by butanol and measurement of the quantity of ^{32}P ($T_{1/2}$ = 14.3 d) in the re-extracts[145].

A number of methods have been proposed for determining silicon, phosphorus, and germanium in steels, bronzes, and solutions, based on the polarographic reduction of heteropolycomplexes in the organic phase[53,69-71,73,91,92,95,96,122-124,179]. A method has been proposed for determining small quantities of elements from the chemiluminescence of the compounds formed by heteropolyacids with luminol after extraction by solvent mixtures[199,200].

Extraction is also used to determine elements which are not typical complex-forming elements in heteropolycompounds. Thus an extraction–photometric method has been proposed for determining down to 0.04 μg ml^{-1} niobium[104] and antimony[173]. Methods have been developed for extracting caesium by nitrobenzene in the presence of molybdophosphoric acid[162-165]. Extraction can also be used to determine elements which act as ligands in heteropolycomplexes. Methods have been described for the photometric determination of down to 25 μg ml^{-1} vanadium, involving the extraction of vanadotungstophosphoric acid by methyl isobutyl ketone[172] and isobutyl alcohol[201]; for the polarographic determination of molybdenum, involving the extraction of vanadomolybdophosphoric acid by isopentyl alcohol[93]; for the extraction–photometric determination of vanadium in aluminium with a detection limit of 4×10^{-4}%;[171] and for the determination of tungsten, involving the extraction of tungstophosphate[202].

In the last ten years, indirect methods have been developed for determining elements by the formation and extraction of heteropolyacids. These are based on the extraction of the heteropolycomplex under the conditions of minimum extraction of molybdate ions, decomposition of the heteropolycomplex, and determination of molybdenum(VI). The favourable stoichiometric ratio of the central atom and the ligand makes this method extremely promising for decreasing the detection limit (the multiplication factor in most cases is twelve) and extends the range of reagents and methods.

A large number of indirect methods use the photometric version, based on the formation of coloured complexes of molybdenum(VI). The use of the familiar formation of the complex of molybdenum(V) with thiocyanate ion has made it possible to develop methods for determining phosphorus in solutions (effective molar absorptivity 1.56×10^5),[65] and for determining down to 10^{-6}% phosphorus in iodine and highly pure tin[133]. A number of methods, including the determination of down to 10^{-7}% phosphorus in hydrochloric and nitric acids, are based on the kinetic determination of molybdenum(VI).[117-119] The use of organic reagents for determining molybdenum(VI) is particularly effective. Indirect photometric methods involving the use of phenylfluorone[129], azo-compounds[27], 2-amino-4-chlorobenzenethiol[54], benzidine, and gallic acid in the presence of hydrogen peroxide[203] have been proposed. Conditions have been recommended for determining microquantities of phosphorus and arsenic in rhenium using zinc dithiol (effective molar absorptivity 1.7×10^5 for phosphorus and 2×10^5 for arsenic) and Sulphonitrophenol M ($\bar{\varepsilon}_{eff} = 4.6 \times 10^5$ for phosphorus and 4.5×10^5 for arsenic)[142].

An indirect titrimetric method with complexometric titration of molybdenum(VI) after the extraction of molybdosilicic acid by isopentyl alcohol with subsequent decomposition has been proposed for determining silicon in silicides[204], and titration of Mo^{III} by permanganate after the reduction of Mo^{VI} in a reductor has been recommended for the analysis of silicates containing up to 68% SiO_2.[205] The intense absorption by molybdenum(VI) in the ultraviolet range of the spectrum is used in a number of methods for determining 0.1 μg ml^{-1} silicon and phosphorus[51], 0.3 μg ml^{-1} germanium[48], and 0.48 μg ml^{-1} vanadium[47].

Methods using atomic-absorption spectroscopy are of particular interest. Atomic-absorption spectroscopy is usually employed for the direct determination of metals. The method is inconvenient for determining non-metals, since the resonance lines of non-metals lie in the far ultraviolet range of the spectrum. In this case it is appropriate to use indirect methods combined with extraction separation from the excess of the element via which the measurement is being made. For example, molybdenum has a resonance line at 313.3 nm; the concentrations of phosphorus, vanadium, and other elements can be determined from the intensity of this line. The indirect method is also used to determine a number of metals which form mixed heteropolycomplexes, extracted under definite conditions.

The method was first used to determine down to 0.015 μg ml^{-1} phosphorus in solutions[125,126]. A number of methods, including descriptions of the conditions of formation, extraction by a suitable extracting agent, decomposition of the heteropolycomplex, and elimination of the co-extraction of molybdenum(VI), were later proposed for determining metals and non-metals. Methods have been proposed for determining silicon, phosphorus, arsenic, and germanium[6], down to 0.01 μg ml^{-1} phosphorus and silicon, and 0.025 μg ml^{-1} arsenic[191]; down to 0.08 μg ml^{-1} silicon and phosphorus[55]; silicon in organic compounds[206,207]; down to 0.005 μg ml^{-1} silicon (including the precipitation of lead molybdate)[46]; down to 0.07 μg ml^{-1} arsenic[52]; down to 0.01 μg ml^{-1} arsenic[191]; small quantities of phosphorus[208], arsenic[209], and germanium[210] in water; down to 0.05 μg ml^{-1} germanium[48] and arsenic in sulphides[211]; and down to 0.5 μg ml^{-1} vanadium in solutions[49] and aluminium alloys[60]. Kirkbright and coworkers proposed a number of methods for determining metals, involving the determination of molybdenum by atomic absorption: niobium[56], cerium[61], thorium[57], and titanium[58]. In some procedures, the direct introduction of the extracts into the flame is recommended, avoiding the operations of re-extraction and decomposition of the complexes[196].

Almost all papers giving specific recommendations for the extraction of heteropolycompounds give data on the influence, on the degree of extraction, of various ions present in the solution at the moment of formation of the complex and its extraction into the organic phase; iron(II), iron(III), aluminium(III), chromium(III), tin(IV), tungsten, and others (a total of ~40 ions). In the present review, however, it is not possible to deal with the results of these studies in detail, and readers are referred to the papers dealing with each specific determination.

* * *

The above review shows that in recent years, considerable success has been achieved in the theory and practice of the extraction of heteropolycompounds: experimental material has been accumulated, making it possible to discuss the mechanism of extraction; the limits of detection of elements by extraction methods have been lowered considerably; and the range of materials and elements extracted as heteropolycompounds has been extended. The mechanism of the transfer of a heteropolycompound from the aqueous to the organic phase has not yet been determined (that is the kinetics of the process have not been studied), however, and there is lack of agreement on the mechanism of formation of the compound extracted. The mechanism of the reduction of complexes in the organic phase is not clear, and the mechanism of the influence of added salts on extraction has not been studied. There are no sufficiently clear-cut practical recommendations on the separation of elements having similar properties at low absolute concentrations, or on the determination of a small quantity of a given element in the presence of large quantities of other elements having similar properties.

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