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Applications of Heteroligand Complexes in the Analytical Chemistry of Niobium and Tantalum

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Modern precision spectrophotometric and extraction-spectrophotometric methods for the determination of niobium and tantalum are based on the use of heteroligand (ternary, quaternary, and mixed) complexes of these elements with organic reagents. These methods make it possible to determine niobium and tantalum in complex materials without separating the components, which has greatly extended the scope of analytical methods in the chemistry of niobium and tantalum. The bibliography includes 131 references.

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I. INTRODUCTION

Inorganic chemical analysis has been developing recently in two main directions. On the one hand, much attention has been devoted to problems of specific synthesis of organic reagents used in spectrophotometric, extraction-photometric, chromatographic, and other analytical methods to ensure their greater specificity and sensitivity in relation to inorganic ions. The second trend is associated with more extensive use in inorganic analysis of ternary, quaternary, and multicomponent (mixed) chemical complexes, which are also referred to as heteroligand complexes. In mixed complexes containing different types of groups, the individual characteristics of the elements are manifested more clearly, namely their capacity for coordination (which is not quite so clearly shown in homoligand complexes), the stabilisation of unstable valence states, and the creation of more favourable conditions for transitions from one valence state to another. The use of reactions involving the formation of heteroligand complexes in spectrophotometric analysis has greatly extended the scope of the methods for the determination of many elements, including niobium and tantalum.

The chemistry of heteroligand complexes has been developed in relation to analytical chemistry in studies by Babko[1,2], Alimarin[3], Pilipenko[4], and others. The applications of heteroligand complexes have been reviewed in detail[1-5].

The use of organic reagents has greatly extended the scope of the spectrophotometric analysis of inorganic ions. During the first period, mainly two-component systems

were investigated, while problems of sensitivity and selectivity associated with the employment of metal ion–organic reagent systems were still not adequately solved.

The sensitivity of photometric reactions, expressed by the molar extinction coefficient ϵ, is greatly influenced by the stability of the chelates formed. The maximum value of ϵ can be estimated theoretically [6] as $\epsilon_{max} = 1 \times 10^5$. However, this sensitivity is provided by only a few reagents. To increase the sensitivity, new chromophoric groups are introduced into the organic reagents, using complexing agents which are as selective as possible; it is necessary that the spectrum of the resulting two-component complex should differ markedly from that of the initial reagent. The choice of selective reagents is also difficult because certain metal ions (niobium and tantalum, zirconium and hafnium, molybdenum and tungsten, etc.) have very similar electronic structures, ionic radii, and ionic potentials. An enhanced selectivity can be achieved by changing the ligand, by introducing substituents, and by altering the distances of the electron-donating groups within the molecule. Selectivity in an analytical reaction can be appreciably improved by masking, but this too has its limits, since the analytical reagent can react also with the masked ion.

A great increase of sensitivity and selectivity can be achieved with the aid of heteroligand complexes, using their optical properties. Mention should first be made of ternary complexes, although recently a number of reports have been published on the applications of quaternary complexes in spectrophotometric analysis [7,8].

In many cases (particularly for heavy metals with high valences) the mechanism of complex formation in the interaction of a two-component system MX with a new ligand Y is not based on competitive relations, i.e. on the displacement of one of the previous components by a third component, and the interaction in the system is more complex than the process

$$MX + Y \rightleftarrows MY + X. \qquad (1)$$

The new ligand enters into the composition of the coordination sphere, forming a heteroligand complex:

$$M^{z+} + mH_aX + nH_bY \rightleftarrows [MX_mY_n]^{z-am-bn} + [am + bn]H^+... \qquad (2)$$

The formation of the heteroligand complex is a fairly complicated process. The new ligand can form an associated ionic species with the initial homoligand complex; it can displace water molecules from the coordination sphere, although in principle complexes such as $M(H_2O)_nX_m$ and MH_nX_m belong to the group of heteroligand complexes themselves. In many cases heteroligand complexes are also formed in extraction processes.

Complexes with different metals, obtained in accordance with the equation

$$pM^{z+} + qM'^{u+} + H_aX \rightleftarrows (M_pM'_qX)^{pz+qu-a} + aH^+, \qquad (3)$$

are less important in analytical chemistry, because in practice one employs an excess of the ligands and the formation of such complexes is suppressed. One can quote only a few examples of their employment in analytical practice: (a) indirect polarographic determination of zirconium as zirconium lead tartrate [9] and photometric determination of cadmium as cadmium iron tartrate [10]; (b) the tin–iron–dimethylglyoxime system has been investigated by Babko and Mikhel'son in relation to analytical chemistry [11,12]; the complex has been used by Elinson and Tsvetkova [13] to develop a method for the determination of tin in alloys with zirconium and niobium; (c) the formation of complexes of the type $M_pM'_qX$ can explain the extraction of metal ions by two other metal ions, which has been observed by Alimarin and Gibalo [14].

Coordination compounds formed in accordance with Eqn. (2) by one metal with two or several ligands are particularly important. It has been shown in a number of studies that the electrostatic interaction in the complex and the ligand effect promote the formation of a heteroligand complex. Electrostatic calculations have demonstrated that the formation of heteroligand complexes is always energetically more favourable than the formation of homoligand complexes [15–20]. Heteroligand complexes can be formed in two ways. They can be produced when complex formation with one ligand gives rise to coordination-unsaturated compounds. The second ligand can then be incorporated by occupying some or all the remaining coordination sites at the metal ion. The second possibility occurs when a single-ligand complex is in fact saturated but not all the valences of the inorganic ion have been compensated. Under these conditions, the heteroligand complex is formed by association of the second ligand and the first charged complex. The formation of the association complex of chlorogallate with diantipyrinylmethane or its detivatives ($GaCl_4$–DAPM), which can be extracted with chloroform, as well as numerous association complexes described by Blyum [21] and other workers [22–26] may serve as typical examples.

The chemistry of transition metal complexes in solution is to a large extent concerned with the chemistry of heteroligand complexes. The wide variety of heteroligand complexes (MX_mY_n) can be accounted for by their higher stability in solution compared with complexes containing identical ligand species. The formation of complexes with different ligand species also leads to appreciable changes in the physicochemical properties of the compounds: changes in their optical properties, an increase or decrease of solubility, and the appearance of capacity to be extracted by organic solvents; it is therefore useful to employ the extraction of coloured heteroligand complexes containing an organic complex-forming agent (for example polyphenols) as one of the ligands. However, one of the main advantages of heteroligand complexes is the possibility of a great increase in the sensitivity and selectivity of analytical reactions owing to their high coordination capacity. The absorption spectra of such complexes differ from those of homoligand systems.

Here, one should emphasise that, since analytical chemistry is concerned with solution chemistry, the majority of analytical reactions are based on the use of heteroligand complexes and, according to Pilipenko and Tananaiko [27], the formation of heteroligand complexes in solution is the rule rather than the exception. The contrary view was held previously. Bearing in mind that, apart from the main components, a homoligand complex can include water or organic solvent molecules as well as hydroxide ions, which are formed on hydrolysis, the vast majority of analytical systems will prove to be of the heteroligand type.

The role of heteroligand complexes in analytical chemistry can be hardly overestimated. Hundreds of spectrophotometric and extraction-photometric methods for the determination of inorganic ions are based on the use of heteroligand complexes. During the last 8 years (1966 to 1973), more than 600 papers dealing with such complexes were published. The text below deals with the applications of heteroligand complexes in one of the most difficult branches of analytical chemistry, namely the analysis of niobium and tantalum [28].

II. SPECTROPHOTOMETRIC DETERMINATION OF NIOBIUM AND TANTALUM IN HETEROLIGAND COMPLEXES

1. METAL COMPLEXES WITH TWO DIFFERENT ELECTRONEGATIVE LIGANDS

Until recently, it was believed that reagents such as metallochromic indicators do not undergo colour reactions with niobium and tantalum. The explanation was that hydrolysis results in the formation of various relatively inactive hydrolysed and polynuclear species, incapable of reacting with the metallochromic indicators used in weakly acid solutions. However, experiments showed that, in the presence of powerful complex-forming agents (tartrate, oxalate, and fluoride ions, etc.), certain organic reagents undergo highly differentiating colour reactions with niobium and tantalum owing to the formation of heteroligand complexes. One of the ligands decomposes polymeric niobium or tantalum ions and maintains them in solution, while the other (the metallochromic indicator) serves as the chromophore in the stable ternary complex formed [29]. In the chemistry of niobium and tantalum heteroligand complexes play a special role, which serves as a basis for the most highly differentiating, sensitive, and selective modern spectrophotometric methods for the determination of these elements [28].

(a) Complexes with Polyphenols

Tantalum–pyrogallol complexes can serve as an example of heteroligand complexes with two electronegative ligands. In the absence of other complex formation agents, tantalum forms with pyrogallol a colourless complex in an acid medium (with an absorption band at 340 nm); when oxalate ions are introduced into the solution of the tantalum–pyrogallol complex, the band at 340 nm is weakened and a new band appears at 420 nm. The formation of this heteroligand complex constitutes the basis of familiar photometric methods [30-34].

Babko and Lukachina [35] examined the pyrogallol method for the determination of tantalum and niobium in their joint presence, based on the fact that in an acid medium a coloured ternary tantalum oxalate–pyrogallol complex is formed, while the niobium gives rise to a colourless oxalate complex. Thus the differentiating ligand for niobium and tantalum in an acid medium is not pyrogallol but the third component, in the present instance oxalic acid. With increase of pH, the concentration of $C_2O_4^{2-}$ and pyrogallol (Pg^{2-}) ions increases. However, oxalic acid is a stronger acid and therefore at $pH > pK_2$, i.e. at $pH > 4$, and a constant overall oxalic acid concentration, the concentration of $C_2O_4^{2-}$ does not increase, while that of the Pg^{2-} ions derived from the weaker acid (pyrogallol) continues to rise. As a result, with increase of pH, the $C_2O_4^{2-}$ ions are displaced from the coordination spheres of tantalum and niobium and only the pyrogallol complexes remain: the coloured niobium complex and the colourless tantalum complex. On the other hand, in a more acid medium ($pH < 4$), the equilibrium shifts towards the formation of colourless niobium oxalate complexes with displacement of Pg^{2-} from the coordination sphere. The study optimised conditions for the determination of niobium and tantalum. Niobium is determined in a weakly alkaline medium at pH 7–8 with $[Pg^{2-}_{tot}] = 0.2$ and $[C_2O_4^{2-}]$ 0.1 M. Tantalum is determined in the heteroligand complex $[TaOC_2O_4Pg_2]^{3-}$ at 400 nm and pH 2–3 with $[Pg^{2-}] = 1.3$ to 1.4 M and $[C_2O_4^{2-}] \geq 0.2$ M.

The formation of heteroligand niobium complexes with pyrogallol and ethylenediaminetetraacetic acid (EDTA) has been noted. Pyrogallol complexes have been used to develop extraction-photometric methods for the determination of tantalum in the presence of niobium, which are discussed below. Among other polyphenols, heteroligand complexes are formed by tantalum with catechol in the presence of $C_2O_4^{2-}$. A photometric method for the determination of tantalum has been developed on this basis [36,37]. It has been modified [38] by the introduction of EDTA. The author [38] drew attention to the fact that EDTA, which usually decolorises the majority of metal complexes, actually enhances the colour of the catechol complex of niobium and enters into the composition of the heteroligand complexes. Thus one can claim that coloured heteroligand compounds of the type of MX_mY_n are formed in those cases where the chromophore is not one of the ligands but the central atom. The complex was investigated in detail in later studies [39,40]. Nevertheless, the method remains relatively unselective and insensitive. In the measurements of the optical density of the complex in the region of 385–395 nm the influence of niobium is to a large extent eliminated, but titanium interferes.

A number of methods involving tetraphenylarsonium have been described [41,42]. Methods in which tetraphenylarsonium and thiocyanate ions are both used are of considerable interest. Niobium and tantalum peroxide complexes with various organic dyes [43] as well as niobium thiocyanate complexes with benzoylphenylhydroxylamine (BPHA) [44] and with dihydroxy-3,4-phenyl-4-azobenzene [45] can also be included among heteroligand complexes.

Niobium and tantalum tartrate, oxalate, citrate, and peroxide complexes with many metallochromic indicators form part of the group of complexes with different electronegative ligands. Reagents containing hydroxypyridylazo- and *oo*-dihydroxyazo-groups are the most sensitive and give rise to contrasting and deep colours with niobium. These include 4-(2-pyridylazo)resorcinol (PAR) and its derivatives, analogues of lumogallion–bisazo-derivatives of chromotropic acid, and monoazo-compounds based on the R-salt. Azo-compounds with complexone groups are also promising reagents for niobium. Arylmethanes and other basic dyes are the most sensitive and selective reagents for tantalum.

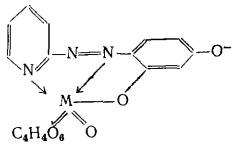
(b) Heteroligand Niobium and Tantalum Complexes of Pyridylazo-compounds

Pyridylazo-compounds are known as reagents forming stable ternary metal–reagent–ligand complexes with niobium and tantalum [46]. Complexing agents used to solubilise these elements, namely peroxide, oxalate, tartrate, and citrate ions, are normally used as the third components.

Among reagents of the pyridine series, 4-(2-pyridylazo)resorcinol has been most thoroughly investigated. It has been proposed as a highly sensitive reagent (molar extinction coefficient of about $3.5\ 10^4$) for the photometric determination of niobium and tantalum in weakly acid solutions (pH 5–6) in tartrate [47-49], peroxide [50], or oxalate [51] solutions. Pyridylazo-compounds are highly reactive but relatively unselective. The explanation is that salt-forming compounds of the type of PAR give rise to complexes with ions having small radii and high positive

charges, i.e. heavy metal and transition metal ions, which thereby complete their *d* and *f* shells[52]. Apart from niobium and tantalum, PAR forms coloured complexes with 40 elements (U, Co, Ga, In, the lanthanides V, Pb, Cu, etc.)[53,54].

In order to choose conditions under which the greatest sensitivity and selectivity of the reactions of niobium and tantalum with PAR are attained, a detailed study was made of the complexes formed by PAR and its analogues with the above elements[55,56]. It has been established that coloured niobium and tantalum complexes are formed by reagents of the pyridyl series (12 such compounds have been investigated) which contain the OH group in the *ortho*-position relative to the diazo-group. In these compounds OH groups or other electron-donating groups, which are in the *para*-position relative to the azo-group, play the role of groups active in analysis, which sharply increase the sensitivity of the reagents. It has been demonstrated[55,56] that niobium and tantalum form heteroligand complexes with pyridylazo-compounds and complex-forming ligands (tartrate, oxalate, fluoride, etc.) with a valence bond via the hydroxy-group in the *ortho*-position relative to the diazo-group and a coordinate bond via the nitrogen of the azo-group:



The high reactivity of PAR in reactions with niobium and tantalum can be explained to some extent by the formation of such compounds. The tartrate ions (or other similar ligands), which enter into the composition of the complex as the third component, disrupt the polymeric niobium and tantalum ions and maintain them in solution in a monomeric form, while the organic reagent—the metallochromic indicator (PAR) and its analogues—plays the role of the chromophore in the ternary complex. The existence of such heteroligand complexes has been demonstrated experimentally. 5-(3,5-Dibromo-2-pyridylazo)-monoethylamino-*p*-cresol (3,5-di-Br-PAAC), which forms a coloured sparingly water-soluble complex with niobium in the presence of tartrate ions, has been synthesised. Analysis of the heteroligand complex isolated in a crystalline form showed that its composition can be described by the formula

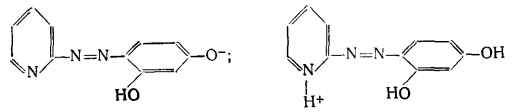
$$\text{Nb - 3,5-di-Br-PAAC - } C_4H_4O_6^2 \cdot 5H_2O,$$

and its molecular weight is 778, i.e. direct confirmation of the formation of a ternary complex with the component ratios Nb : R : tartrate = 1 : 1 : 1 was obtained.

The calculated instability constants of the complexes showed that the most stable complexes are formed by brominated pyridylazo-compounds, which react with niobium or tantalum in more acid media. Consequently, electronegative substituents in the pyridine ring increase the selectivity of the reagents. Two new selective and sensitive reagents were suggested on this basis: 5-(5-bromo-2-pyridylazo)-2-monoethylamino-*p*-cresol (5-Br-PAAC) and 4-(5-bromo-2-pyridylazo)resorcinol (5-Br-PAR), which give rise to a marked bathochromic effect ($\Delta\lambda$ = 130–160 nm) and high molar extinction coefficients (4.17×10^4 and 3.8×10^4 respectively). The determination of niobium and tantalum with the aid of the proposed reagents in highly acid solutions (up to an HCl concentration of 2 M) is not interfered with by molybdenum, tungsten, uranium, zirconium, titanium, iron, rhenium, and other elements.

4-(2-Thiazolylazo)resorcinol (TAR) has a structure similar to that of PAR and like the latter forms with niobium coloured complexes in weakly acid solutions (pH 5–5.5). However, thiazolylazo-compounds, containing the less basic thiazole ring instead of the pyridine ring, should give rise to niobium complexes in more acid media and hence should be more selective than pyridylazo-compounds. 5-(2-Thiazolylazo)-2-monoethylamino-*p*-cresol (TAAC) is of considerable interest in this respect; a method for the determination of niobium in alloys containing uranium, zirconium, and molybdenum involving the use of TAAC has been developed[57].

Studies have shown that, in contrast to other media, in tartrate solutions the heteroligand PAR complex of niobium is formed not only at pH 5–6 but also at higher acidities (HCl concentrations in the range 0.5–1 M),[49] different compounds being formed, since the ionic state of PAR depends greatly on the acidity. At pH 5–6 a proton dissociates initially from the OH group in the *para*-position with formation of a singly charged ion in solution[53,58]. In the solution where [HCl] = 1 *N* PAR exists in the form of a singly charged cation as a result of the protonation of the heterocyclic nitrogen of the pyridine ring:



(pH 5–6) (1 M HCl)

The absorption spectra of these compounds differ from one another[59]. The ternary complex has an absorption maximum in 1 M HCl solution only in the region of 405 nm, while at pH 5–6 the maximum is at 520–540 nm (depending on the nature of the third complex-forming component). Furthermore, in weakly acid media a second indistinct maximum is also observed in the region of about 400 nm, which is extremely characteristic of heteroligand complexes. Since the absorption maximum of the complex in an acid solution is close to that of the reagent (395 nm), a differential curve with a maximum at 540 nm was used in practice. In an acid solution we have the ratio Nb : PAR = 1 : 2 (instead of 1 : 1 at pH 5–6). With increase of acidity, there is a sharp increase of the selectivity of PAR. Iron, aluminium, titanium, zirconium, molybdenum, tungsten, the lanthanides, and other elements do not interfere with the determination of niobium.

Methods have been developed for the determination of niobium under such conditions in steels[60], minerals[59], and complex copper-based alloys[61]. A differential method has been devised for the determination of large amounts of niobium in alloys and ferroalloys[62], particularly in ferroniobium.

Masking of tantalum with a large excess of tartrate ions made it possible to develop a procedure for the determination of niobium and tantalum without their separation[63]. In tartrate solution tantalum is bound in a stable polynuclear complex, with a polymerisation factor of about 670, which does not form compounds with PAR, and therefore in 3–4% ammonium tartrate solutions at pH 4.5–4.8 tantalum does not interfere with the development of the colour of the PAR complex of niobium. The method proved to be extremely effective and permits the determination of 0.1%

of niobium and more in tantalum concentrates and in metallic tantalum. The heteroligand PAR complex of tantalum has been used to determine tantalum in steels and alloys with a high tantalum content [64]. It has been shown that, in the presence of ligands used to solubilise niobium and tantalum (oxalate, citrate, etc.), PAR forms coloured complexes with both tantalum and niobium. The most sensitive and stable complex is formed in 0.01 M citrate solution at pH 5.4. Under these conditions, niobium does not form a coloured compound. However, a concentration corresponding to more than 1 mg of niobium in 50 ml increases the optical density of the tantalum solution. Stable and reproducible results can be obtained only for the same reactive tantalum species, which is achieved by selecting identical conditions for the preparation of solutions of the sample and standard solutions (boiling of the initial solutions at the same pH 2.3–2.8 after dissolving the alloys, introduction of nickel into standard tantalum solutions). When the steel specimen contains less than 5% of tantalum, the latter is determined relative to a standard steel specimen and not with the aid of a calibration graph [64].

Thus, using heteroligand PAR complexes, it is possible to increase greatly the selectivity in the determination of niobium and tantalum. Ways of increasing the selectivity still further, involving the use of reagents with electronegative substituents and the ligands of the heteroligand complex as masking agents (tartrate and citrate) as well as an increase of acidity in the preparation of PAR complexes of niobium, have been discussed [65].

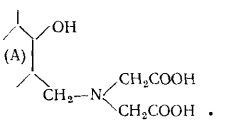
Other complexes of resorcinol derivatives have also been investigated. A method has been determined for the determination of niobium as a heteroligand complex with H_2O_2 and sulphonaphtholazoresorcinol [66]. In another study H_2O_2 was used in combination with morin [67]. The fluorescence method developed with the aid of these reagents makes it possible to determine niobium with a sensitivity of 0.004 $\mu g\ ml^{-1}$.

(c) Heteroligand Niobium Complexes with *oo'*-dihydroxyazo-compounds

Organic compounds containing the *oo'*-dihydroxyazo-group undergo extremely characteristic colour reactions with niobium. Compounds of this type can be divided into two groups on the basis of their structural features. The first includes Lumogallion and many bisazo-derivatives of chromotropic acid—structural analogues of Arsenazo III (Sulphochlorophenol S, Sulphomethanylphenol Nitrosulphophenol S, and others) and the second group includes Anthracene Chrome Violet and other monosubstituted R-salt derivatives (Picramine R, Magneson, Picramine-epsilon, etc.); they all form heteroligand complexes with the niobium tartrate complex or with niobium complexes of other hydroxy-acids. In the first group of reagents Sulphochlorophenol S or 3,6-bis[(5-chloro-2-hydroxy-3-sulphophenyl)azo]-4,5-dihydroxynaphthalene-2,7-disulphonic acid (SCPS) is of greatest interest. This dye is widely used to determine niobium [68–72]. The most interesting compound in the second group is Picramine R or 3-hydroxy-4-[(2-hydroxy-3,5-dinitrophenyl)azo]naphthalene-2,7-disulphonic acid. Both reagents, SCPS and Picramine R, form coloured complexes with niobium at a high acidity of the solution, are satisfactorily selective, and permit the determination of niobium in metals and alloys without the separation of components. SCPS and its analogues are three times more sensitive ($\epsilon = 3.6 \times 10^4$) than Picramine R ($\epsilon = 1.1 \times 10^4$). SCPS is used to determine microamounts of niobium in metals [73], while Picramine R is used for the determination by photometric or differential methods of large amounts of niobium in alloys and intermetallic compounds containing up to 70–80% of niobium [74].

(d) Heteroligand Niobium Complexes with Metallochromic Indicators Containing Complexone Groups

The importance of heteroligand complexes for the determination of niobium and tantalum can be readily demonstrated for reagents containing complexone groups: Xylenol Orange (XO) and Methylthymol Blue (MTB). It appeared likely that these reagents, which do not contain an OH group in the *ortho*-position relative to the azo-group (a characteristic of niobium and tantalum reagents), are capable of forming complexes with these metals. Indeed, in the first relevant reports the reaction of niobium with Xylenol Orange was classified as insensitive, because the experiments were performed without additional ligands (oxalate or tartrate ions) at room temperature. Later it was found that, in the presence of either of these ligands, an intensely coloured complex is formed on heating. A fairly stable niobium complex is known to be formed at pH 3–3.5 with EDTA, while tantalum forms a fairly weak complex with this substance. Similarly, XO and MTB, which contain complexone groups, form in oxalate or tartrate solution at pH 2–4 fairly stable brightly coloured complexes with niobium and interact only weakly with tantalum. XO has been proposed as a reagent for niobium by Babko and Shtokalo [75] and has been used to determine niobium in certain alloys [76]. MTB has been investigated as a reagent for niobium by Elinson and Mirzoyan [74]. The fact that niobium reacts with MTB in 1 : 1 molar proportions, while in the absence of sufficient oxalate or other similar ligands the niobium–MTB complex is not formed at all suggests that, as for pyridylazo-compounds, oxalate ions enter into the composition of the coloured compound, forming a heteroligand complex with the component ratios $Nb : C_2O_4^{2-} : MTB = 1 : 1 : 1$. Oxalate and tartrate ions decompose polymeric niobium ions. At pH 2–3 niobium readily hydrolyses and in the absence of these ligands could not compete with the MTB or XO protons in the formation of a complex. Experiments have shown that the formation of MTB and XO complexes of niobium is due to the group (A), i.e. to the most reactive hydroxy-, amino-, and carboxy-groups:



2. DETERMINATION OF NIOBIUM AND TANTALUM IN THE FORM OF COMPLEX HETEROPOLYACIDS

Niobium and tantalum form heteroligands phosphorus–niobium–molybdenum complexes which are more stable and more soluble than the usual heteropolyacids. The absorption bands of these complexes are displaced further towards the visible region, while the reduced binary tantalum–molybdenum complex absorbs in the infrared ($\lambda = 820$ nm). [78] The phosphorus–niobium–molybdenum complex can be reduced to a blue complex, the intensity of

the colour of which is proportional to the concentration of niobium (sensitivity 0.1 μg ml^{-1}). The conditions governing this reaction have been refined [79] and methods have been developed for the determination of niobium in ores together with a differential spectrophotometric method for the determination of large amounts of niobium [80]. Titanium interferes with the determination of niobium; the influence of tungsten can be eliminated by an excess of phosphate. Methods for determination of niobium and titanium in alloys [81] and of niobium in steels [82] have been developed on the basis of the formation of heteroligand heteropolycomplexes. A technique has been devised for the determination of low niobium concentrations based on the formation of niobium–molybdenum blue [83].

3. COMPLEXES WITH TWO DIFFERENT ELECTROPOSITIVE ATOMS AND ONE ELECTRONEGATIVE LIGAND

Complexes with two electropositive metals have not found such extensive application as heteroligand complexes with two electronegative ligands. However, it is possible to quote certain instances of the formation of mixed niobium and tantalum complexes with an electronegative ion, whereupon tantalum becomes an obstacle, which is difficult to overcome, to the determination of niobium when the two metals are present jointly in large amounts. For example, compounds are formed by mixtures of niobium and tantalum with H_2O_2. Niobium combines with one H_2O_2 molecule so strongly that in a weakly acid medium it is not titrated by potassium permanganate. When an excess of a standardised H_2O_2 solution is added, the concentration of niobium can be determined in the absence of tantalum by titrating the free H_2O_2 with permanganate [84], but in the presence of tantalum niobium does not retain the H_2O_2 molecule in consequence of the formation of a mixed niobium–tantalum peroxide complex. In the presence of phosphoric acid the niobium peroxide complex decomposes, whereupon only tantalum forms a stable peroxide [85].

Another example involves the formation of mixed niobium–tantalum complexes with tartrate ions. In the method developed for the determination of niobium in the presence of large amounts of tantalum with the aid of PAR [63] at pH 4.5–4.8 it is possible to bind tantalum with a large excess of tartrate ions into a stable relatively unreactive polynuclear complex and thus avoid the formation of a mixed niobium–tantalum complex with PAR. Niobium can then be determined with a high accuracy even in metallic tantalum [63]. In the determination of large amounts of niobium (10–80%) by a differential spectrophotometric method with PAR more than 50 μg of tantalum in 1 M HCl solution [62] is already sufficient to interfere with the determination, since in such a solution the tantalum tartrate complex is not sufficiently stable to prevent the formation of a mixed complex with niobium and PAR.

Such interference by tantalum in the determination of niobium has been called by some investigators (Babko, Belcher) "the loss of individual properties", which does not accurately reflect the true behaviour of these elements in solution. We believe it to be a typical instance of the formation of a mixed complex of different metals not with loss but with manifestation of the individuality of elements with similar physicochemical properties (the copolymerisation and complex formation phenomena when the ionic radii are similar, etc.).

Mixed tantalum–zirconium tartrate complexes can serve as an example of mixed complexes of two different metals [86]. Studies by the equilibrium shift and isomal series [continuous variations] methods established that, in 0.5 M tartaric acid solution at pH 2 and in the presence of a tenfold excess of zirconium, a complex with the component ratios Ta : Zr : Tart = 1 : 1 : 2 is formed. The tantalum in the mixed tartrate complex does not react with PAR, [28] which must be taken into account in the analysis of such systems.

III. THE USE OF HETEROLIGAND NIOBIUM AND TANTALUM COMPLEXES IN EXTRACTION PROCESSES

1. EXTRACTION-PHOTOMETRIC METHODS FOR THE DETERMINATION OF NIOBIUM

A number of compounds which constitute the basis of extremely sensitive and selective extraction-photometric methods for the determination of niobium and tantalum belong to the group of heteroligand complexes formed when niobium or tantalum interact with two electronegative ligands.

Extraction is a widely used procedure for improving the sensitivity and selectivity of analytical reactions; in this way it is possible to increase sharply the sensitivity of photometric methods.

Extraction with formation of heteroligand complexes can be described by the equation

$$M^{z+}(w) + mH_aX(w) + hH_bY(o) \rightleftarrows MX_mY_n(o) + (am + bn)H^+(w), \quad (4)$$

where w is the aqueous fraction and o the organic fraction. Numerous extraction-photometric methods are based on the measurement of the optical density of the compound $MX_mY_n(o)$ formed in the organic phase. If the partition coefficient of MX_m is very small, the affinity of HbY for MX_m plays a significant role. The equilibrium in the system shifts continuously during the extraction process towards the formation of MX_mY_n and a higher partition coefficient may be obtained for MX_mY_n than for MX_m.

The extraction of complexes in the presence of hydrophobic organic bases is especially important in analytical chemistry. Studies have shown, for example, that the chelate complex of molybdenum and catechol can be extracted from the aqueous phase by organic solvents in the presence of tetraphenylarsonium (as well as in the presence of pyridine) [87]. In this case the occurrence of extraction has been explained by a synergic effect, but the latter is based on the formation of a heteroligand complex. The use of tetraphenylarsonium as well as tetraphenylphosphonium for the extraction of niobium proved to be a fairly effective procedure. In the presence of tetraphenylarsonium niobium also forms with thiocyanate ions the heteroligand complex $[(C_6H_5)_4As]_2[NbO(NCS)_5]$, which can be extracted by organic solvents. The formation of this complex constitutes the basis of the extraction-photometric method for the determination of niobium [88]. Compounds formed by dioctylaminoethanol (DOAE) and fluoride ions with niobium or tantalum are similarly extracted by chloroform as $(DOAE)_2[NbOF_5]$. [89]

In particular complexes of the type $MX_mY_n^0$ or $[MX_m(RY)_n]^0$, where Y is the organic base, can be formed in the extraction process. Whereas in the former case Y provides an electron-donating atom for the formation of an electron pair, coordinating the metal ion, in the latter case Y enters into the association complex in the form of an 'onium compound. Anionic complexes which become capable of forming hydrates by combining with the SO_3H

group form solvates with ammonium, arsonium, or phosphonium cations and are extracted in the form of associated ionic species. A number of extraction-photometric methods based on the extraction of these two types of heteroligand complexes are described below.

In combination with diphenylguanidine, the chlorosulphophenol described above has been used in the extraction-photometric determination of niobium with the aid of 1-butanol. Iron, molybdenum, and zirconium are bound by thioglycolic acid and the complexone [90].

The extraction of complexes containing sulpho-, carboxy-, or hydroxy-groups is based on the fact that alkyl- and aryl-amines and their salts form with niobium complexes substituted ammonium salts (R_3NR) which are readily extracted. Thus heteroligand complexes which are extracted by chloroform are formed in the niobium–salicylic acid–organic base systems [91].

An extraction-photometric method has been proposed for the determination of niobium in the presence of tantalum, titanium, uranium, zirconium, iron, and tin; it is based on the formation of a 1 : 2 : 2 extractable heteroligand complex with SCN^- ions and pyrrolidinedithiocarbamate [92].

The usual catechol and pyrogallol methods for the determination of niobium have been improved by the extraction of polyphenol complexes of niobium in the presence of quaternary ammonium bases having a long hydrocarbon chain, with a consequent sharp increase of the sensitivity of the determination of niobium [93,94]. The influence of tantalum, which is also extracted by the above reagents, was eliminated by selecting optimal conditions. Best results were achieved in the extraction of niobium by polyethoxy-15-stearylmethylammonium chloride [Ethoquad 18125].

A large group of niobium complexes containing two organic reagents, one of which forms with niobium a soluble inner complex and the other a sparingly soluble complex, has been investigated [95,96]. The following compounds (with 1 : 2 : 2 component ratios) are of interest: niobium–pyrrolidine dithiocarbamate–catechol, niobium–BPHA–catechol, niobium–BPHA–pyrrogallol, niobium–cupferron–catechol, and niobium–catechol–diantipyrinylpropylmethane. The compounds are almost completely extracted by chloroform. The method is also interesting because niobium can be determined in the presence of a 20-fold excess of titanium and tantalum. The molar extinction coefficient is $\epsilon = 1.4 \times 10^4$.

The extraction of a number of metals forming heteroligand complexes with Arsenazo I and diphenylguanidine has been studied [97,98]. Niobium, tantalum, titanium, zirconium, hafnium, and thorium can be extracted from acid solutions by pentyl, isopentyl, and butyl alcohols; iron, aluminium, beryllium, scandium, yttrium, lanthanum, and copper can be extracted from weakly acid and neutral solutions. The extraction of niobium and a number of other elements in the form of heteroligand complexes which they form with *o*-carboxy-, *oo'*-dihydroxy-, and hydroxyazo-compounds (Acid Chrome Dark-blue, Eriochrome Black T, Magneson, Acid Chrome Red, and others) and organic cations has been investigated [99]. The extraction takes place over a wide pH range. It has been suggested that ionic association complexes in which inner complexes behave as anions are extracted.

The heteroligand complexes of a large group of metals, including niobium, with Chromazurol and diphenylguanidine are readily extracted and permit the determination of many elements with a high sensitivity [100,101]. Peroxo-complexes of niobium and tantalum react with oxalate ions to form compounds which can be extracted by trioctylamine [102]. Niobium and tantalum can be separated in this way from iron, titanium, manganese, vanadium, aluminium, and other elements. Trioctylamine and certain *N*-substituted amines have been used in inorganic acid solutions for the separation of niobium and tantalum by extraction using chloroform [103–105].

An extraction-photometric method, based on the formation of a heteroligand niobium complex with catechol (CA) and thenoyltrifluoroacetone (TTFA) in the proportions Nb : CA : TTFA = 1 : 2 : 3, which can be extracted by chloroform, has been developed for the determination of niobium. The complex absorbs at 414 nm ($\epsilon_{414} = 7.7 \times 10^3$) and the sensitivity is 2 μg/ml Nb. [106] It was shown recently that mixed niobium–catechol–phenylbenzoylpyrazolone and niobium–thiocyanate–phenylbenzoylpyrazolone complexes with component ratios of 1 : 2 : 1 are readily extracted by organic solvents [107].

The extraction of heteroligand organic complexes of niobium and tantalum by oxine in chloroform [108] or by isobutyl methyl ketone from citrate and chloride solutions and also by 50% solutions of tributyl phosphate in chloroform or cyclohexane [109] is used in the radiometric analysis of tantalum–niobium preparations.

It was pointed out above that quaternary heteroligand complexes are used in spectrophotometric analysis, particularly when extraction processes are resorted to. A typical example is provided by the extraction of niobium in the form of a heteroligand complex with Catechol Violet (CV), pyridine, and potassium bromide [110]:

$$2Nb(OH)_2^{3+} + PyH^+ + H_3CV^- + 3Br^- \rightarrow \{[Nb(OH)_2]_2CVPyH\}^{3+}Br_3^- + 3H^+.$$

In this compound pyridine is bound to the sulpho-group of Catechol Violet, and Br^- is an outer-sphere anion, which neutralises the positive charge of the complex formed. A quaternary system is produced with the component ratios Nb : CV : Py : Br = 2 : 1 : 1 : 3. The coloured compound is formed immediately after mixing the solutions and remains stable for 32 h. The coloured solutions obey Beer's law in the presence of 15–100 μg of niobium in 25 ml ($\epsilon = 3 \times 10^4$).

2. EXTRACTION-PHOTOMETRIC METHODS FOR THE DETERMINATION OF TANTALUM

The extraction-photometric methods for the determination of tantalum are based on the use of heteroligand ionic association complexes. Such association complexes are formed when tantalum fluoride complexes interact with basic dyes. The coloured heteroligand complexes formed can be extracted by inorganic solvents, such as benzene, toluene, xylene, chloroform, etc. Under certain conditions, the pure dye is hardly extracted by these solvents. The formation reactions of the extractable ionic association complexes are fairly sensitivity and specific. The following dyes are used as the reagents: triarylmethane dyes (Methyl Violet, Brilliant Green, Crystal Violet, Malachite Green, etc.), xanthene dyes (Rhodamine 6G, Rhodamine S, and Rhodamine 3B), oxazine dyes (Nile Blue, Meldola's Blue, New Blue, etc.), and thiazine dyes (Methylene Blue, Methylene Green, etc.). In the association complexes formed tantalum in the form of the negatively charged fluorotantalate ion substitutes the acid residue (Cl^-, HSO_4^-) in the dye. A number of studies have been made on the use of triarylmethane dyes (TAMD) and xanthene dyes for the determination of tantalum in various materials. These procedures have been reviewed in detail in a monograph [28].

Recently much attention has been devoted to the problem of the mechanism of the formation of association complexes of fluorotantalate with triphenylmethane dyes (TPMD). Most investigators tend to regard the complex anion TaF_6^- as the reactive species in the interaction of fluoride solutions of tantalum with TPMD.[111,112] Elemental analysis of the organic phase in the extraction of the fluorotantalate of Brilliant Green with chloroform established that the compound extracted has the formula $RTaF_6$,[113] where R is the cation of the basic dye. This was confirmed in other investigations.

It was suggested previously that the extractability of ionic association complexes depends on the charge, the relative dimensions of the anion and cation, and the presence of hydrophobic groups in one or both ions. The ratio of the charge to the number of atoms in the ion was proposed as a criterion of extractability. The extractability of the association complex should improve with decrease of "the specific charge". Lomonosov and coworkers[114-117] demonstrated the inadequacy of these ideas, which fail to take into account the individual characteristics of the cation and anion structures. They showed that the overall effective positive charge in the region of the dye cation involved in association can serve as a criterion governing the choice of TAMD for extraction. It was suggested that the part of the cation bounded by the two most basic parts of the dye is responsible for association. The substituents in the amino-groups in the *para*-positions relative to the central carbon (or nitrogen) atom play an important role here. The presence of such substituents leads to an increase of the positive charge at the ends of the molecule and to the stabilisation of the ionic association complexes formed by the reagent with these substituents. Two reagents of the group of oxazine dyes proposed recently for the extraction-photometric determination of tantalum can serve as typical examples, namely Capri Blue[118] and Meldola's Blue[119]. With Capri Blue, which contains a much greater number of substituents than Meldola's Blue, a more stable structure is produced: the fluorotantalate interacts simultaneously with two substituted groups and this is accompanied by a greater localisation of the positive charge than in Meldola's Blue.

The basicity of the dye, which in the case of TAMD is determined by the electron density at the central carbon atom, can serve as a criterion of the extractability of ionic association complexes. The extractability of TPMD increases steadily in the series Crystal Violet < Malachite Green < Brilliant Green, i.e. with increase of the overall positive charge on two dialkylamino-groups. In extraction at high pH values the conversion of the ionic form of the dye into a carbinol is very important, while at high acidities (2 M H_2SO_4) the influence of protonation becomes more marked. In the case of Brilliant Green, which has more positive electron-donating groups than Malachite Green, this factor has a decisive influence on the extraction. Brilliant Green proved to be the most sensitive dye in the TPMD group and has recently been used widely not only for the extraction-photometric determination of tantalum[28,120,121] but also for the extraction-gravimetric determination of large amounts of this metal[122].

The assortment of reagents used in the form of ionic association complexes with fluorotantalate has been greatly extended during the last 5–6 years as a result of the employment of thiazine dye cations, namely those of Methylene Blue and Methylene Green[123], dimethylthionine, trimethylthionine, and Toluidine Blue[124,125].

The use of oxazine dyes (Capri Blue, Meldola's Blue) has already been discussed[118,119]. Studies are being continued on the Rhodamines (Rhodamine 6G) and the TPMD group is being expanded as a result of additions to the TAMD group—Victoria Blue 4R and B[126] and others. The association complex formed by fluorotantalate and tetra-n-pentylammonium bromide $[(C_5H_{11})_4N][TaF_6]$, is used for the gravimetric determination of tantalum[127].

IV. HETEROLIGAND COMPLEXES IN TITRIMETRIC AND GRAVIMETRIC METHODS FOR THE DETERMINATION OF NIOBIUM AND TANTALUM

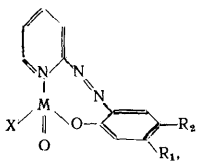
Classical gravimetric and titrimetric methods involving complex processes for the separation of niobium and tantalum and their separation from other elements do not meet modern requirements for production control and only spectrophotometric methods employing organic reagents are widely used nowadays. Nevertheless, as a result of the application of heteroligand complexes, gravimetric and volumetric methods for the determination of niobium and tantalum are again resorted to, albeit not very frequently. The methods where the precipitants are quaternary ammonium and tetraphenylarsonium salts, which permit the development of highly selective and sensitive gravimetric procedures, are of special interest. Thus a method has been devised for the precipitation of niobium or tantalum from fluoride solutions (1–8 M) with the aid of tetraphenylarsonium chloride, which permits a quantitative separation of these elements from those in adjacent Groups: tungsten, molybdenum, titanium, and zirconium[128].

Niobium can be separated from tantalum in the form of the complex $[Fe(o\text{-phen})_3][NbO_2(C_4H_4O_5)_2]$ with the aid of ferroin in a solution containing tartrate ions; a gravimetric method for the determination of niobium has been developed on this basis[129]. In the presence of H_2O_2 niobium forms with complexones (ethylenediaminetetraacetate and nitrilotriacetate) ternary complexes with the component ratios Nb : H_2O_2 : complexone = 1 : 1 : 1. Optimal conditions for the existence of these complexes obtain at pH 2–7. In the titrimetric determination niobium peroxide is titrated with nitrilotriacetic acid using Xylenol Orange as an indicator[130]. Owing to the low stability of niobium complexonates, complexometric methods cannot be regarded as sufficiently accurate.

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In the theory and practice of the application of heteroligand complexes there are still many obscure and unsolved problems, which are particularly complicated in the analytical chemistry of niobium and tantalum, bearing in mind the complexity of their ions and compounds and their unusual behaviour when present jointly in solutions and in the presence of other metals and organic ligands. Koch and Ackermann[131] showed in a number of instances that the addition of an auxiliary complex-forming agent leads to an appreciable improvement of the reproducibility of the photometric reactions. In particular, referring to a study of niobium–tartrate–PAAC ternary complexes by Elinson and Mal'tseva[55], they suggest that the formation of the heteroligand complex plays an important role in the suppression of the hydrolysis of niobium. The auxiliary ligand can also influence the kinetics of the complex formation reactions and can promote the formation of coloured ions by reaction with the metallochromic indicator.

It has been shown[56] that the niobium complexes formed with pyridylazo-compounds and tartrate or oxalate ions have the following structure:



where $X=C_4H_4O_6^{2-}$ or $C_2O_4^{2-}$;

$R_1=-OH, -N<^{H}_{C_2H_5}$ or $-N<^{C_2H_5}_{C_2H_5}$;

and $R_2=-H, \quad -CH_3$.

This structure of the complex, involving the formation of the two most probable stable five-membered rings, is justified from the standpoint of the energy state of the system. It has been stated in the literature that in the synthesis of heteroligand complexes five- and six-membered complexes are formed in most cases. Accurate measurements of the dependence of the stability of the complexes on the number of rings formed have not so far been made in relation to binary systems. The number of experimental data is still less adequate for the solution of this problem in relation to heteroligand complexes.

The affinity of the metal ions for specific electron-donating atoms of the complexing agents (usually for O, N, and S) found for binary chelates applies also to heteroligand complexes, but in this case account must be taken of the more complicated interaction with the third component.

Studies have shown[28] that compounds containing hydroxypyridylazo-, *oo'*-dihydroxyazo-, and complexone groups are the most sensitive and selective reagents for niobium. These groups, which are involved in colour reactions with the niobium present in heteroligand complexes, contain two OH groups in the *ortho*-position relative to the azo-group (*oo'*-dihydroxyazo-compounds) or one OH group with the heterocyclic nitrogen atom playing the same role as the second OH group (pyridylazo-compounds), while in compounds containing complexone groups, which play the role of azo-groups, there are two OH groups in the *ortho*-positions in relation to them.

Sensitive colour reactions with niobium are undergone only by those reagents which contain, apart from ring-forming groups, also auxochromes; many electron-donating and electron-accepting substituents, frequently in the *para*-position relative to the azo-group, behave as auxochromes.

The most sensitive and selective reagents for tantalum are those capable of forming heteroligand complexes in the form of associated ionic species with fluorotantalate. These include basic triarylmethane dyes and their analogues.

Studies on heteroligand niobium and tantalum complexes with the above groups of reagents led to the development of precision methods for the determination of niobium and tantalum in various materials in the presence of many elements without their separation.

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