168. K. Auwers and W. Jülicher, Ber., 55B, 2167 (1922).
169. K. Auwers and K. Ziegler, Annalen, 425, 217, 280, 295 (1921).
170. K. Auwers, Annalen, 352, 219 (1907).
171. R. Woodward, J. Amer. Chem. Soc., 62, 1208 (1940).
172. S. Winstein and R. Baird, J. Amer. Chem. Soc., 79, 756 (1957).
173. R. Baird and S. Winstein, J. Amer. Chem. Soc., 79, 4238 (1957).
174. N. M. Emanuel' and Yu. N. Lyaskovskaya, "Tormozhenie Protsessov Okisleniya Zhirov" (Inhibition of Oxidation in Fats), Pishchepromizdat, Moscow, 1961, p. 130.
175. J. Hogg, D. Lohmon, and K. Russell, Canad. J. Chem., 39, 1588 (1961).
176. A. Bickel and E. Kooijman, J. Chem. Soc., 2215 (1956).
177. E. Müller, "Neuere Anschauungen der organischen Chemie" (Translated into Russian), Inostr. Lit., Moscow, 1960, p. 506.
178. E. Müller *et al.*, Annalen, 645, 1 (1961).
179. W. Hatchard, R. Lipscomb, and F. Stacey, J. Amer. Chem. Soc., 80, 3636 (1958).
180. G. Cavill, E. Cole, P. Gilmann, and D. Methigh, J. Chem. Soc., 2785 (1954).
181. R. Moore and W. Waters, J. Chem. Soc., 243 (1954).
182. S. Cosgrove and W. Waters, J. Chem. Soc., 388 (1951).
183. A. Bickel and E. Kooyman, J. Chem. Soc., 3211 (1953).
184. C. Cook, J. Org. Chem., 18, 261 (1953).
185. W. Hatchard, J. Amer. Chem. Soc., 80, 3640 (1958).
186. K. Dimroth, F. Kalk, and G. Neubauer, Chem. Ber., 90, 2058 (1957).
187. S. Goldschmidt, Ber., 55, 3194 (1922); Annalen, 438, 202 (1924); 445, 123 (1925).
188. E. Müller, K. Shurr, and K. Scheffler, Annalen, 627, 132 (1959).
189. C. Cook, R. Woodworth, and P. Fianu, J. Amer. Chem. Soc., 78, 4159 (1956).
190. H. Blanchard, J. Org. Chem., 25, 264 (1960).
191. H. Gersmann and A. Bickel, J. Chem. Soc., 2711 (1959).
192. J. Conradi and G. Laren, J. Amer. Chem. Soc., 82, 4745 (1960).
193. G. Coppinger, J. Amer. Chem. Soc., 79, 2758 (1957).
194. T. Campbell and G. Coppinger, J. Amer. Chem. Soc., 74, 1469 (1952).
195. E. T. Denisov and N. M. Emanuel', Uspekhi Khim., 27, 365 (1958).
196. F. Wessely, G. Lauterbach-keil, and F. Sinwell, Monatsh., 81, 811 (1950).
197. F. Wessely and F. Sinwell, Monatsh., 81, 1055 (1950).
198. F. Wessely, J. Kotlan, and F. Sinwell, Monatsh., 83, 902 (1952).
199. F. Wessely and J. Kotlan, Monatsh., 84, 291 (1953).
200. F. Wessely and E. Schinzel, Monatsh., 84, 426 (1953).
201. F. Wessely and E. Schinzel, Monatsh., 84, 969 (1953).
202. F. Wessely, J. Kotlan, and W. Metlesies, Monatsh., 85, 69 (1954).
203. W. Metlesies, E. Schinzel, H. Vilesek, and F. Wessely, Monatsh., 88, 1069 (1957).
204. F. Wessely, J. Roy. Inst. Chem., 83, 424 (1959).
205. G. N. Bogdanov and V. V. Ershov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 2145 (1962).
206. C. Cook and C. Depatie, J. Org. Chem., 24, 1144 (1959).
207. S. Hünig and W. Daum, Annalen, 595, 131 (1955).

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USE OF REAGENTS OF THE ARSENAZO–THORON GROUP IN ANALYTICAL CHEMISTRY

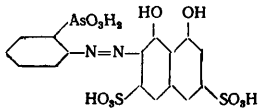
S. B. Savvin

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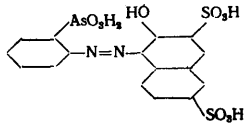
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1. GENERAL REVIEW OF APPLICATIONS

The reagents Arsenazo I [1] and Thoron I [1,2] synthesised by Kuznetsov in 1941 were the first of the general class of reagents of the arsenazo–thoron group:



Arsenazo I



Thoron I

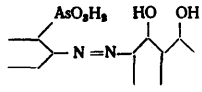
The main use of these reagents is in inorganic spectrophotometric analysis, but they are also used in complexometry, extraction, and coprecipitation methods. More than 40 elements can be detected by reagents of the arsenazo group, and quantitative methods have been developed for the determination of 20 of these in various materials.

Organic reagents containing the arsono-group AsO_3H_2 had previously been used widely in inorganic analysis, the best known being phenylarsonic acid. The presence of the arsono-group causes the formation of particularly stable complexes with several elements, such as zirconium, niobium, and thorium. The reaction products with phenylarsonic acid and many of its derivatives are colourless; the reagents are mainly used for the gravimetric determination of elements or for the removal of interfering elements.

The reagents of the arsenazo group are characterised by the presence of the arsono-group and also an azo-group in the *ortho*-position to it; almost always there is a

hydroxy-group *ortho* to the azo-group. Several dozen reagents of this type are now known, but only certain of them have been widely used.

The very convenient combination of the AsO_3H_2, OH, and azo-groups into a single complex functional group:



has provided a whole series of analytically valuable reagents. The presence of the salt-forming AsO_3H_2 group produces complexes of sufficient stability for complex-formation to take place even in acid solutions, the azo-group provides colour, and because of the hydroxy-group a second six-membered ring containing the cation can be formed, which not only substantially increases the stability of the complex, but also gives a deeper colour.

The relative complexity of the functional group means that reagents of the arsenazo group are not specific for any one element, but are group reagents; this is convenient in that a series of elements can be determined with a single reagent, but the necessary selectivity always requires special working conditions.

The exceptionally valuable analytical properties of arsenazo and its more recently developed analogues have caused them to be widely used in analysis; the relevant literature contains several hundred references, including reviews on the use of Thoron I [3], Arsenazo I [4,5], and Arsenazo III. [6]

The use of reagents of the arsenazo group is a successful complement to the use of dithizone, which is employed mainly for elements of the hydrogen sulphide group; satisfactory photometric methods have long been known for the determination of these elements and for certain others, *e.g.* those which have a chromophoric action or form ammines, but no convenient and sensitive methods were known for the determination of thorium, zirconium, hafnium, uranium, protactinium, beryllium, aluminium, the rare-earth elements, and several others, with a few exceptions [7]; arsenazo has proved to be useful for just these "difficult" elements.

The reagents of the arsenazo group are readily prepared by coupling diazotised *o*-aminophenylarsonic acid or its derivatives with any coupling component. Chromotropic acid is especially suitable as the latter; the resulting reagents are more sensitive than many described in the literature for the spectrophotometric determination of various elements.

2. MAIN PROPERTIES OF THE REAGENTS

Not all the reagents described in this section are equally widely used in analysis. The most widely used are Arsenazo I, Thoron I, and Arsenazo III.

The reagents of the arsenazo group are dark red powders, readily soluble in water to give a pink solution. The orange-red Thoron I and II dissolve to give an orange-yellow solution. Arsenazo I, II, and III form violet, blue, or even, with Arsenazo III, green complexes with elements. Complex formation with reagents of the thoron group, derivatives of R-salt, etc., produces less deep crimson colours.

Arsenazo I

The first studies of the properties of arsenazo [1,2,8] showed it to be a very valuable analytical reagent, primarily because it gives colour reactions with elements for which no convenient methods of determination had previously been known. The high sensitivity of these colour reactions (the molar extinction coefficients are of the order of several tens of thousands) enables micro-quantities of the elements (from 0.05 to 0.1 $\mu g\ ml^{-1}$) to be detected. Finally, the relatively high stability of the complexes enables elements to be determined even in acid solution, which is extremely valuable in analytical practice.

The high sensitivity of the reactions is due to the relatively large shift of the absorption spectrum of the complex in comparison with that of the reagent; Fig. 1 shows these spectra for the reagent and its thorium complex. The absorption spectra of other complexes resemble closely that of the thorium complex.

Methods have been developed for the determination, using Arsenazo I, of uranium [9-20], thorium [20-32], zirconium [33-38], scandium [39], lanthanum [40], cerium [41], total rare-earth elements [42-46], aluminium [47,48], beryllium [49-51], titanium [52], niobium [33,42,53], tantalum [54], vanadium(IV) [17], and indium [55]. Colour reactions also suitable for their determination have been described for tin, bismuth, gallium, copper, palladium(II), magnesium, and calcium.

One of the features of the use of Arsenazo I is the possibility of obtaining high selectivity by variation of pH, which is not always possible with other reagents, *e.g.* Thoron II. Examples are the selective determination of thorium in the presence of large amounts of rare-earth elements [21], of zirconium and thorium in the presence of UO_2^{2+}, and of UO_2^{2+} in the presence of rare-earth elements, calcium, and others [5,9,33]. The comparatively low stability of Arsenazo I complexes (in comparison with other reagents of this type) enables it to be used as an indicator in the complexometric determination of plutonium [56], thorium [57-59], total rare-earth elements [60-62], and fluoride (by titration with Th) [63-65].

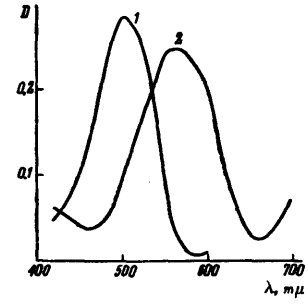
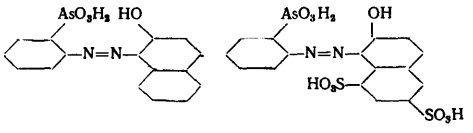


Fig. 1. Absorption spectra of 10^{-5} M solutions (at pH 2.0) of: 1) Arsenazo I; 2) Arsenazo I thorium complex.

Thoron I

Reagents of the thoron group are prepared from R-acid†, β-naphthol, or derivatives of β-naphthol as coupling component. As well as Thoron I [1,2] several analogues are known [4,5], *e.g.*:



extract thoron iso-thoron

Thoron gives somewhat less sensitive colour reactions than arsenazo; because of this, and because of the somewhat simpler analytically functional group, the number of elements which react with thoron is limited, *i.e.* thoron is more selective than arsenazo.

Thoron I has been most used for the determination of thorium [66-89]. The high reproducibility of results, the convenient working conditions (acid medium of pH 0.7–1.2) and the high selectivity make this a very efficient method; thus no interference in the determination of thorium is caused by the presence of more than 100- to 1000-fold quantities of rare-earth elements, UO_2^{2+}, and other elements. With the extraction-photometric variants of the determination described below, the tolerable ratio of thorium to certain other elements reaches 1 : 10^6.

Thoron I is used to a lesser extent for the photometric determination of plutonium [90], neptunium [91], total rare-earth elements [40], uranium(IV) [92,93], zirconium [94], beryllium [50,95,96], and lithium [97-100], and for the complexometric determination of thorium [101], uranium [102], bismuth [103,104], fluoride [105-107], and sulphate [108,109].

Table 1 gives the absorption maxima of various reagents and their thorium complexes, the shift of the maximum $\Delta\lambda$, which determines the contrast‡ of the reaction, and the working value of λ selected so as to reduce the effect of the excess of reagent as much as possible.

TABLE 1. Spectrophotometric data on reagents and their complexes.

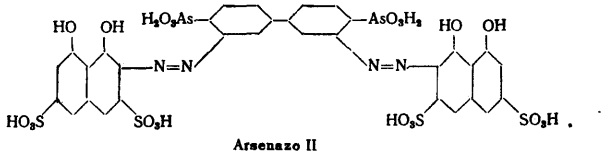
Reagent	Absorption maximum, mμ		Δλ	λ (working)
	reagent	thorium complex		
Arsenazo I	500	555	55	580
Thoron I	475	505	30	545
Arsenazo II	510	550	40	600
Thoron II	480	520	40	560
Arsenazo III	540	665	125	665

† 2-Hydroxynaphthalene-3,6-disulphonic acid (Ed. of Translation).

‡ The term "contrast" is used here apparently synonymously with selectivity (Ed. of Translation).

Arsenazo II

The reagent Arsenazo II [5] is an analogue of Arsenazo I in which the analytically functional group appears twice:



Arsenazo II

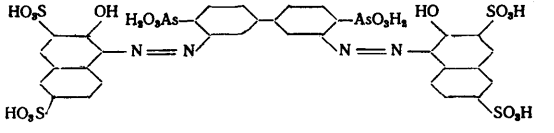
Its preparation has been described by Kuznetsov and Savvin [110]. A feature of the reagent is the substantially increased stability of its complexes, so that the optimum pH values for its reaction with elements is in the more acid region: thus Th and Zr can be determined in 0.1–0.6 *N* HCl. Interference due to masking anions (sulphates, phosphates, fluorides) is much reduced.

The selectivity of action of Arsenazo II is about the same as that of Arsenazo I; it reacts in acid solution with zirconium, hafnium, titanium, thorium, uranium(IV), and iron(III); in weakly acid and neutral solution with aluminium, indium, gallium, uranium(VI), rare-earth elements, copper, and beryllium; and in alkaline solution with calcium, magnesium, barium, zinc, cadmium, lead, and manganese.

Procedures have been developed for the determination of thorium in monazites [111,112], UO_2^{2+} in uranium ores [113], and scandium [39]. The reagent may apparently also be used for the determination of zirconium, hafnium, total rare-earth elements, vanadium(IV), beryllium, and gallium [5].

Thoron II

This is also the analogue of the corresponding monoazo-compound with two analytically functional groups [5]:



Thoron II

Its preparation has been described by Kuznetsov and Savvin [110]. An important feature of Thoron II, not shared by Thoron I, Arsenazo II, or many other reagents, is its ability to form with thorium, zirconium, uranium(IV), and the rare-earth elements very stable complexes which are not decomposed even in strongly acid solution. The reagent has been used to determine thorium [114], and its use for the determination of zirconium and certain rare-earth elements looks very promising [5,114]. A disadvantage of this reagent is the low contrast of the reaction.

Arsenazo III

Arsenazo III was prepared by Savvin in 1959 [115]; its properties have been described [6].

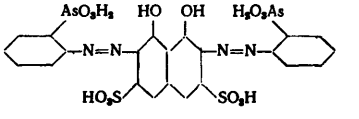


TABLE 2. Colour reactions of Arsenazo III.

Element	Colour of complex*	Reaction conditions	Conditions for maximum sensitivity		Molar extinction coefficient**
Th	green	0.01 – 10 *N* HCl	9 *N* HCl	665 λ, mμ	130 000
Zr	green	0.2 – 12 *N* HCl	9 *N* HCl	665 λ, mμ	120 000
Pa	green	1 – 10 M HCl or H_2SO_4	7 M H_2SO_4	660 λ, mμ	22 000
Hf	green	0.2 – 12 *N* HCl	9 *N* HCl	665 λ, mμ	95 000
U^{IV}	green	0.05 – 10 *N* HCl	4 *N* HCl	670 λ, mμ	100 000
UO_2^{2+}	green	pH 1 – 4	pH 2.0	665 λ, mμ	53 000
Sc	violet	pH 1 – 4	pH 1.7	675 λ, mμ	19 000
I	green	pH 3 – 4	pH 3.0	655 λ, mμ	55 000
La	green	pH 3 – 4	pH 3.0	655 λ, mμ	45 000
Ce	green	pH 3 – 4	pH 3.0	655 λ, mμ	47 000
Ca	blue	pH 4 – 5	pH 5.0	655 λ, mμ	10 000
Pb	blue	pH 4 – 5	pH 5.0	655 λ, mμ	10 000
Bi	violet	pH 1.5 – 4.5			
Fe^{III}	violet	pH 1.5 – 3			
Cu	violet	pH 4.5 – 5			
Ba	blue	pH 4.5 – 5			

* The reagent is pinkish crimson.

** Approximate data

Arsenazo III gives colour reactions with many elements, although with a smaller number than Arsenazo I. Its main distinguishing feature is the ability to form particularly stable inner complexes, so that elements can be determined in strongly acid media [*e.g.* thorium, zirconium, hafnium, protactinium, and uranium(IV) in up to 10 *N* HCl] and in the presence of complex-forming anions which normally interfere in the direct determination of the elements.

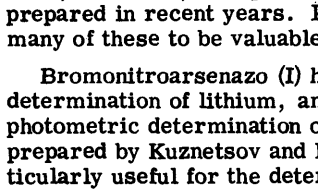
The sensitivity of the colour reactions can reach 0.01 – 0.05 μg of elements per ml. The most sensitive methods are those for the determination of thorium, zirconium, uranium, protactinium, scandium, and the rare-earth elements, and the least sensitive, those for lead, bismuth, iron, copper, calcium, and barium; methods with the greatest selectivity are those developed for the determination of thorium[97,116-125], uranium[115,126-128], zirconium[6,129-135], hafnium[131], rare-earth elements[136], and protactinium[137] in various materials. The analytical use of Arsenazo III and the mechanism of its reaction have been reviewed[6,139].

Table 2 lists the elements which give colour reactions with Arsenazo III, the resulting colours, the reaction conditions, and the sensitivity.

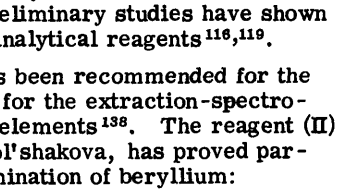
Other Arsenazo Analogues

A large number of derivatives and analogues of Arsenazo I, Thoron I, and particularly Arsenazo III have been prepared in recent years. Preliminary studies have shown many of these to be valuable analytical reagents[116,119].

Bromonitroarsenazo (I) has been recommended for the determination of lithium, and for the extraction-spectrophotometric determination of elements[138]. The reagent (II) prepared by Kuznetsov and Bol'shakova, has proved particularly useful for the determination of beryllium:

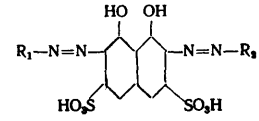


(I)

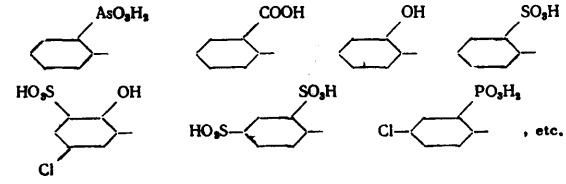


(II)

Arsenazo III analogues of analytical value are the bisazo-compounds obtained from chromotropic acid and various amines, of the general formula:

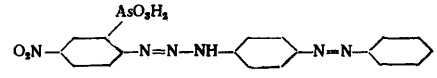


where R_1 and R_2 are the residues of the substituted anilines:



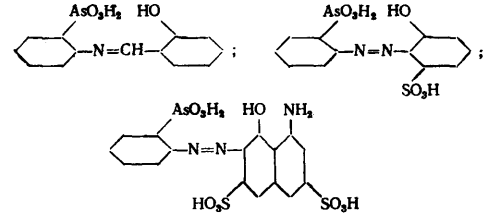
A general feature of these last reagents is that they form highly stable complexes with elements, and many have proved of interest for the determination of niobium, zirconium, hafnium, uranium, strontium, scandium, barium, and many other elements[140-145].

The use of "Arsazen":



has been suggested for the extractive determination of lead[146].

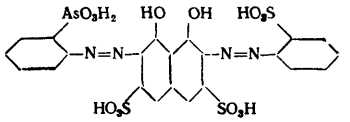
Many monoazo-compounds derived from *o*-aminophenylarsonic acid and various coupling components have been described, *e.g.* [2,147-149]:



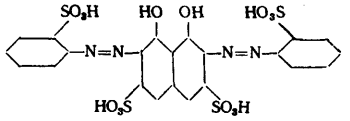
These all give colour reactions with thorium, zirconium, and several other elements in a near-neutral medium; the resulting complexes are relatively unstable and are readily decomposed by many masking complex-forming reagents (sulphates, phosphates, etc.). These reagents and others do not match up to those based on chromotropic acid and R-salt, and have not found wide analytical use.

Reagents which do not contain the AsO_3H_2 group do not belong formally to the arsenazo group of reagents (*i.e.* those containing arsenic and an azo-group), but a very close analogy in their analytical behaviour makes it convenient to consider them together with reagents containing the AsO_3H_2 group; the nature of the salt-forming group affects only the selectivity of the reagents, and not the mechanism of the complexing and colour reactions. We shall give a few examples.

The reagents (III) and (IV) are of use for the determination of barium and strontium in acid media (to pH 1)§ [142]:

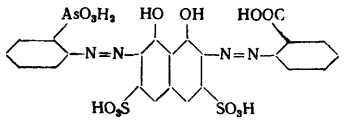


(III)

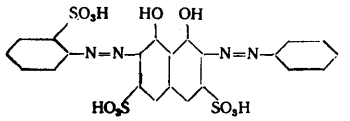


(IV)

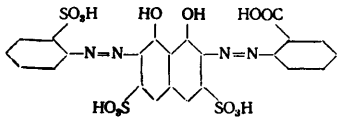
Reagents (III) and (V)–(VIII) have been used as indicators for barium ion in the volumetric determination of sulphate [142-143]:



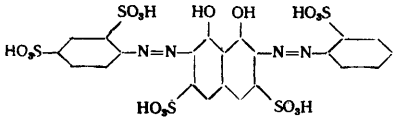
(V)



(VI)

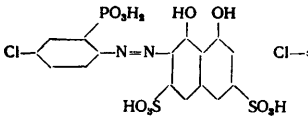


(VII)

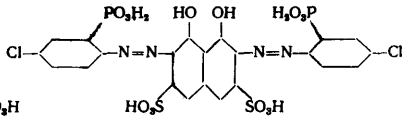


(VIII)

Reagents (IX) and (X) have been recommended for the determination of uranium [144,145]:

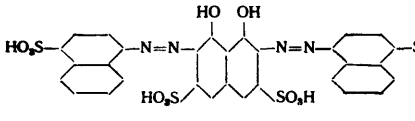


(IX)



(X)

Datta and other Indian workers have described a whole series of reagents based on chromotropic acid, which are useful for the photometric determination of thorium, zirconium, and others [140,141]. The best known is di-SNADNS, which is often used as an indicator for metal ions [150]:

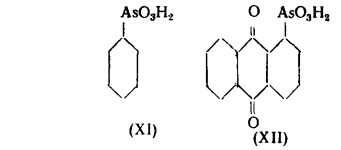


We cannot mention here all the reagents of this type, since the number derived from chromotropic acid, H-acid¶, and other naphthalene sulphonic acid coupling components described in the literature is so great that they would require a separate review.

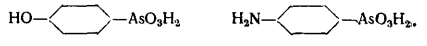
Other Reagents Containing the AsO_3H_2 Group

Colourless reagents containing the arsono-group are mainly used as precipitants for heavy metals and for their subsequent gravimetric determination or separation from other elements. We shall consider them here in less detail.

Phenylarsonic acid (XI) is the best known reagent of this group. It is used mainly for the precipitation of zirconium to separate it from other elements [151-153]; precipitates are also formed only with tin, titanium, niobium, tantalum, and cerium(IV), and the influence of these elements can be removed by adding hydrogen peroxide, after first removing tin. Phenylarsonic acid is also used for the detection of niobium and tantalum [154,155], tin(IV) [156,157], and thorium in monazite sands in the presence of rare-earth elements [158].



(XI) (XII)



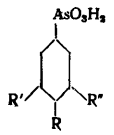
(XIII) (XIV)

Anthraquinone-α-arsonic acid (Anthraquas) (XII) is used to precipitate small amounts of tin(IV), zirconium, and titanium from dilute solutions [159]; because of the increased size of the molecule there is a certain increase in sensitivity as compared with phenylarsonic acid.

p-Hydroxyphenylarsonic acid (XIII) is used for the precipitation and gravimetric determination of titanium [160] and zirconium [161]. Arsanilic acid (XIV) is used for the detection of cerium by a colour reaction (appearance of a reddish-brown colour because of the chromophoric action of cerium) [162] and for the detection of zirconium (formation of a white precipitate) [163].

Propylarsonic acid, allylarsonic acid, and other alkylarsonic acids are used to precipitate zirconium [164,165].

A group of reagents of general formula:



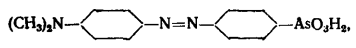
(where R is H, OH, NH_2, CH_3, C_6H_5, $NHCOCH_3$, or $NHCH_2$. .COOH and R′ and R″ are H, Cl, NO_2, or COOH) have been described; they are suitable for the precipitation of tin(IV), zirconium, and thorium [166-168], but have not found wide use.

§ In these compounds the grouping containing the AsO_3H_2 group does not take part in the reaction with barium and strontium.

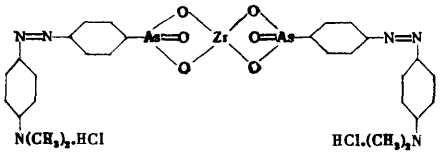
¶ 1-Amino-8-hydroxynaphthalene-3,6-disulphonic acid (Ed. of Translation).

This class of precipitating agents contains the coloured compounds having an arsono-group in a position other than *ortho* to an azo-group. In this case the reaction produces simple salts of the AsO_3H_2 group; there is no formation of inner complexes or any sharp colour change.

The most studied reagent of this type is *p*-dimethylaminophenylazophenylarsonic acid:

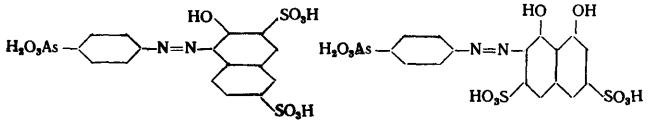


which forms with zirconium the brownish red salt[169-172]:



The sensitivity of the reaction is 10 μg ml^{-1}; many elements do not interfere.

Azo-dyes derived from arsanilic acid, with R-salt and chromotropic acid as coupling components[2,147-149]:



form simple salts with zirconium, thorium, and other elements, and may be used for their precipitation.

3. THE ATTAINMENT OF SELECTIVITY

The simplest method of increasing selectivity is by adjustment of the acidity of the solution, since the optimum pH for the reaction of a reagent with an element depends on the latter. For reagents of type ROH there is a definite correlation between colour reactions and hydrolysis[173]; thus colour reactions with coloured reagents are only given in strongly acidic media by elements whose cations are readily hydrolysed: zirconium, hafnium, uranium(IV), and thorium; in moderately acid solutions colour reactions are given, in addition to the above, by iron(III), aluminium, and UO_2^{2+}; in weakly acid and neutral solutions by rare-earth elements, iron(II), and copper; and in alkaline solutions by calcium, strontium, and magnesium. This series is not of course absolute in character, and applies only to reagents of type ROH.

The reaction conditions depend on the reagent used, but for each reagent the optimum pH depends on the element in the same way: readily hydrolysed elements react in a more acidic medium, and other elements in a less acidic medium.

Variation of the acidity is not the only method for increasing the selectivity. It is often recommended that the interfering elements present should be complexed as stable colourless complexes; this is only possible when under the given conditions (at a definite pH) the complexes formed by the complexing agent with the element to be determined and the impurity have greatly differing stabilities. A well-known example is the system UO_2^{2+}–Trilon B–other elements. When uranium is determined with Arsenazo II, aluminium is readily masked with sulphosalicylic acid†, and titanium with tartaric acid[113]. In the determination of uranium with Arsenazo III thorium is masked with fluorides[126]. In the determination of thorium with Arsenazo III zirconium is very selectively masked with oxalic acid[115]. Many other examples could be given.

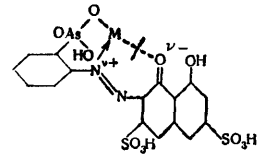
The so-called confirmatory reactions, when under the given conditions only the element to be determined is selectively masked, are sometimes very useful. By measuring the optical density before and after the addition of the masking agent, the interference due to the presence of other elements can be estimated. The use of hydrogen peroxide has been suggested in the determination of uranium with Arsenazo I,[9] sodium hexametaphosphate in the determination of thorium with Arsenazo III,[120] and phosphates in the determination of the rare-earth elements[42].

Another method for increasing selectivity is to use the so-called extraction–photometric procedure, which has only recently been described[138,174]; this combines extraction and photometry in one operation, and gives high selectivity with certain elements (thorium[116,119], UO_2^{2+} [126]).

In many cases a combination of these methods for thorium, protactinium, zirconium, hafnium, uranium(IV), plutonium, neptunium, and UO_2^{2+} will ensure a good selectivity in the determination. When materials of complex composition or of low content of the elements to be determined are analysed it is usually necessary to remove interfering elements before the determination.

4. NATURE OF THE COLOUR REACTIONS

The mechanism of the colour reaction has been discussed in many papers[21,95,136,175,176]. For example, the complex of arsenazo with bivalent elements may be represented:



With aluminium, copper, and certain other elements the hydroxy-groups of the naphthalene residue may participate in the formation of the complex.

In general, a colour reaction occurs if the element reacts with the dyestuff molecule in such a way that there is a direct effect on the atom or group of atoms of the reagent molecule which are responsible for its colour, *i.e.* on the chromophoric group[177,178]. In azo-dyes the –N=N– group is usually considered to be the chromophore, but it is more accurate to treat the molecule as a whole as a single conjugated system with π-bonds; therefore, if groups directly attached to the conjugated system (*e.g.* the OH group) take part in the formation of the complex, a colour reaction will occur. It is an established experimental fact, however, that direct action on the azo-group of a dyestuff molecule produces a larger optical effect than action on the peripheral part of the molecule; for instance, the aluminium complex of arsenazo is red-violet, while the UO_2^{2+} complex is blue. This has been established by studying the absorption spectra of the pure reagents in concentrated sulphuric acid, when the azo-group is protonated and deep violet,

† 2-Hydroxybenzoic-5-sulphonic acid (Ed. of Translation).

blue, and green colours are observed, corresponding to those of the complexes of UO_2^{2+}, Th, and other elements; and in alkalis, where the naphthalene hydroxy-groups are ionised and less deep red-violet colours are obtained, corresponding to the colours of aluminium and copper complexes.

The greatly increased depth of colour when complex--formation occurs is thus due firstly to the formation of a certain positive charge on the "chromophoric centre of the molecule" (the azo-group), and secondly to the formation of a certain negative charge on the residue of the naphthalene hydroxy-group. In order to indicate the partially ionic character of the $M^{\nu+}-O^{\nu-}$ bond, we here use the symbol M.../...O (intramolecular ionisation, after Kuznetsov[175,179-181]). The dipole formed at the ends of the system of conjugated bonds causes a sharp change in the colour of the reagent, *i.e.* it produces the corresponding colour reaction. The metal cation thus acts as an independent very strongly positive auxochrome, and at the same time the two six-membered rings which are formed, and which have almost aromatic properties, produce substantial stabilisation of the molecule.

Complex-formation with Arsenazo III shows a number of interesting features[115,136,139]. It has been shown that in the free state the Arsenazo III molecule is symmetrical but not planar, because of steric hindrance caused by the AsO_3H_2 groups. When complex-formation takes place, the planarity of the molecule may be partially restored, which is another factor producing a considerable deepening in colour[139].

The two analytically functional groups of the Arsenazo III molecule form part of two weakly interacting almost isolated conjugated systems, only one of which participates in complex-formation; this destroys the symmetry and creates two absorption bands in the complex in the visible region (Fig. 2). The reduced reactivity of the second analytically functional group when the first takes part in complex-formation may be related to the possible production of a certain positive charge on the second azo-group,

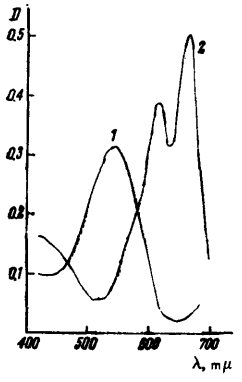


Fig. 2. Absorption spectra of 10^{-5} M solutions in 9 *N* HCl of: 1) Arsenazo III; 2) Arsenazo III thorium complex.

which hinders the formation of a second $M^{n+}-N$ bond. The longer conjugation system in Arsenazo III as compared with Arsenazo I, and the resulting possibility for the spread of the positive charge produced on the first azo-group, may be reasons for the increase in the stability of the M–N bond, which determines the stability of the whole complex[139].

Several studies have been devoted to the determination of the dissociation constants of Arsenazo I and Thoron I[182-184] and the instability constants of their complexes with a number of elements[176,185]. The very interesting quantitative data obtained require a special review.

5. FIELDS OF USE

Spectrophotometry is the main field in which the reagents of the arsenazo group are used. They show two typical features. The first is their ability to form stable complexes, which is of obvious interest for analysis, since it allows the use of strongly acid solutions, where there is no hydrolysis, conversion of the ions of the element into slowly reacting multinuclear ions, or other undesirable effect. The reproducibility of results and the reliability of the determination are greatly increased, there is no need for careful maintenance of the pH, and the experimental procedure is simplified; the influence of anions is reduced to the minimum. Particularly stable complexes are formed by the bisazo-derivatives of chromotropic acid, Arsenazo III and its analogues.

The second feature is the high sensitivity of the colour reactions: for some elements the determinable minimum concentration is 0.01–0.1 μg ml^{-1}, with molar extinction coefficient $100-150 \times 10^3$.[116,119] The high sensitivity is due to the nature of the absorption spectra of the complex and reagent, and to the high stability of the complexes formed, which enables the element to be completely complexed even at high dilution[119,187,188].

Arsenazo I has been employed as an ingredient in an *organic coprecipitant*, which can concentrate plutonium[189,190], americium[190], and rare-earth elements[191] from dilute solutions. The theory of the action of organic coprecipitants and the features of their analytical application have been discussed by Kuznetsov[192]. Methyl violet and certain other highly coloured basic dyestuffs have been used in the coprecipitants, but colourless organic coprecipitants may also be used; in this case the filtered precipitates can be dissolved in a small volume of organic solvent and the coprecipitated element determined directly by photometry of its complex with the reagent. In this way the element is simultaneously concentrated and determined. Ashing of the organic precipitate or its decomposition with acids are not required. These methods are exceptionally convenient for the determination of elements in extremely dilute solutions[138]. A method has been described for the coprecipitation of the diphenylguanidinium salt of the Arsenazo III complex of thorium with diphenylguanidinium anthracene-α-sulphonate as carrier, which can determine thorium at a dilution of 1 in 10^9.[119]

Another new use for reagents of the arsenazo group is in the so-called *extraction–spectrophotometric* methods of analysis[138,174]. The selectivity and sensitivity can be increased by combining spectrophotometry with preliminary extraction of the element; the spectrophotometry is best carried out directly in the organic phase, without re--extraction, but for this purpose only reagents soluble in organic solvents, such as dibenzoylmethane, can be used,

while the sulphonato-group-containing reagents of the arsenazo group are insoluble in non-aqueous solvents.

It has been shown that the hydrophilic action of the sulphonic acid groups and their anionic constitution, which hinder the extraction, can be removed by forming simple salts with heavy organic cations containing at least 10–12 carbon atoms; the most suitable is the diphenylguanidinium cation $[(C_6H_5NH)_2CNH_2]^+$.[138,174] When triply- and in some cases quadruply-charged cations are used for complex-formation with the reagent some of the cationic charge may be retained; this is compensated by adding an anion suitable for extraction. Thiocyanates, perchlorates, and chloroacetates can be used as hydrophobic anions. The hydrophilic action of the complex, caused by the partial charges distributed in different parts of the molecule, can be substantially reduced if the extractant molecules can replace water molecules in the solvates[193]. The most convenient solvents are butanol and pentanol, but hexanol, benzyl alcohol, cyclohexanone, and a solution of ethanol in chloroform can also be used[138,148].

The extraction of inner complexes has been considered from the point of view of the coordination saturation or unsaturation of the central atom[193]; extraction is thought to occur only when all the coordination positions of the central atom are saturated by the reagent used, by molecules of other substances present which can take part in coordination, by molecules of the organic solvent, and so on. These matters have been considered in detail in Zolotov's review (see p.107).

Examples of the extraction–spectrophotometric method are the determination of uranium[126] and thorium[116,119] with Arsenazo III.

The extraction of known reagents can be increased by using their bromo-, chloro-, or nitro-derivatives.

In the last few years the reagents of the arsenazo group have begun to be widely used as *metal-indicators* in the complexometric determination of elements; methods have been described for the volumetric determination of thorium[57-59,102], rare-earth elements[60-62], and plutonium[56]. For a high sensitivity and accuracy in the volumetric determination there must be a certain relationship between the stabilities of the complexes formed by the element with the indicator and with the complexing agent; this relationship depends on the element concerned, the pH conditions, the concentration, and other factors[60]. In this respect reagents of the arsenazo group show great possibilities. Of the large number of compounds described, it is always possible to select a series of reagents which will give a colour reaction with the given element but form with it complexes of different stabilities. The bisazo-derivatives of chromotropic acid are particularly useful, since by variation of the radical R_z it is possible to retain a colour reaction with the given element, but at the same time to provide reagents which produce complexes of greatly different stabilities[119]. The stabilities of the complexes in such cases can be determined most conveniently by the method of "particular instability indices"[194], which gives exceptionally rapid results. An example is the determination of the rare-earth elements, in which less than 1–2 μg of a particular element per ml can be determined with an accuracy of 1–2%.[60]

In the complexometric determination of readily hydrolysed elements — zirconium, thorium, uranium(IV) — or elements which tend to form oxo-ions (aluminium, chromium), the titration is preferably carried out in strongly acid solution. Certain bisazo-derivatives of chromotropic acid may prove useful here.

The reagents of the arsenazo group have not found wide application as *precipitants*. The precipitation of Zr with Arsenazo I has been described[195]. The separation of Th and Zr from other elements by adsorption of their complexes with Thoron I on activated carbon is of interest[196]. The most useful reagents for these purposes, as for co-precipitation with coloured or colourless precipitants, are those of higher molecular weight: Arsenazo II, Thoron II, and bromo- and nitro-derivatives of Arsenazo III.

The use of these reagents for the *chromatographic separation* of elements has been little studied, although it may reveal new possibilities.

6. QUANTITATIVE ANALYTICAL METHODS

Thorium

This element, which once presented serious difficulties analytically, can now be determined photometrically in almost any material, even in trace amounts. The use of Thoron I has been the most studied. After early work describing the colour reaction, the conditions for the determination and the selectivity[1,2], a series of independent papers appeared describing the determination of thorium in various materials[66-89].

Methods using Arsenazo I are somewhat more sensitive; the reaction has been studied in detail by Kuznetsov and Nikol'skaya[21]. The method has been described in Japanese[29-32] and other[22-28] papers. Zaikovskii and Gerkhard suggested the use of tartaric acid to mask Zr and Ti.[22,23]

The determination of Th with Arsenazo II is carried out in 0.2 *N* HCl under conditions such that the influence of many other elements is reduced to a minimum; zirconium and titanium are masked with phosphates. The determination of thorium in monazites[111], granites, and other minerals[112] has been described.

With Thoron II the determination can be effected in strongly acid media, where the influence of sulphates and phosphates is low; zirconium and titanium are masked with oxalic acid[114]. A method for the determination of micro-quantities of thorium oxide, ThO_2, has been developed[114].

The use of Arsenazo III appears to be the most promising[6,115]. The experimental conditions are: 3.0–9.0 *N* HCl, 1.5–2% oxalic acid to mask zirconium, and 0.002% Arsenazo III; the sensitivity is 0.05–0.1 μg of thorium per ml[6,115]. Sulphates, oxalates, and phosphates do not interfere. Methods have been developed for the determination of micro-quantities of thorium[119] and for the determination of thorium in zircons[117], metallic tungsten[124], products containing niobium and titanium[121], rocks[118,120], and other materials[97,121-123]. An extraction–spectrophotometric method using Arsenazo III has been developed, which can determine for example 1 μg of thorium in 1 litre of solution[119]. Methods have been described for coprecipitating thorium with Arsenazo III with colourless and inert coprecipitants[119,120].

In the absence of zirconium, thorium can be determined in 50% hydrochloric acid (~ 6 M) without adding oxalic acid. The sensitivity is a maximum in 8 M HCl. With a 5 cm photometric cell 0.01 μg of thorium per ml can be

determined[119]. Because of the high acidity, oxidants such as nitric acid and chlorine, which are sometimes found in commercial acids, must be absent. It is best to use distilled hydrochloric acid.

Various procedures have been described for use with specific materials; these differ mainly in the method used to decompose the sample and remove the base material, the photometry being carried out under practically the same conditions in each case. For rocks the following procedure may be used: 0.1–0.5 g of rock containing 0.0001% of thorium or more, *i.e.* assumed to contain 1–25 μg of thorium, is decomposed with hydrofluoric acid, the solution evaporated, the residue moistened with the same acid and treated with water, the filtered residue treated with perchloric–hydrochloric acid mixture, the solution evaporated, the residue dissolved in hydrochloric acid, the reagent is added, and the solution subjected to spectrophotometry[118].

To determine thorium in zircons, 0.1 g of the material is fused with potassium hydrogen fluoride at 800°–900°, the melt treated with sulphuric acid (1 : 1), and the solution evaporated to remove all the fluorine. The residue is dissolved in hydrochloric acid and the solution subjected to spectrophotometry[117].

In the determination of thorium in silicate rocks, zirconium, titanium, and the rare-earth elements are removed by ion exchange on cation-exchange resin KU-2‡ in the hydrogen-form. Titanium is not adsorbed from 1 M hydrochloric acid; the rare-earth elements are eluted with 2 M hydrochloric acid and zirconium with 0.5% oxalic acid, and then thorium is quantitatively eluted with saturated ammonium oxalate solution. The thorium is then determined with Arsenazo III in 5 M hydrochloric acid without removing the oxalates, which do not interfere. The sensitivity corresponds to 10^{-3}–10^{-4}% of thorium in the specimen[125].

The concentration of thorium from sea or river water has been described, with its subsequent photometric determination in the precipitates with Arsenazo III by "wet ignition" and with reprecipitation of the thorium to remove impurities present in the water. Quantities as low as 0.5–1 μg of thorium can be separated and determined from 20 litres of sea or river water[120].

Because of its high sensitivity combined with good selectivity, especially with respect to anions, the method using Arsenazo III is recommended for the rapid determination of micro-quantities of thorium present as ThO_2. The material is dissolved in sulphuric acid and the ThO_2 determined without removing the sulphates. Such determinations are required in the extraction and evaporation of solutions, and in the determination of thorium in aerosols, biological materials, blood and other cases requiring its determination for medical and health purposes.

Uranium

The highly sensitive reaction with Arsenazo I is most frequently used for the determination of uranium[1,9-20]; zirconium, thorium, titanium, aluminium, iron, the rare-earth elements, and some other elements interfere. With low contents of other elements their influence can be eliminated by adding Trilon B or by utilising the decomposition of the complex of UO_2^{2+} with arsenazo when hydrogen peroxide is added[9,197]. The determination is carried out at pH 4.5–6. A successful method for increasing the selectivity is to combine extraction with spectrophotometry[126,197,198]. Another method for greatly increasing the selectivity is to reduce the uranium to uranium(IV) and determine the latter in the same way as for thorium.

A complexometric method for the determination of uranium(IV) using Arsenazo I as metal indicator has been described. Methods for the chromatographic separation of uranium from impurities have been suggested[199]. An extremely useful method for determining uranium involves preliminary extraction of uranium(VI) with ethyl methyl ketone in the presence of Complexone III.[200]

Thoron I has been proposed for the determination of uranium(IV)[92,93] in 0.1–0.3 *N* HCl; many elements do not interfere.

A method for the determination of uranium in ores with Arsenazo II has been developed, using readily fusible extractants to separate uranium from impurities[113]; sulphates and relatively large amounts of phosphates do not interfere. Iron(III), vanadium(IV), copper, the rare-earth elements, and in part aluminium, titanium, and thorium are masked by adding the calcium salt of Trilon B; aluminium is readily masked with sulphosalicylic acid, titanium with tartaric acid, and thorium with fluorides[113].

Arsenazo III can be used to determine both UO_2^{2+} (pH 1.5–2) and uranium(IV) (4–10 *N* HCl)[115]. An extraction–spectrophotometric procedure has been developed for determining uranium in ores, comprising the extraction of the UO_2^{2+}–Arsenazo III complex with butanol from a solution saturated with Trilon B and containing potassium fluoride to mask thorium and other elements[126]. A highly selective method developed for the determination of uranium(IV)[127] comprises the reduction of uranium with zinc metal and ascorbic acid in one aliquot of the solution, addition of the reagent to this and a fresh aliquot, adjustment of the acidity to 4.5 *N* HCl, and measurement of the optical density of the second solution against the first. The influence of other elements is thus eliminated. Zirconium is masked with oxalic acid. Large quantities of thorium interfere. The determination of uranium in particularly complex materials requires the removal of at least the main mass of interfering elements. Methods for the separation of uranium, thorium, and plutonium have been reviewed[4].

A method for determining uranium in complex ores, minerals, and solutions comprises extraction of uranyl ion with a 20% solution of tributyl phosphate in carbon tetrachloride from a solution containing ammonium nitrate and Complexone III, re-extraction of the uranium with Arsenazo III solution, and photometry; the method can determine contents of uranium of 0.002 μg per ml or more of solution[128].

Zirconium and Hafnium

Zirconium is another element for which reagents of the arsenazo group are widely used analytically. Methods are known using Arsenazo I[33-38] and Thoron I,[94] and colour reactions with Arsenazo II and Thoron II have been described[5].

‡ KU-2 is a monofunctional, strongly acid cation-exchange resin with $-SO_3H$ active groups, prepared by treating a swollen styrene–divinylbenzene copolymer with chlorosulphonic acid, then saponifying the sulphonyl chloride (Ed. of Translation).

Good results have been obtained with Arsenazo III. The possibility of working in strongly acid media (2–11 *N* HCl), *i.e.* under conditions where there is practically no hydrolysis or formation of polynuclear zirconium ions, gives highly stable results and good reproducibility [6,129-135]. Many anions and cations, with the exception of thorium, hafnium, uranium(IV), fluorides, and oxalates, do not interfere. Therefore, in most cases, even in the determination of zirconium in complex materials (ores [130,133], alloys based on aluminium, copper, magnesium, and titanium [131,132], and other materials), other elements need not be removed nor the zirconium concentrated.

The optical absorption of the zirconium–Arsenazo III complex, and hence the sensitivity of the reaction, is greatly dependent on the acidity of the solution; the sensitivity is several times greater in 9 *N* than in 2 *N* HCl. [6]

Hafnium is determined under approximately the same conditions and with the same selectivity as zirconium. A slight difference in the behaviour of the zirconium and hafnium complexes with Arsenazo I [201] when the acidity is varied has enabled methods to be developed for the separate determination of zirconium and hafnium when both are present.

Hafnium can be determined with Arsenazo III under approximately the same conditions and with the same selectivity as zirconium. The variation of sensitivity with acidity is as great as with zirconium; the sensitivity is maximum in 6–11 *N* HCl.

The following method can be used to determine zirconium and hafnium when both are present: the combined solution is subjected to spectrophotometry at two pH values, such that the intensities of colour of the corresponding zirconium and hafnium complexes combine or show the greatest divergence respectively; it is then easy to calculate the contents of zirconium and hafnium from the results obtained. According to Elinson and Mirzoyan, in the case of Arsenazo III 1 *N* HCl and 4 *N* HCl should be used [131]; the procedure is as follows. Metallic hafnium (10–20 mg) is dissolved in hydrofluoric acid, the solution fumed with sulphuric acid, and the residue dissolved in 4 *N* HCl and made up to 500 ml. An aliquot of the solution (> 50 μg hafnium) is heated and cooled, 2 ml 0.05% Arsenazo III solution is added, and the solution made up to 50 ml with 4 *N* HCl and the extinction measured, with the reagent solution as comparison solution. The zirconium content is found from a calibration curve. Thorium, uranium(IV), and titanium interfere. The accuracy of the method is ±20% with 0.5% zirconium and ±10% with 1% zirconium.

Plutonium

The determination of plutonium(IV) with Thoron I in 0.05–0.25 *N* HNO_3 or HCl has been described; uranium(IV), thorium, zirconium, and to a lesser extent cerium(III), iron(III), and uranium(VI) interfere. The accuracy is ±1%. [90] Arsenazo I is used as metal indicator in the complexometric determination of 0.1–0.2 mg of plutonium(IV) per ml with Trilon B in 0.1–0.2 *N* HNO_3; up to 140-fold amounts of UO_2^{2+} can be tolerated [56].

A method for the coprecipitation of plutonium has been developed; coprecipitation is practically complete with the arsenazo–methylene blue system at pH 2–6.3 and a dilution of 1 in 2×10^9 (0.1 μg of Pu in 200 ml) [189].

Neptunium

In 0.3–0.5 *N* HNO_3 Thoron I forms with neptunium(IV) a coloured complex of molar extinction coefficient 14 500; 0.5–5 μg of neptunium can be determined to within ±2–4% with photometry at 540 mμ. [91] Neptunium(IV) can be determined with Arsenazo III in 4–6 *N* HNO_3; the molar extinction coefficient at 665 mμ is 100 000. Uranium, plutonium(IV), thorium, and zirconium are removed by extraction of their complexes with di-(2-ethylhexyl)orthophosphate in carbon tetrachloride [210]. The reactions of protactinium(V) with Arsenazo III [211] and Chlorophosphonazo III [212] have been described.

Americium

Traces of americium can be precipitated from dilute solutions by using coprecipitants containing reagents of the arsenazo group, especially Arsenazo I. [190] Basic dyes such as methylene violet are used to provide the heavy organic cations. The coprecipitation is carried out at pH 5–8, and is practically complete at a dilution of 1 in 10^{12} (0.00002 μg of americium in 200 ml). Each 200 ml portion of solution requires 200–400 mg of the coprecipitant components [190].

Protactinium

A highly selective reaction for protactinium has been described, using Arsenazo III, which gives a colour reaction with protactinium(V) over a wide acidity range: from weakly acid to 10 M or more sulphuric acid. The complex is green, and is stable for more than 24 h. The reaction can also be carried out by the extraction–photometric procedure. The complex of protactinium with Arsenazo III is fully extracted from sulphuric acid solutions (> 4 *N*) by isopentyl alcohol [137]; the molar extinction coefficient of the complex is 2.2×10^4 and Beer's law is obeyed over the concentration range 0.3–3.1 μg of protactinium per ml.

The possibility of extracting the complex of protactinium with Arsenazo III from strongly acid solutions makes the reaction highly selective; in addition to protactinium, the extract contains only traces of thorium, uranium(IV), and zirconium, and the influence of these elements can be completely eliminated by washing the extract with a solution of oxalic acid in 7 *N* H_2SO_4.

The procedure is as follows: 0.2–1 ml of the initial solution, containing 1–10 μg protactinium, is taken in a tube with a ground glass stopper, 0.8 ml 10^{-4} M Arsenazo III is added, and then concentrated sulphuric acid to give a final acid concentration of 7–8 *N*. The solution is extracted with 2 ml isopentyl alcohol saturated with 7 *N* H_2SO_4, the extract is transferred to a centrifuge tube, the extraction is repeated with 1 ml of the alcohol, and the extracts combined and centrifuged for better separation of the phases. The upper organic layer is transferred to a 10 mm cell and the extinction measured, against the reagent, at 660 mμ. If thorium, uranium(IV), and zirconium are present, before centrifuging the extract is washed with 1 ml of ~ 0.5 M oxalic acid in 7 *N* H_2SO_4. [137] The reaction of protactinium with Chlorophosphonazo III has been described [213].

Rare-Earth Elements

Arsenazo I and Thoron I have been proposed for the determination of the rare-earth elements in various materials. Arsenazo I is used at pH 6–8; the sensitivity is 0.2–0.4 μg ml^{-1}.[40-46,202,203] Many elements interfere; a confirmatory reaction is the immediate disappearance of the colour when phosphates are added[42]. Spectrophotometry at two different temperatures has been used for the direct determination of rare-earth elements in the presence of thorium; the optical density at 576 mμ of the thorium complex of Arsenazo I in a solution of pH 3.7 is the same at 20° as at 80°, while the optical density of the corresponding rare-earth complexes is greater at the higher temperature. By using a calibration curve 1.2% or more of rare-earth elements can be determined in thorium products[202].

A method for the determination of individual rare-earth elements with Arsenazo III has been developed[136]; the pH used is 1.5–3.5 and the sensitivity is 0.01–0.05 μg ml^{-1} of the element. Aluminium, iron, magnesium, sodium, potassium, sulphate, chloride, and dihydrogen phosphate do not interfere; many other elements greatly affect the determination. A method for the successive complexometric determination of thorium and total rare-earth elements has been described[204].

The spectrophotometric titration of rare-earth elements with Complexone III using Arsenazo I as indicator has been described[205]; 5–500 μg of rare-earth elements can be determined with an accuracy of ±6%.

Scandium

Scandium is determined with Arsenazo I at pH 6; the molar extinction coefficient is 11 500, and the sensitivity 0.04 μg of scandium per ml[39]. With Arsenazo II at pH 5.0 the sensitivity is 0.1 μg per ml[39]. With Arsenazo III more acid solutions can be used (pH 1.8), where there is no formation of polynuclear scandium cations; as with zirconium, this is of particular importance.

Scandium is determined spectrophotometrically by adding 0.5 ml of 0.1% Arsenazo III solution to ~9 ml 0.08 *N* HCl containing 5–30 μg of scandium, diluting to 10 ml, and measuring the extinction in a 1 cm cell at 680 mμ against water[208]. The use of Arsenazo III as complexometric indicator in the volumetric determination of scandium has been described. The use of an acid medium (pH ≃ 1) gives a rapid reaction and high selectivity.

The reaction of scandium with Chlorophosphonazo III has been described[214,215]. The colour is developed at pH 3–4; the molar extinction coefficient at 680 mμ is 9113.

Beryllium

Beryllium is detected with Arsenazo I at pH 6–6.5 (urotropine and hydrochloric acid); the sensitivity is 0.02 μg of beryllium per ml[49-51]. Many elements can be selectively masked: aluminium with tartrates or Trilon B; iron(III), rare-earth elements, and copper with oxalates; uranium with hydrogen peroxide; and thorium with tungstates[49]. Beryllium is determined with Thoron I at pH 12.4 (borate buffer mixture); methods have been developed for determining beryllium in aluminium alloys[95-97].

Aluminium

Arsenazo I has been used to determine aluminium[8,47,48]; the reaction is carried out at pH 4.3, with sensitivity 0.05 μg ml^{-1}. No interference is caused by iron(II), magnesium, manganese, alkali or alkaline earth metals, or sulphates. The experimental conditions are of great importance. Because aluminium tends to form oxo-ions and polynuclear ions, the pH must be adjusted by careful addition of sodium acetate or urotropine only after the reagent has been added. Certain *o*-hydroxy-diazo-derivatives of chromotropic acid can be used to determine aluminium in a more acid medium. Thermospectrophotometry can be used to determine aluminium in the presence of indium, gallium, and other elements[202].

Indium

The determination of indium with Arsenazo I has been described, at pH 4.8; 0.8–50 μg of indium per ml can be determined. Alkali or alkaline earth metals, ammonium, cobalt, nickel, zinc, cadmium, and palladium do not interfere[55].

Vanadium

Vanadium gives a typical colour reaction with Arsenazo I[17]; it is determined at pH 6. Complex-forming agents used for masking interfere. A colour reaction of vanadium(IV) with Arsenazo II has been described[113].

Niobium

Niobium can be detected with Arsenazo I[33,42,53] at pH 2, sensitivity 0.5–1 μg ml^{-1}. There is little colour contrast in the reaction.

Tantalum

A colour reaction of tantalum with Arsenazo I has been described[42,54]. A method has been developed for determining 0.5–30% of tantalum in titanium alloys. The sensitivity is 0.3 μg of tantalum per ml, in 1–2 *N* HCl.

Titanium

The determination of titanium in titanium and chromium borides with Arsenazo I at pH 2.5–3 has been described; the sensitivity is 0.01–0.25 mg of titanium in 100 ml[52]. The use of dichlorochromotropic acid offers better prospects[216,217].

Lithium

Thoron, nitrothoron, nitroarsenazo, and various other derivatives have been suggested for the determination of lithium[98]. The reaction is carried out in 2% potassium hydroxide solution, and the detectable minimum is 1 μg of lithium; calcium and magnesium do not interfere[99,101]. The determination of lithium in aluminium and copper alloys has been described. The best method is spectrophotometry of 0.1–0.7 mg of lithium in a volume of 50 ml at pH 14 in the presence of 0.7 ml of 0.1% thoron solution[100].

Barium and Strontium

Certain analogues of arsenazo — *e.g.* reagents (III) and (IV) — have been suggested for the determination of barium and strontium[142]. The determination is carried out at pH 1–2; the sensitivity is 0.04–0.1 μg of element per ml.

Bismuth

Methods have been described for the photometric[103] and complexometric determination of bismuth at pH 1.3 using Thoron I as metal indicator[104]. At pH 1.5–4.5 Arsenazo III gives a clear colour reaction[6].

Sulphates

Several methods have been described for the volumetric determination of sulphates by titration with barium chloride or barium perchlorate solution; Thoron I[108,109], reagent (V)[143], and reagents (VI) and (VII)[142] have been suggested as indicators for barium.

Fluorine

A number of methods are known for the volumetric determination of fluorine by titration with thorium salts; Thoron I[105,107] and Arsenazo I[63,65] have been suggested as indicators for thorium(IV) cation. The method with Thoron I has been most widely used. Several methods are based on the masking of fluorides with elements other than thorium, *e.g.* aluminium in the presence of Arsenazo I[208,209].

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Reagents of the arsenazo group occupy a foremost place in inorganic photometric analysis, by virtue of the scale of their use, their universality, and the efficiency of their analytical action. A feature of these reagents is their high sensitivity (to 0.01 μg of element per ml) and the high stability of the complexes formed; because of the latter, strongly acid media can be used for the determinations. The determination of elements producing highly charged cations (palladium, thorium, zirconium, hafnium, plutonium, neptunium, and certain others) with Arsenazo III is highly selective. In many cases these elements can be determined without removal of other elements, and several methods have accordingly been used for rapid process control determinations. In addition to photometry, the reagents are widely used as coprecipitant components in the concentration of elements from dilute solutions, as metal indicators in volumetric complexometric determinations, and in the extraction–photometric determination of elements.

The ready synthesis of the basic reagents (Arsenazo I, Thoron I, and Arsenazo III) and their derivatives and the availability of the necessary starting materials favours an even wider use of the reagents of the arsenazo group in inorganic analysis. The wide choice of readily-prepared compounds ensures that in each particular case the determination of the elements in the given combinations can be carried out with the most suitable reagent in respect of selectivity, ease of extraction, completeness of precipitation, or required stability of the complex.

1. V.I.Kuznetsov, Dokl.Akad.Nauk SSSR, 31, 895 (1941).
2. V.I.Kuznetsov, Zhur.Obshch.Khim., 14, 914 (1944).
3. M.B.Johnston, A.H.Barnard, Jnr., and W.C.Broad, Rev. Univ.Ind., Santander, Colombia, 2, 137 (1960).
4. V.I.Kuznetsov, S.B.Savvin and V.A.Mikhailov, Uspekhi Khim., 29, 525 (1960) [Russ.Chem.Rev., 243 (1960)].
5. V.I.Kuznetsov, Zhur.Anal.Khim., 14, 7 (1959).
6. S.B.Savvin, Talanta, 8, 673 (1961).
7. F. Feigl, "Spot Tests" (Translated into Russian), Goskhimtekhizdat, Moscow-Leningrad, 1933.
8. V.I.Kuznetsov, Dokl.Akad.Nauk SSSR, 50, 227 (1945).
9. V.I.Kuznetsov, Zhur.Anal.Khim., 13, 220 (1958).
10. V.I.Kuznetsov and I.V.Nikol'skaya, Zavod.Lab., 26, 266 (1960).
11. H.P.Holcomb and J.H.Yoe, Analyt.Chem., 32, 612 (1960).
12. J.S.Fritz and M.Johnson-Richard, Analyt.Chim.Acta, 20, 164 (1959).
13. S.Shibata and T.Matsumae, Bull.Chem.Soc.Japan, 31, 377 (1958).
14. C.E.Bricker and P.B.Sweetser, Analyt.Chem., 25, 764 (1953).
15. S.Ahrland and R.Larsson, Acta Chem.Scand., 8, 137 (1954).
16. Emi, Toki, Furunawa, J.Chem.Soc.Japan, 79, 681 (1958).
17. V.I.Kusnetsov, Dokl.Akad.Nauk SSSR, 52, 39 (1946).
18. A.F.Kuteinikov and G.A.Lanskoi, Metodicheskie Materialy Vses.Nauch.-Issled.Inst.Metrologii i Standartizatsii, Moscow, Byul.No.5, 169 (1957).
19. M.V.Sobolev and I.A.Pudovkina, "Mineraly Urana.Spravochnik" (Handbook of Uranium Minerals), Gosgeoltekhizdat, Moscow, 1957, p.16.
20. J.S.Fritz and E.C.Bradford, Analyt.Chem., 30, 1021 (1958).
21. V.I.Kuznetsov and I.V.Nikol'skaya, Zhur.Anal.Khim., 15 299 (1960).
22. F.V.Zaikovskii and L.I.Gerkhard, Zhur.Anal.Khim., 13, 274 (1958).
23. F.V.Zaikovskii and L.I.Gerkhard, Zhur.Anal.Khim., 13, 513 (1958).
24. A.F.Kuteinikov and G.A.Lanskoi, Byul.Nauch.-Tekh.Inform. Min.Geol. i Okhrany Nedr SSSR, No.4 (9), 76 (1957).
25. A.E.Klygin and V.N.Pavlova, Zhur.Neorg.Khim., 5, 1516 (1960) [Russ.J.Inorg.Chem., 734 (1960)].
26. E.S.Przheval'skii, A.P.Golovina, and A.F.Kuteinikov, Vestn.Moskov.Gos.Univ., Ser.Matem., Mekhan., Astronom., Fiz., Khim., No.6, 99 (1958).
27. L.I.Gerkhard, Zhur.Anal.Khim., 14, 434 (1959).
28. F.V.Zaikovskii, Zhur.Anal.Khim., 14, 440 (1959).
29. M.Ischibashi and S.Higashi, Japan Analyst, 4, 14 (1955).
30. M.Ischibashi and S.Higashi, Japan Analyst, 5, 135 (1956).
31. Takahashi Takeo and Miyake Shingo, Talanta, 3, 155 (1959).
32. R.Emi and T.Hayami, J.Chem.Soc.Japan, 76, 1291 (1955).
33. V.I.Kuznetsov, L.M.Budanova, and T.V.Matrosova, Zavod. Lab., 22, 406 (1950).
34. N.S.Poluektov and L.I.Kononenko, "Analiz Mineral'nogo Syr'ya" (Analysis of Mineral Raw Materials), Gosgeolizdat, 1956, p.775.
35. L.I.Kononenko and N.S.Poluektov, Trudy Kom.Anal.Khim. Akad.Nauk.SSSR, 12, 132 (1960).
36. L.I.Kononenko and N.S.Poluektov, Zavod.Lab., 25, 1050 (1959).
37. V.F.Luk'yanov and E.M.Knyazeva, Zhur.Anal.Khim., 15, 69 (1960).
38. V.G.Goryushina and V.M.Vladimirova, Zavod.Lab., 22, 1177 (1956).
39. V.I.Titov and I.E.Pokrovskaya, Metodicheskie Materialy Vses.Nauch.-Issled.Inst.Metrologii i Standartizatsii,, Moscow, Byul.No.8 (184), 15 (1958).

40. S. Shibata, F. Takenchi, and T. Matsumae, Analyt. Chim. Acta, 21, 177 (1959).
41. S. Shibata and T. Matsumae, Rep. Govt. Ind. Res. Inst., Nagoya, 8, 408 (1959); Ref. Zhur. Khim., 30 464 (1960).
42. V. I. Kuznetsov, Zhur. Anal. Khim., 7, 226 (1952).
43. A. F. Kuteinikov and G. A. Lanskoi, Metodicheskie Materialy Vses. Nauch.-Issled. Inst. Metrologii i Standartizatsii, Moscow, Byul. No. 5, (169) (1957).
44. A. F. Kuteinikov, Zavod. Lab., 24, 1050 (1958).
45. J. S. Fritz, M. J. Richard, and W. J. Lane, Analyt. Chem., 30, 1776 (1958).
46. C. V. Banks, J. A. Thompson, and J. O'Laughlin, Analyt. Chem., 30, 1792 (1958).
47. V. I. Kuznetsov and R. B. Golubtsova, Zavod. Lab., 21, 1421 (1955).
48. V. I. Kuznetsov, G. G. Karanovich and D. A. Drapkina, Zavod. Lab., 26, 787 (1950).
49. V. I. Kuznetsov, Zhur. Anal. Khim., 10, 276 (1955).
50. A. P. Adamovich and B. V. Yuuis, Ukrain. Khim. Zhur., 22, 523 (1956).
51. S. Shibata, F. Takeuchi, and T. Matsumae, Bull. Chem. Soc. Japan, 31, 888 (1958); Ref. Zhur. Khim., 56 836 (1959).
52. E. I. Nikitina, Zhur. Anal. Khim., 14, 431 (1959).
53. E. I. Nikitina, Zavod. Lab., 27, 663 (1961).
54. E. I. Nikitina, Zhur. Anal. Khim., 13, 72 (1958).
55. V. I. Kuznetsov and I. S. Levin, Izv. Sibir. Otd. Akad. Nauk SSSR, 131 (1958).
56. P. I. Palei and Chang Wên-ch'ing, Zhur. Anal. Khim., 15, 598 (1960).
57. Yu. A. Chernikhov, R. S. Tramm, and N. S. Pevzner, Zavod. Lab., 26, 921 (1960).
58. Yu. A. Chernikhov, V. I. Luk'yanov, and A. B. Kozlova, Zhur. Anal. Khim., 14, 567 (1959).
59. R. S. Volodarskaya, Zavod. Lab., 26, 925 (1960).
60. V. I. Kuznetsov and L. A. Okhanova, Zavod. Lab., 25, 1162 (1959).
61. A. F. Kuteinikov, Metodicheski Materialy Vses. Nauch.-Issled. Inst. Metrologii i Standatizatsii, Moscow, Byul. No. 8, 1 (1959).
62. J. S. Fritz, R. T. Oliver, and D. L. Pietrzyk, Analyt. Chem., 30, 1111 (1958).
63. A. F. Kuteinikov, Zhur. Anal. Khim., 16, 327 (1961).
64. E. Koichi, H. Tadashi, and T. Hiroshi, J. Chem. Soc. Japan, 80, 731 (1959).
65. E. Koichi and H. Tadashi, J. Chem. Soc. Japan, 80, 735 (1959).
66. P. F. Thomason, M. A. Perry, and W. M. Byerly, Analyt. Chem., 21, 1239 (1949).
67. J. C. Ingles, Canad. Chem. Processing, 35, 397 (1951).
68. R. J. Geest, Canad. Dept. Mines Tech. Surveys, p. 24 (1953).
69. C. V. Banks, D. W. Klingman, and C. H. Byrd, Analyt. Chem., 25, 992 (1953).
70. D. W. Margerum, C. H. Byrd, S. A. Reed, and C. V. Banks, Analyt. Chem., 25, 1219 (1953).
71. F. S. Grimaldi and M. H. Fletcher, Analyt. Chem., 28, 812 (1956).
72. C. V. Banks and C. H. Byrd, Analyt. Chem., 25, 416 (1953).
73. J. Clinch, Analyt. Chim. Acta, 14, 162 (1956).
74. D. A. Everest and J. V. Martin, Analyst, 84, 312 (1959).
75. M. H. Fletcher, F. S. Grimaldi and L. B. Jenkins, Analyt. Chem., 29, 963 (1957).
76. H. Levine and F. S. Grimaldi, Geochim. Cosmochin. Acta, 14, 93 (1958).
77. L. Kosta, Reports "J. Stefan" Inst., 3, 163 (1956).
78. J. Korkisch and P. Antal, Z. anal. chem., 173, 126 (1960).
79. E. Cerrai and F. Gazzarrini, Energia nucl., 7, 358 (1960).
80. D. A. Everest and J. V. Martin, Analyst, 82, 807 (1957).
81. Kwank Shean-wei, Acta Chim. Sinica, 26, 103 (1960).
82. M. G. Mellon and D. F. Bolts, Analyt. Chem., 28, 559 (1956).
83. M. Ishibashi and S. Higashi, Japan Analyst, 3, 213 (1954).
84. A. Mayer and G. Bradshaw, Analyst, 77, 154 (1952).
85. G. W. C. Milner and J. H. Nunn, Analyt. Chim. Acta, 17, 494 (1957).
86. A. E. Taylor and R. T. Dillon, Analyt. Chem., 24, 1624 (1952).
87. O. A. Nietzel, B. W. Wessling, and M. A. DeSasa, Analyt. Chem., 30, 1182 (1958).
88. A. L. Arnfelt and J. Edmundsson, Talanta, 8, 473 (1961).
89. I. E. Starik, D. E. Starik, and K. F. Lazarev, Zhur. Anal. Khim., 14, 306 (1959).
90. T. V. Healy and P. E. Brown, Atomic Energy Res. Estab. Rep., N C/R 1287 (1958); Ref. Zhur. Khim., 38 306 (1959).
91. R. D. Britt, Analyt. Chem., 33, 969 (1961).
92. J. K. Foreman, C. J. Riley, and T. D. Smith, Analyst, 82, 89 (1957).
93. H. M. Ockenden and J. K. Foreman, Analyst, 82, 592 (1957).
94. A. D. Horton, Analyt. Chem., 25, 1331 (1953).
95. L. P. Adamovich and R. S. Didenko, Uch. Zap. Khar'kov. Univ., 54; Trudy Khim. Fak. i Nauch.-Issled. Inst. Khim. Khar'kov. Gos. Univ., 12, 195 (1954).
96. L. P. Adamovich and A. P. Mirnaya, "Sovremennye Metody Analiza v Metallurgii" (Modern Methods of Analysis in Metallurgy), Moscow, Metallurgizdat, 1955, p. 172.
97. V. I. Kuznetsov, Zhur. Anal. Khim., 3, 295 (1948).
98. L. P. Adamovich and T. T. Alekseeva Uch. Zap. Khar'kov. Univ., 54; Trudy Khim. Fak. i Nauch.-Issled. Inst. Khim., Khar'kov. Gos. Univ., 12, 209 (1954).
99. T. J. Hayes, U. K. Atomic Energy Authority Prod. Grod., P. G. Rep., 41 (S), 10 (1961).
100. P. F. Thomason, Analyt. Chem., 28, 1527 (1956).
101. F. V. Zaikovskii, Zhur. Anal. Khim., 14, 440 (1959).
102. P. N. Palei and Hsü Li-yüan, Zhur. Anal. Khim., 16, 51 (1961).
103. K. N. Bogdasarov, P. N. Kovalenko, and A. A. Rabtsun, "Fiziko-Khimicheskie Metody Analiza i Kontrolya Proizvodstva" (Physicochemical Methods of Analysis and Process Control), Rostov-on-Don, Rostov Univ., 1961, 115.
104. G. Rady and L. Erdey, Z. analyt. Chem., 152, 253 (1956).
105. A. D. Horton, Analyt. Chem., 25, 1331 (1953).
106. A. D. Horton, P. F. Thomason, and F. J. Miller, Z. analyt. Chem., 138, 202 (1953).
107. F. S. Grimaldi, B. Ingram, and F. Cuttita, Analyt. Chem., 27, 918 (1955).
108. J. S. Fritz and S. S. Yamamura, Analyt. Chem., 27, 1461 (1955).
109. J. S. Fritz and M. O. Freeland, Analyt. Chem., 26, 1953 (1954).
110. V. I. Kuznetsov and S. B. Savvin, Zhur. Prikl. Khim., 32, 2329 (1959).
111. V. I. Kuznetsov and S. B. Savvin, Zhur. Anal. Khim., 15, 175 (1960).
112. S. B. Savvin, M. P. Volynets, Yu. A. Balashov, and V. V. Bagreev, Zhur. Anal. Khim., 15, 446 (1960).
113. V. I. Kuznetsov and S. B. Savvin, Radiokhimiya, 1, 589 (1959).
114. V. I. Kuznetsov and S. B. Savvin, Radiokhimiya, 1, 583 (1959).
115. S. B. Savvin, Dokl. Akad. Nauk SSSR, 127, 1231 (1959).
116. V. I. Kuznetsov and S. B. Savvin, Mitteilungsblatt Chem. Gesellschaft in DDR, Anal. Chem. Sond., 161 (1960).
117. V. F. Luk'yanov, S. B. Savvin, and I. V. Nikol'skaya, Zavod. Lab., 25, 1155 (1959).
118. S. B. Savvin and V. V. Bagreev, Zavod. Lab., 26, 412 (1960).
119. V. I. Kuznetsov and S. B. Savvin, Radiokhimiya, 3, 79 (1961).
120. V. I. Kuznetsov, T. G. Akimova, and O. P. Eliseeva, Radiokhimiya, 4, 188 (1962).
121. V. M. Vladimirova and N. K. Davidovich, Zavod. Lab., 26, 1210 (1960).
122. V. F. Luk'yanov, I. V. Nikol'skaya, and E. S. Kozlova,

Radiokhimiya, 3, 239 (1961).
123. V.M.Vladimirova and N.K.Davidovich, Nauchnye Trudy Gos.Nauch.-Issled.Inst.Redkikh Metalov, Vol.3, Gos. Nauch.-Tekh.Izd.Lit.po Chernoi i Tsvetnoi Metallurgii, Moscow, 1961, p.24.
124. L.I.Il'ina, in "Metody Opredeleniya i Analiza Redkikh Elementov" (Methods for the Determination and Analysis of Rare Elements), Izd.Akad.Nauk SSSR, Moscow, 1961, p.566.
125. M.P.Volynets, *ibid.*, p.392.
126. V.I.Kuznetsov and S.B.Savvin, Radiokhimiya, 2, 682 (1960).
127. V.F.Luk'yanov, S.B.Savvin, and I.V.Nikol'skaya, Zhur. Anal.Khim., 15, 311 (1960).
128. P.N.Palei, A.A.Nemodruk, and A.V.Davydov, Radiokhimiya, 3, 181 (1961).
129. V.G.Goryushina, E.V.Romanova, and T.A.Archakova, Zavod.Lab., 27, 795 (1961).
130. V.G.Goryushina and E.V.Romanova, Zavod.Lab., 26, 415 (1960).
131. S.V.Elinson and N.A.Mirzoyan, Zavod.Lab., 27, 798 (1961).
132. V.G.Goryushina and E.V.Romanova, Nauchnye Trudy Gos. Nauch.-Issled.Inst.Redkikh Metalov, 3, 5 (1961), Gos. Nauch.-Tekh.Izd.Lit.po Chernoi i Tsvetnoi Metallurgii, Moscow.
133. V.G.Goryushina and E.V.Romanova, in "Metody Opredeleniya i Analiza Redkikh Elementov" (Methods for the Determination and Analysis of Rare Elements), Izd.Akad. Nauk SSSR, Moscow, 1961, p.329.
134. A.I.Ponomarev, "Metody Khimicheskogo Analiza Silikatnykh i Karbonatnykh Gornykh Porod" (Methods for the Chemical Analysis of Silicate and Carbonate Rocks), Izd.Akad.Nauk SSSR, Moscow, 1961.
135. S.V.Elinson and K.I.Petrov, "Tsirkonii: Khimicheskie i Fizicheski Metody Analiza" (Zirconium: Chemical and Physical Methods of Analysis), Atomizdat, Moscow, 1960.
136. S.B.Savvin and A.A.Muk, Bull.Inst.Nuclear Sci. "Boris Kidrich", 12, No.259, 97 (1961).
137. E.S.Pal'shin, B.F.Myasoedov, and P.N.Palei, Zhur.Anal. Khim., 17, 471 (1962).
138. V.I.Kuznetsov and S.B.Savvin, Dokl.Akad.Nauk SSSR, 140, 125 (1961).
139. S.B.Savvin Zhur.Anal.Khim., 17, 785 (1962).
140. S.K.Datta, Naturwiss., 43, 250 (1956).
141. S.K.Datta, Z.analyt.Chem., 149, 328 (1959).
142. S.B.Savvin, Yu.M.Dedkov, and V.P.Makarova, Zhur. Anal.Khim., 17, 43 (1962).
143. K.F.Novikova, N.I.Basargin, and M.F.Tsiganova, Zhur. Anal.Khim., 16, 348 (1961).
144. A.A.Nemodruk, Yu.P.Novikov, A.M.Lukin, and I.D.Kalinina, Zhur.Anal.Khim., 16, 292 (1961).
145. A.A.Nemodruk, Yu.P.Novikov, A.M.Lukin, and I.D.Kalinina, Zhur.Anal.Khim., 16, 180 (1961).
146. A.M.Lukin, L.S.Chernaya, G.S.Petrova, and A.I.Sosnina, Zavod.Lab., 28, 398 (1962).
147. V.I.Kuznetsov, Dokl.Akad.Nauk SSSR, 33, 45 (1941).
148. W.A.Jacobs, M.Heidelberger, and I.P.Rolf, J.Amer. Chem.Soc., 40, 1583 (1918).
149. S.Shibata and T.Matsumae, Rep.Govt.Indust.Res.Inst., Nagaya, 8, 725 (1959).
150. S.K.Datta, Z.analyt.Chem., 149, 270 (1956).
151. I.P.Alimarin and O.A.Medvedeva, Zavod.Lab., 11, 254 (1945).
152. A.C.Rice, H.C.Fogg, and C.James, J.Amer.Chem.Soc., 48, 895 (1926).
153. O.Hackl, Z.analyt.Chem., 122, I (1941).
154. I.P.Alimarin and B.I.Frid, Mikrochem., 37, 17 (1937).
155. I.P.Alimarin and B.I.Frid, Zavod.Lab., 6, 823 (1937).
156. V.I.Kuznetsov, Zhur.Prikl.Khim., 13, 1512 (1940).
157. R.H.Bullard, J.Chem.Educ., 14, 312 (1937).
158. L.E.Kaufman, Zhur.Prikl,Khim., 10, 1648 (1937).
159. V.I.Kuznetsov, Zavod.Lab., 11, 263 (1945).
160. C.T.Simpson and G.C.Chandlee, Ind.Eng.Chem., Analyt., 10, 642 (1938).
161. C.T.Simpson and G.C.Chandlee, Ind.Eng.Chem., Analyt., 10, 642 (1938).
162. I.M.Korenman, Z.analyt.Chem., 90, 115 (1932).
163. R.Chandelle, Bull.Soc.chim.belges, 48, 12 (1939); 50, 185 (1941).
164. F.Arnold and G.C.Chandlee, J.Amer.Chem.Soc., 57, 8 (1935).
165. H.Geist and G.C.Chandlee, Ind.Eng.Chem., Analyt., 9, 169 (1937).
166. L.M.Kul'berg, "Organicheskie Reaktivy v Analiticheskoi Khimii" (Organic Reagents in Analytical Chemistry), Goskhimizdat, 1950.
167. M.A.Chepelevskii, Trudy Vses.Konf.po Anal.Khim., 1, 22 (1939).
168. V.I.Kuznetsov, Zavod.Lab., 11, 263 (1945).
169. F.Feigl, P.Krumholz, and E.Rajmann, Mikrochem., 9, 395 (1931).
170. F.S.Grimaldi and C.E.White, Analyt.Chem., 25, 1886 (1953).
171. V.A.Nazarenko and N.S.Poluektov, "Polumikrokhimicheskii Analiz Miniralov i Rud" (Semimicro Chemical Analysis of Minerals and Ores), Goskhimizdat, 1950.
172. V.A.Nazarenko, Zhur.Prikl.Khim., 10, 1096 (1937).
173. V.I.Kuznetsov, Zhur.Anal.Khim., 2, 67 (1947).
174. V.I.Kuznetsov and S.B.Savvin, Russ.P. 133 257 (10.11.1960).
175. V.I.Kuznetsov, Trudy po Khim.i Khim.Tekhnol., No.3, 559 (1960).
176. L.P.Adamovich and V.M.Rutman, Uch.Zap.Khar'kov. Univ., 54; Trudy Khim.Fak.i Nauch.-Issled.Inst.Khim., Khar'kov.Gos.Univ., 12, 203 (1954).
177. I.M.Kogan, "Khimiya Krasitelei" (Chemistry of Dyes), Goskhimizdat, Moscow, 1956.
178. A.N.Terenin, "Fotokhimiya Krasitelei i Rodstvennykh Organicheskikh Soedinenii" (Photochemistry of Dyes and Related Organic Compounds), Izd.Akad.Nauk SSSR, Moscow, 1947.
179. V.I.Kuznetsov, Zhur.Obshch.Khim., 20, 807, 816 (1950).
180. V.I.Kuznetsov, Uspekhi Khim., 21, 175 (1952).
181. V.I.Kuznetsov, Trudy Kom.Anal.Khim.Akad.Nauk SSSR, 7 (10), 174 (1956).
182. V.A.Mikhailov, Zhur.Anal.Khim., 16, 141 (1961).
183. A.F.Kuteinikov, Metodicheskie Materialy Vses.Nauch.-Issled.Inst.Metrologii i Standartizatsii, Moscow, No.7, 19 (1956).
184. A.E.Klygin and V.P.Pavlova, Zhur.Anal.Khim., 14, 167 (1959).
185. A.R.Palmer, Analyt.Chim.Acta, 19, 458 (1958).
186. V.I.Levchenko and N.A.Makarova, Kirgiz.Filial Akad. Nauk SSSR, Trudy Khim.Inst., No.1, 19 (1946).
187. V.I.Kuznetsov, Trudy Kom.Anal.Khim.Akad.Nauk SSSR, 8 (11), 52 (1958).
188. V.I.Kuznetsov and T.T.Akimova, Atomnaya Energiya, 8, 148 (1960).
189. V.I.Kuznetsov and T.T.Akimova, Radiokhimiya, 2, 357 (1960).
190. V.I.Kuznetsov and T.T.Akimova, Radiokhimiya, 3, 737 (1962).
191. V.I.Kuznetsov and G.V.Myasoedova, Trudy Kom.Anal. Khim.Akad.Nauk SSSR, 9 (12), 76 (1958).
192. V.I.Kuznetsov, Zhur.Anal.Khim., 9, 199 (1954).
193. Yu.A.Zolotov and I.P.Alimarin, Dokl.Akad.Nauk SSSR, 136, 603 (1961).

194. V.I.Kuznetsov, Zhur.Neorg.Khim., 6, 1042 (1961) [Russ. J.Inorg.Chem., 532 (1961)].
195. J.C.Dalton and S.J.Thomson, Geochim.Cosmochin.Acta, 5, 74 (1954).
196. F.V.Zaikovskii and V.S.Bashmakova, in "Metody Opredeleniya i Analiza Redkikh Elementov" (Methods for the Determination and Analysis of Rare Elements), Izd.Akad. Nauk SSSR, Moscow, 1961, p.156.
197. V.I.Kuznetsov and V.Blechta, Coll.Czech.Chem.Comm., 26, 1092 (1961).
198. A.E.Klygin, N.A.Nikol'skaya, D.M.Zavransova, and N.S. Kolyada, Zhur.Anal.Khim., 16, 110 (1961).
199. V.F.Luk'yanov, L.M.Moiseeva, and N.M.Kusnetsov, Zhur. Anal.Khim., 16, 448 (1961).
200. V.I.Kuznetsov and T.N.Kukisheva, Zavod.Lab., 26, 1344 (1960).
201. L.I.Kononenko, R.S.Lauer, and P.S.Poluektov, Ukrain. Khim.Zhur., 25, 633 (1959).
202. V.I.Kuznetsov and T.V.Petrova, Zhur.Anal.Khim., 14, 404 (1959).
203. E.M.Gel'man, in "Metody Opredeleniya i Analiza Redkikh Elementov" (Methods for the Determination and Analysis of Rare Elements), Izd.Akad.Nauk SSSR, 1961, p.154.
204. Yu.A.Chernikhov, R.S.Tramm, and K.S.Pevzner, Zavod. Lab., 26, 921 (1960).
205. V.M.Peshkova, M.I.Gromova, I.P.Efimov, and A.V.Isachenko, Vestnik Moskov.Gos.Univ., Khimiya, No.4, 59 (1961).
206. V.I.Kuznetsov, Ni Chê-ming, G.B.Myasoedova, and L.A. Okhanova, Acta Chim.Sinica, 27, 74 (1961).
207. E.N.Nikitina, in "Metody Opredeleniya i Analiza Redkikh Elementov" (Methods for the Determination and Analysis of Rare Elements), Izd.Akad.Nauk SSSR, Moscow, 1961, p.523.
208. V.M.Brodskaya, A.F.Kuteinikov, and G.A.Lanskoi, Byull. Nauch.-Tekh.Inform.Min.Geol.i Okhrany Nedr SSSR, No.1 (29), 104 (1961).
209. A.F.Kuteinikov, Zhur.Anal.Khim., 16, 327 (1961).
210. E.G.Chudinov and G.N.Yakovlev, Radiokhimiya, 4, 506 (1962).
211. E.G.Chudiniv and G.N.Yakovlev, Radiokhimiya, 4, 505 (1962).
212. E.G.Chudinov and G.N.Yakovlev, Radiokhimiya, 4, 601 (1962).
213. E.G.Chudinov and G.N.Yakovlev, Radiokhimiya, 4, 605 (1962).
214. I.P.Alimarin and V.I.Fadeeva, Acta Chimica, 32, 171 (1962).
215. V.I.Fadeeva and I.P.Alimarin, Zhur.Anal.Khim., 17, 1020 (1962).
216. V.I.Kuznetsov and N.N.Basargin, Zhur.Anal.Khim., 16, 573 (1961).
217. N.N.Basargin, A.N.Tkachenko, L.R.Stupa, and L.N.Borodaevskaya, Zav.Lab., 28, 1311 (1962).

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HYDRATION AND SOLVATION OF ACIDS AND SALTS UNDERGOING EXTRACTION

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Recent experimental investigations of the mechanism of the extraction of iron from chloride solutions and also of some simple inorganic acids by oxygen-containing solvents[1-5,70-72] have led to conclusions extending insignificance beyond these systems. The results obtained, combined with existing data, gave an orderly picture of the mechanism of the extraction of simple and complex acids (partly in relation to the hydration and solvation of the compounds extracted). It has also been found that in several cases the extraction of salts, too, has much in common with that of acids. An attempt is made below to present this picture as a whole.

1. SOME EXPERIMENTAL DATA

It might be supposed that tervalent iron is extracted from hydrochloric-acid solutions by oxygen-containing solvents (ethers, esters, ketones, alcohols) in the form of compounds of general formula $HFeCl_4.nH_2O.mS$, where S represents a molecule of the organic solvent. Examination of the infra-red spectra of the iron compounds extracted from hydrochloric-acid solutions by esters (ethyl, butyl, and isopentyl acetates) has enabled several conclusions to be drawn concerning the character of the hydration and solvation of these compounds[1,3-5].

The extracts containing iron showed shifts in the band due to stretching vibrations of the C=O group of the esters by 30–40 cm^{-1} compared with the spectra of the pure solvents and those of solutions of water in these solvents, where hydrogen bonds may be formed between the water and solvent molecules. These shifts indicate combination of the solvent, *i.e.* that it forms part of the extracted compounds.

The changes in the spectra of extracts containing iron do not differ in character from those observed in extracts containing hydrochloric acid alone, and also in solutions of hydrochloric acid in organic solvents. The spectra of extracts of iron show no changes other than the above shift in the C=O band and the associated shift in the C–O band. The spectra of solutions of $KFeCl_4$ in anhydrous organic solvents show no displacements of the C=O band. These