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1961

SovietRxiv

Abstract

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Chemistry

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Extraction of Colored Complex Compounds of Reagents of the Arsenazo-Thoron Group

(Presented by Academician A. P. Vinogradov on 6 February 1961)

The organic reagents proposed earlier—arsenazo and thoron (^{1})—have become widely used for photometric determinations of uranium, thorium, plutonium, aluminum, rare-earth elements, and a number of other elements. The reagents arsenazo II, thoron II (^{2}), and especially arsenazo III (^{3}), described later, also proved valuable. All these reagents are readily soluble in water and practically insoluble in organic solvents. Therefore, up to the present time photometric determinations have been carried out only in aqueous solutions, while extraction-photometric methods, known for a number of other reagents, were impossible in the case of reagents of the arsenazo-thoron group.

In the present article we describe techniques that make it possible to carry out colored reactions of this type in the extraction variant. Let us consider the schematic structural formula of a complex, for example Th with arsenazo:

[structural formula of the Th-arsenazo complex shown]

The complex is an ion already because of the presence of two sulfo groups, which impart a negative charge. At the same time, however, another part of the molecule has a positive charge, since the thorium atom entering into the complex has retained its cationic charge. In addition, owing to the presence in the molecule of an intramolecular ionic state (^{4}), responsible for the color of the complex, partial charges amounting to fractions of a whole unit of charge occur at various sites in the complex molecule. These charges are distributed over many atoms of the complex molecule and are sites of solvation. The strongly pronounced solvation of the complexes, together with the presence of negative charges of the sulfo groups and, for a number of elements, the possible positive charge of the metal entering into the complex, is the reason preventing their extraction.

Compensation of the negative charges on the sulfo groups can be achieved by introducing salts of suitable heavy hydrophobic organic cations. According to the literature, this can be achieved by introducing tributylamine, which forms tributylammonium cations (^{5,6}), or other suitable cations, for example tetraphenylarsonium cations $((C_6H_5)_4As)^+$ (^{7}). At the same time, it is also necessary to ensure compensation of the positive charge of the element ion by introducing an anion now suitable for extraction. The latter should preferably also be sufficiently hydrophobic and heavy. But simultaneous introduction into the solution of a heavy hydrophobic anion and cation leads to extraction of the salt formed by this cation and anion, whereas the complex of interest to us remains in the aqueous phase. Therefore the nature and concentration of the introduced cation, as well as of the anion, must be properly selected.

When salts of diphenylguanidine are used as the supplier of cations, chlorides, sulfates, or nitrates sometimes prove to be suitable anions. In some cases, however, it is necessary to introduce more hydrophobic anions: rhodanides, perchlorates, chloroacetates, trichloroacetates ([8]).

Diphenylguanidine is especially convenient as a supplier of cations because of its availability and the ease with which it can be obtained in a completely colorless form.

state, complete stability, even in solutions, in air, good solubility of its salts in organic solvents, and excellent extraction properties. Diphenylguanidine is a fairly strong base and is suitable for work in systems from 6–7 N HCl to pH 8–9. In individual cases pyramidon, antipyrine and its analogs of the diantipyrylphenylmethane type, colorless aromatic amines, β-naphthylamine, and many others may be suitable. When working in sufficiently acidic solutions, oxonium cations formed by trialkylphosphine oxides, cyclohexanone, tributyl phosphate, β-naphthol, and other compounds are also suitable.

The hydrophilicity of the complex, caused by the presence of partial charges distributed at different sites of the molecule, can be considerably reduced if extractants are used whose molecules are capable of replacing water molecules in the solvates. There are certain indications of the possibility of such a process in the literature ([9], [10]). As extractants, the use of butyl and amyl alcohol proved most convenient. It is also possible to use hexyl and benzyl alcohol, cyclohexanone, a solution of C_2H_5OH in chloroform, and certain other solvents.

Taking all the considerations indicated into account, with some empirical selection of the most suitable systems and working conditions, made it possible to carry out extraction of the group of complex compounds under consideration and thereby to perform extraction-photometric determinations of many elements. These methods of determination, being more selective, also possess higher sensitivity than the corresponding photometric methods, since in extraction of complexes a reduction in volume is readily achieved.

Extraction proceeds more readily, i.e., at a lower concentration of diphenylguanidine salts or in the presence of less suitable anions, if the reagents contain not two but only one sulfo group, or contain $-Br$, $-Cl$, $-NO_2$, and other groups that promote an increase in the hydrophobicity of the reagent molecule.

In Table 1 we give an incomplete list of color reactions that may be used for extraction-photometric determinations. The practical execution will be explained with several examples.

Extraction of the complex of hexavalent uranium with the reagent arsenazo I. To a weakly hydrochloric-acid solution of a uranyl salt are added a solution of arsenazo, then a 30% solution of urotropine until the color is fully developed, and then, for each 5 ml of the resulting solution, 0.5 ml of a neutral 20% aqueous solution of diphenylguanidine chloride. Extraction is carried out with butyl or amyl alcohol. Arsenazo gives a pink extract. In the presence of uranium, the extract has a violet color of various shades, up to pure blue when uranium is in excess.

Extraction of complexes of rare-earth elements with the reagent nitroarsenazo. To a weakly hydrochloric-acid solution of rare-earth elements are added the reagent solution, a urotropine solution until the violet or blue-violet color is fully developed, and diphenylguanidine. Extraction is carried out with butyl alcohol.

Extraction of the thorium complex with the reagent thoron. To 2–5 ml of a thorium-containing solution with an acidity of ~0.05 N in HCl are added 1-2 ml of a 40% solution of monochloroacetic acid or 20–50 mg of trichloroacetic acid, 0.5–1 ml of a 20% solution of diphenylguanidine chloride, 3–4 ml of butyl or amyl alcohol, and the mixture is extracted. Depending on the amount of thorium, the color of the extract varies from yellow to red.

Extraction of thorium complexes with the reagent arsenazo III. Extraction is possible both from hydrochloric-acid and from sulfuric-acid solutions:

a) To 2–3 ml of a thorium-containing solution with an acidity of ~0.1 N HCl are added 0.5 ml of a 40% solution of monochloroacetic acid, -

···arsenazo III solution until an excess of reagent is reached, which can be observed from the transition of the initially formed green color to mixed violet or blue; add 0.5–1 ml of a 20% solution of diphenylguanidinium chloride and extract with amyl or butyl alcohol. The extract is photometered at $\lambda = 665$ mμ.

c) To 5 ml containing thorium in 0.1 N H_2SO_4, add an excess of arsenazo III, diphenylguanidinium chloride, and extract with a small volume of butyl or amyl alcohol. The thorium concentration in the original aqueous solution, equal to 0.01—0.02 γ/ml thorium, can be determined.

Extraction of hexavalent uranium with arsenazo III. In view of the considerable stability of the UO_2^{2+}—arsenazo III complex, extraction becomes possible from a solution saturated with complex III, which masks many elements. This ensures good selectivity of the determination of uranium ([11]).

To 1–2 ml of an almost neutral test solution containing 1–50 γ of uranium, add 2–3 ml of a 5% aqueous solution of ethylenediaminetetraacetic acid sodium salt, 1 ml of 0.1 N HCl, 1.00 ml of a 0.05% arsenazo III solution, 0.5 ml of a 20% solution of diphenylguanidinium chloride, and 5.00 ml of butyl alcohol, and extract. The extract is photometered at 660 mμ. At low contents—

Table 1

Reagent	Possible extraction-photometric determinations
Arsenazo I[[structural formula shown in the original table]]	UO_2^{2+}, Th, Zr, Hf, ΣTR, FeIII, VO^{2+}, Al, Be, Ti, Cu, Ga, In, Sc
Arsenazo II[[structural formula shown in the original table]]	UO_2^{2+}, Th, La, Be, Cu, etc.
Arsenazo III[[structural formula shown in the original table]]	UO_2^{2+}, Th, Zr, Hf, FeIII, VO^{2+}, Pb, Ca, Cu, ΣTR
Thoron[[structural formula shown in the original table]]	Th, Zr, Hf, Bi, etc.
Thoron II[[structural formula shown in the original table]]	Th, Zr, Hf, Bi, etc.
Nitrotoron[[structural formula shown in the original table]]	Th, La, Bi, etc.
Nitroarsenazo[[structural formula shown in the original table]]	UO_2^{2+}, Th, Zr, Hf, La, VO^{2+}, Al, Be, Pb, etc.
Tetrabromoarsenazo III[[structural formula shown in the original table]]	Th, UO_2^{2+}, U^{IV}, Zr, Pb

in the case of uranium the extract is pink; with a larger amount it is violet, blue, or green.

The practical sensitivity of extraction-photometric reactions can be increased very greatly if a combined procedure of extraction and coprecipitation with organic collectors is used.

Organic collectors ([12]) make it possible to isolate elements from very dilute solutions. One of the possible methods of coprecipitation is the coprecipitation of elements in the form of complex compounds formed by them with reagents of the arsenazo-thoron group ([12–14]). Methyl violet and certain other basic dyes, all of which are intensely colored, are used as the ingredient of the collectors. It is possible, however, to use colorless organic collectors. In this case the precipitates obtained after filtration can be dissolved in small volumes of organic solvents, where the coprecipitated element is determined directly photometrically from the color of its complex with the reagent. Thus concentration is combined with simultaneous determination. Ashing of the organic precipitate or its decomposition with acids is not required. Such procedures provide exceptional possibilities with respect to the convenience of determining elements in their extremely dilute solutions.

As colorless collectors one may use sparingly soluble sulfates, perchlorates, rhodanides, trichloroacetates, naphthalene-β-sulfonates, anthracene-α-sulfonates, and other salts of suitable sufficiently hydrophobic organic cations, for example, diphenylguanidinium.

A collector suitable for each particular case is selected experimentally. The collector must dissolve well in the organic solvent employed and must ensure complete coprecipitation of the element complex, while leaving the major portion of the excess reagent in solution. This possibility is connected with a definite ratio of the solubilities of the simultaneously formed precipitates: the colorless collector—the salt of the heavy organic cation with a suitable anion; the salt of this same organic cation with the colored complex anion (in the form of which the element is coprecipitated); and the salt of the same organic cation with the anion of the colored reagent used. As an example, we shall cite a method for the combined determination of thorium in solutions at a thorium dilution equal to $1 : 1 \cdot 10^9$ ([15]).

To 1 l of 0.2 N HCl containing, for example, 1 γ Th, add 5 ml of a 0.05% solution of arsenazo III, 50 ml of a 20% solution of diphenylguanidinium chloride, and 50 ml of an approximately 1% solution of the potassium salt of anthracene-α-sulfonic acid. The precipitate is filtered off and dissolved in 5-10 ml of a mixture of butyl alcohol with an equal volume of conc. HCl. The extract is photometered at 665 mμ. One drop of a saturated solution of sodium hexametaphosphate, which destroys the Th–arsenazo III complex, is added, and the solution is again photometered, thus estimating the amount of reagent coprecipitated together with the complex. Thorium is determined by using a calibration curve.

The authors express their gratitude to V. P. Makarova for assistance in the work.

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Received
15 XII 1960

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