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Abstract

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EXTRACTION OF TECHNETIUM-99 FROM AQUEOUS SOLUTIONS BY QUINOLINE, TRIBUTYL PHOSPHATE, AND CERTAIN OTHER ORGANIC SOLVENTS

Technetium can be extracted from acidic, neutral, and alkaline media. For the purpose of its recovery, various classes of organic compounds have been investigated—alcohols, ethers, ketones, and amines (1-6). However, the published works do not make it possible to select an optimal extractant suitable for practical purposes. It is of interest to study the processes of technetium extraction by extractants not yet investigated for it, such as quinoline, tributyl phosphate (TBP), acetone, acetylacetone, thenoyltrifluoroacetone in benzene, and triphenylguanidinium chloride* in *n*-butyl alcohol. For comparison with the latter, tetraphenylarsonium chloride and tetraphenylphosphonium chloride were also used as complexing agents in extraction with chloroform.

In the investigations the long-lived isotope Tc^{99} was used. Methods for its isolation and purification have been described earlier (8,9). Extraction was studied on pure solutions of sodium pertechnetate with a concentration of 6-8 mg/l. The radiochemical purity of the preparation was checked by beta-spectral analysis, which

Table 1

Extraction of Tc(VII) by various extractants

Extractant and complexing agent	Medium	Distribution coefficient, *K*
Quinoline, C_9H_7N	NaOH, pH 8	83
Tributyl phosphate, $(C_4H_9)_3PO_4$	HNO_3, 0.5 *N*	14.7
Acetone, C_3H_6O	NaOH, 3*N*	5
Acetylacetone, $C_5H_8O_2$	HNO_3, pH 4	1.3
Thenoyltrifluoroacetone, $C_8H_5O_2F_3$(0.2 *M* solution in benzene)	HNO_3, pH 3NaOH, 1*N*	<0.001<0.001

Extractant and complexing agent	Medium	Distribution coefficient, K
Triphenylguanidinium chloride, $(C_{19}N_3H_{17})Cl(10^{-3}M$ aqueous solution). Extractant—*n*-butyl alcohol	pH 6-7	6.6
Extractant—chloroform, $CHCl_3$a) Complexing agent—tetraphenylarsonium chloride, $(C_6H_5)_4AsCl(10^{-4}M$ aqueous solution)	Na_2CO_3, pH 10	106
b) Complexing agent—tetraphenylphosphonium chloride, $(C_6H_5)_4PCl(10^{-4}M$ aqueous solution)	Na_2CO_3, pH 10	107

established that the spectrum obtained was single-component and had a limiting energy of 0.29 ∓ 0.01 MeV. The experiments were carried out at room temperature. Before the experiment, the sodium pertechnetate solution was additionally oxidized with hydrogen peroxide in an alkaline medium. The alkalinity and acidity in the samples were brought to the required value. The time of shaking the solutions in separatory funnels was 5 min. The working volume was 1 ml.

The amount of technetium was determined by a radiometric method. To calculate the distribution coefficient, the following formula was used:

$$K = \frac{(C_1 - C_2)V_{\text{aq. ph.}}}{C_2 V_{\text{org. ph.}}},$$

where C_1 is the amount of technetium in the aqueous phase before extraction, and C_2 is the same after extraction.

The results of the preliminary experiments are given in Table 1.

Readily available extractants—quinoline, tributyl phosphate, and acetone—characterized by high distribution coefficients, were studied in greater detail. It was found that, with the aid of quinoline and acetone,* radiochemically pure

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* The preparation was synthesized by V. I. Kuznetsov and N. N. Basargin and kindly provided to us. The synthesis method has been published (7).

technetium-99 can be fairly simply extracted from neutron-irradiated molybdenum.

Extraction of technetium with quinoline and its re-extraction from the organic phase. The highest value of the distribution coefficient was obtained near the neutral point, at pH 8 (*K*-83). Under conditions of high alkalinity of the solution, a certain decrease in the distribution coefficient is observed.

The isolation of technetium from quinoline can be carried out by distilling off the extractant in vacuum. But this method is unsuitable because of the presence, in the residue, of quinoline decomposition products. An attempt to re-extract technetium from quinoline with aqueous solutions containing reducing agents (0.2 *M* sulfuric hydrazine solution, 0.2 *M* sodium thiosulfate solution) did not give satisfactory results. Nor was it possible to isolate technetium from quinoline in the form of sparingly soluble compounds—$CsTcO_4$, $RbTcO_4$. It was found that the addition to the quinoline-water system of the nonpolar solvent chloroform, in a volume equal to the volume of quinoline, leads to an almost complete (99.7%) transfer of technetium into the aqueous phase.

Fig. 1. Dependence of the distribution coefficient of technetium on the acidity and alkalinity of a sodium pertechnetate solution during extraction with tributyl phosphate.

Table 2

Extraction of technetium from TBP as a function of the composition of the washing solution

Re-extracting solution	Concentration, *N*	Degree of technetium extraction, %	Re-extracting solution	Concentration, *N*	Degree of technetium extraction, %
Water	–	–	HNO_3	8.0	80.4
$(NH_4)_2CO_3$	4	0.5	HNO_3	10.0	90.8
HCl	2.2	0.1	HNO_3	12.5	99.0
HCl	5.6	0.8	Oxalic acid	4.0	0.01
HNO_3	4.0	34.2	Citric acid	4.0	0.03
HNO_3	5.0	63.0	NaOH	3.0	24.0
HNO_3	6.0	74.8	NaOH	4.0	50.0
HNO_3	7.0	71.8			

Extraction of technetium with tributyl phosphate and its re-extraction from the organic phase. The extraction of technetium with TBP was studied by the method described above. The influence of additions of nitric acid and alkali on the distribution coefficient is shown in Fig. 1.

The process of extraction of technetium(VII) in an acidic medium, i.e., derivatives of $HTcO_4$, probably proceeds as in the $HClO_4$—TBP system ([10,11]). The greatest—

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* Studies on the extraction of technetium with acetone will be published separately.

The highest distribution coefficient was obtained in the case of $0.5N$ HNO_3 ($K = 14.7$). At this acidity of the solution, the number of TBP molecules in the extracted complex was determined by a graphical method—from the dependence of the technetium distribution coefficient on the TBP concentration in a bilogarithmic coordinate system, from the tangent of the angle of inclination of the straight line. In this case the number of TBP molecules corresponded to ~ 2.8. Hence the composition of the complex may be represented as $HTcO_4 \cdot 3TBP$.

The re-extraction of technetium from TBP was studied in a series of experiments by washing the extractant with solutions of various composition. Water, solutions of HCl and HNO_3 of different concentrations, $4N$ solutions of citric and oxalic acids, and also solutions of $(NH_4)_2CO_3$ and NaOH were used as the washing liquid. The results of the studies are given in Table 2.

The best results for the re-extraction of technetium from TBP were obtained when 10-12N HNO_3 and $4N$ NaOH were used as the washing solution.

It may be concluded that both extractants studied—quinoline and TBP—are, under certain conditions, suitable for the extraction of technetium from aqueous solutions.

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Note: Figure translations are in progress. See original paper for figures.