

TECHNETIUM (VII) EXTRACTION BY MONO AND BIDENTATE NEUTRAL ORGANOPHOSPHORUS COMPOUNDS FROM NITRIC ACID SOLUTIONS

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Leading place between different methods of radionuclides' isolation from man-caused systems belongs to liquid extraction. Extraction schemes were put into basis of not only technology of irradiated nuclear fuel reprocessing (PUREX process) but also high level active waste (HLW) partitioning. Extraction partitioning of HLW is aimed for deep isolation of, mostly, Cesium-137, Strontium-90, minor actinides as well as technetium. For the most known technologies of HLW partitioning such as DDFK process [1], STN process [2], TRUEX process [3] and others it is proposed to isolate Tc in the stream together with platinum group elements [1,2] or uranium [3]. However technologies mentioned above do not imply possibility of isolation into separate fraction of such dangerous and long lived radionuclide as ^{99}Tc . Therefore development of original flow sheets schemes for HLW partitioning including technetium isolation stage is very important.

Up to present date a great material is accumulated on Tc (VII) extraction properties study from acidic as well as from neutral and alkaline media. Great group of extractants of different types was investigated such as alcohols, ketons, aldehydes and other compounds. However, almost all of them are unacceptable in technology and others have weak extraction abilities.

The goal of present research is investigation of Tc (VII) extraction by prevailing mono and bidentate neutral organophosphorus reagents (NOPC). Bidentate NOPC are known [5] to be the most effective reagents in technological flow sheets of radionuclides separation and partitioning. Between perspective monodentate neutral organophosphorus compounds dialkylmethylphosphonates were chosen as the products of military substances reprocessing.

In spite of lower efficiency compared to bidentate NOPC they cost much less.

Nitric acid solutions containing ^{99}Tc (VII) were used for experiments. Organic reagents were synthesized in **INEOS RAS** (scientific supervisor, Corresponding Member of RAS, professor T.A. Mastrjukova) from compounds of tetracoordinated phosphorus by the method of etherification of methylchlorphosphonate. All used alcohols, amines and diluents were dehydrated by standard procedures and had constants described in literature [6]. Reaction progress was controlled by nuclear magnetic resonance of ^{31}P using Bruker CXP-200 hardware. Nuclear magnetic resonance spectrums of ^1H were detected in solutions of C_6D_6 using Bruker AMX-400 hardware.

Diluents such as 1,2 - dichloroethane, methanitrobenzotrifluoride (MNBTF) and synthine were used without primary purification. Reagent solutions in diluents were prepared by precise weight amount.

Extraction was performed by shaking of prepared solution with equal reagent volume in appropriate diluent for three minutes (sufficient time for equilibrium achievement). Aliquots were taken after phase separation by centrifuging, samples' activity was determined and distribution coefficients of element (D_{Tc}) were calculated.

In Technetium (VII) extraction experiments by monodentate NOPC dialkylmethylphosphonates with common structure $(\text{RO})_2\text{CH}_2\text{P}(\text{O})$ were synthesized and used in dichloroethane, MNBTF with radicals R having proper titles as follows:

R	Titles of synthesized compounds
$\text{CH}_3\text{-CH}(\text{C}_2\text{H}_5)\text{-(CH}_2)_4\text{-}$	Diisooctylmethylphosphonate (DIOMP)
Cyclo- C_6H_{12}	Dicyclohexylmethylphosphonate (DCHMP)
$\text{CH}_3\text{-C}_6\text{H}_5\text{-O-CH}_2\text{-CH}_2\text{-}$	Di - 2-phenoxyethylmethylphosphonate (D2POEMP)

During Tc extraction experiments by bidentate NOPC tetraphenylethylenediphosphineoxide (TPEDP) and diphenyldibutylcarbamoylmethyl phosphineoxide (Ph_2Bu_2) were synthesized and investigated.

During Tc (VII) extraction by dialkylmethylphosphonates from nitric acid solutions it

was shown that nature of alkoxy- substitute at phosphorus atom do not actually influence on Tc (VII) isolation degree. Maximum D_{Tc} is close to 4 during extraction by 4 M DCHMP in MNBTF from 3 M HNO_3 .

Coefficient of Tc extraction by $(RO)_2CH_3P(O)$ significantly decreases while nitric acid concentration increases in solution. For instance, D_{Tc} at $[R] = 0.1$ M within range of $[HNO_3]$ from 0.5 to 5.0 M changes from 0.21 to $2.7 \cdot 10^{-3}$. Since actinide elements (Np, Pu, Am) are extracted by dialkylmethylphosphonates at high nitric acid concentrations (maximum of D_{Am} is observed at ~ 3 M) separation of those elements from Tc is possible.

For extracted complex structure determination Technetium (VII) extraction was investigated for solutions of DCHMP in MNBTF and Ph_2Bu_2 in DCE from 3 M and 0.1 M HNO_3 respectively. It was shown that increase of reagents' concentrations leads to Technetium extraction increase. For example, D_{Tc} at $[HNO_3] = 3$ M within range of $[DCHMP]$ from 0.1 to 4 M changes 0.011 to 4.1. Technetium extraction (D_{Tc}) from 0.1 M HNO_3 by Ph_2Bu_2 solutions in DCE within range of $[Ph_2Bu_2]$ from 0.001 to 0.1 M increases from 0.07 to 3.2. Graphs slopes of D_{Tc} dependences as the function of given extragents concentrations are close to 2 which is the reason to suppose formation of complex with two molecules of reagent.

Extraction abilities of both studied bidentate NOPC in the processes of Tc isolation were close however comparing to monodentate NOPC they are significantly higher. For instance, at $[R] = 0.1$ M in MNBTF and $[HNO_3] = 0.5$ M (volumes ratio of aqueous and organic phases is 1:1) ratio $D_{Tc}(TPEDP)/D_{Tc}(DCHMP)$ is about 100.

On the basis of obtained information it is planned to develop original flow sheet schemes of technetium isolation from HLW.

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