Separation and Refinement of Tc in the Sulfuric Acid Leachate after the Denitration of the Nuclear Fuel Reprocessing Solution

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Abstract We have separated fissile elements and Tc, Mo, and Ru, by denitrating the fuel reprocessing solution, leaching by sulfuric acid and extracting the leachate with tri-*n*-octylamine(TOA).

We have prepared the final product, NH_4TcO_4, removing the molybdenium by the reextraction of the back extract with the di-2-ethylhexylphosphate(HEDHP) and removing the ruthenium by the distillation.

Key words Tc, nuclear fuel reprocessing solution, radiopharmaceuticals

Introduction

The great leader Comrade **Kim Il Sung** said as follows.

"**We must open new fields of science, introduce the latest achievements of science and technology throughout the national economy, and actively develop the important areas of the basic sciences**."("**KIM IL SUNG** WORKS" Vol. 15 P. 197)

The reactions between the coordination compounds of ^{99m}Tc and the various polyaminocarboxylic acid(PACA) have been investigating widely worldwide because they occupy more than 85% of radiopharmaceuticals [2−5]. ^{99}Tc which uses in the basic researches of such radiopharmaceuticals are taken from the nuclear fuel reprocessing solution.

We have already found that the tiny amount of fissile elements including Tc, Ru, Mo exist when the fuel reprocessing solution is denitrated and then the precipitate is leached by sulfuric acid [1].

In this paper we described the preparation of final product, NH_4TcO_4, removing the tiny amount of fissile elements by the extraction of this leachate by the tri-*n*-octylamine(TOA), removing the molybdenum by reextraction of the back extract with the di-2-ethylhexylamine(HEDHP), and removing the ruthenium by the distillation [6−8].

1. Experimental Method

1.1. Analytical method of element

Tc and Pd were measured with the γ ray liquid scintillator of type "FJ-353" by labeling ^{99m}Tc and ^{102}Pd separately, and Zr, Ce, Fe, Sb and Re were measured with the β-ray automatic discharge counter of type "FH-408" by labelling ^{95}Zr–^{95}Nb, ^{144}Ce–^{144}Pr, ^{59}Fe, ^{124}Sb and ^{188}Re separately.

Mo and Rh were analyzed with the specific flame atomic extinction method. In the case of Mo, the wavelength is 313nm, the basic transformer is 5μg Pd$+3\mu$g MgNO$_3$, the ashing temperature is 1 500℃ and the temperature of atomization is 2 400℃. In the case of Rh, the wavelength is 343nm, the basic transformer is not used, the ashing temperature is 900℃ and the temperature of atomization is 2 200℃.

1.2. Removing trace fission elements from the sulfuric acid leachate by TOA

The extractant is the mixture of 10% TOA/10% *n*-hexanol/80% kerosene (v/v/v).

The sulfurric acid leachate was extracted for 5 min by the same volume of the extractant and then the organic phase was washed with the same volume of 0.1 mol/L HNO$_3$.

The separated effect was determined by the tracer method and the specific flame atomic extinction method.

$$\text{Distribution ratio}(D) = \frac{\text{The total content of corresponding component in organic phase}}{\text{The total content of corresponding component in aqueous phase}}$$

$$\text{Extraction rate}(\%) = \frac{100D}{D + (V_a/V_o)}$$

1.3. Removing Mo by HEDHF

The extractant is the mixture of 20% HEDHF / 80% kerosene(v/v).

The back extractant of TOA was extracted for 5min by the same volume of the extractant. The separated effect was determined with above mentioned method.

1.4. Removing Ru by the distillation

The solution was distilled at 100℃ for the content of Ru to find the effect on the loss of Tc during the distillation of Ru, the chlorine gas flowing through the distiller.

After the distillation the removing coefficient of Ru and the loss(%) of Tc were calculated by measuring the specific radio activities of [103]Ru and ^{99m}Tc in the solution

$$\text{The removing coefficient of Ru} = \frac{\text{The original specific radioactivity}}{\text{The specific radioactivity after distillation}}$$

$$\text{The loss of Tc} = \frac{\text{The original specific radioactivity} - \text{The specific radioactivity after distillation}}{\text{The original specific radio activity}} \cdot 100$$

2. Experimental Result and Discussion

2.1. Removing the trace fissile elements from the sulfuric acid leachate by TOA

Table 1 shows the distribution ratio(*D*) of the fissile elements by TOA.

Table 1. The distribution ratio(D) of the fissle elements by TOA

[H$^+$] /(mol·L^{-1})	Fissile elements								
	Tc	Ru	Mo	Pd	Zr	Fe	Sh	Ce	Rh
0.1	240	$4.3\cdot10^{-1}$	409	$1.8\cdot10^{-2}$	$3.0\cdot10^{-3}$	$2.2\cdot10^{-3}$	$7.1\cdot10^{-3}$	$1.7\cdot10^{-4}$	$<10^{-4}$
1	67.7	$9.3\cdot10^{-2}$	909	$3.2\cdot10^{-2}$	$9.5\cdot10^{-4}$	$1.3\cdot10^{-4}$	$6.5\cdot10^{-4}$	$2.8\cdot10^{-4}$	$<10^{-4}$
10	$6.2\cdot10^{-1}$	$2.6\cdot10^{-2}$	$6.2\cdot10^{-3}$	$5.8\cdot10^{-2}$	$-$	$2.9\cdot10^{-4}$	$5.9\cdot10^{-4}$	$9.5\cdot10^{-4}$	$-$

As shown in table 1, when the acidity of solution increases, the extractive distribution ratio(D) decreases. Most of Tc and Mo and some of Ru were extracted at the H$^+$ ion concentration from 0.1 to 1 mol/L and the other fissile elements were removed.

The mechanism of the extraction and the stripping can be represented as follows [9].

$$TcO_4^- + R_3NH^+ \rightarrow [R_3NHTcO_4] \tag{1}$$

$$[R_3NHTcO_4] + OH^- \rightarrow R_3N + TcO_4^- + H_2O \tag{2}$$

After the loading organic phase was stripped by NaOH solution of 2mol/L at A/O ratio of 1/3, Ru and Mo in organic phase did not appear.

This showed that Mo and Ru had been stripped into the aqueous phase with Tc completely.

2.2. Removing Mo by HEDHF

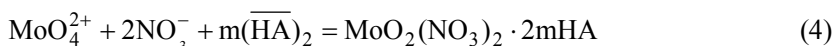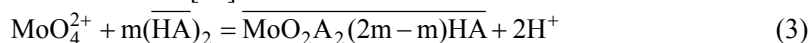The important impurities in the stripping solution were Ru and Mo.

Table 2 given the results reextracted the stripped solution in HNO$_3$ by HEDHF.

Table 2. The distribution ratio(D) of the fissile elements by HEDHF

[H$^+$] /(mol·L^{-1})	Fissile elements							
	Mo	Tc	Pd	Ce	Fe	Ru	Sh	Zr
1	79.4	$7.9\cdot10^{-4}$	60.4	$2.3\cdot10^{-2}$	2.46	$5.0\cdot10^{-1}$	250	3.5
2	198	$1.6\cdot10^{-3}$	54.0	$4.2\cdot10^{-3}$	$9.1\cdot10^{-1}$	$4.3\cdot10^{-1}$	226	6.1
4	358	$1.7\cdot10^{-3}$	33.0	$2.0\cdot10^{-2}$	1.55	$2.8\cdot10^{-1}$	225	5.8

As shown in table 2, Mo reached at its distribution ratio(D) over 198 and its extraction rate over 99% at the concentration of H$^+$ ion over 2 mol/L, but Tc was not extracted. And the trace fissile elements also were extracted.

The extraction of Mo(VI) in HNO$_3$ takes place with the additive coordination combination and the ionic coordination combination [10].

$$MoO_4^{2+} + m\overline{(HA)_2} = \overline{MoO_2A_2(2m-m)HA} + 2H^+ \tag{3}$$

$$MoO_4^{2+} + 2NO_3^- + m\overline{(HA)_2} = MoO_2(NO_3)_2 \cdot 2mHA \tag{4}$$

where HA is the HEDHP. Tc was not extracted because of the existence of TcO$_4^-$.

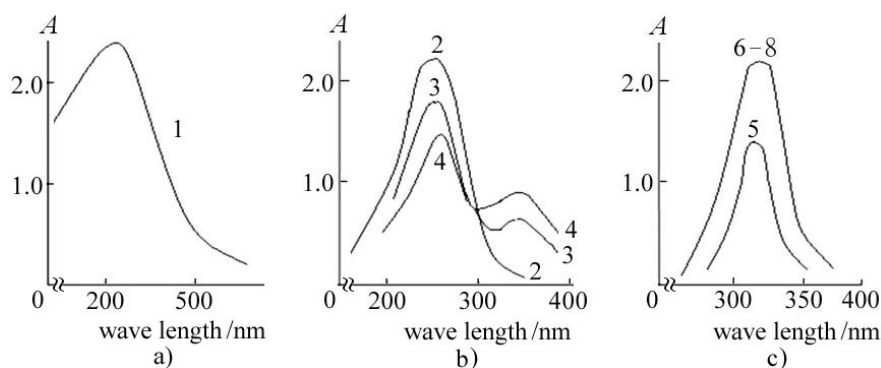The UV–Vis spectra of MoO$_4^{2-}$ in HNO$_3$ were shown in Fig.

Fig. UV–Vis spectra of MoO_4^{2-} in various concentration of HNO_3
a) neutral media ($1-[HNO_3]=0.01mol/L$), b) acid media of 0.5(2), 1.0(3) and
2.0(4)mol/L HNO_3, c) acid media of 3.0(5), 4.0(6), 6.0(7) and
10(8)mol/L HNO_3

Fig. shows that Mo(VI) exists as MoO_4^{2-} in neutral media, that the absorption peak appears on the wavelength of 206nm at the No.1, that if the acidity of media increase it appears on the wavelength of 250, 255, 259nm at the No. 2, 3 and 4, respectively and that when the concentration of HNO_3 is 2mol/L it appears on the wavelength of 328nm at the No. 5, 6, 7 and 8, respectively. This shows that Mo, existing as MoO_4^{2-} in neutral media, forms the polyvalent acid by the condensation of MoO_4^{2-} when the acidity increases and forms the bioxidation-coordination compound MoO_4^{2-} of MoO_4^{2-} when the concentration of HNO_3 reaches more than 2mol/L [9－12].

2.3. Removing Ru by the distillation

Table 3 shows the loss(%) of Tc during the distillation.

Table 3. The loss(%) of Tc during the distillation

Content of Ru in Solvent $/(mol \cdot L^{-1})$	1.07	0.50	0.79	0.99
Content of Tc in Solvent $/(mol \cdot L^{-1})$	0.005	0.005	0.005	0.005
Removal coefficient of Ru $(\cdot 10^{-3})$	1.0	4.5	5.9	7.7
Loss of Tc /%	0.4	0.5	0.7	0.7

As shown in table 3, Ru was removed by distilling and the loss of Tc was very small. Ru exists as RuO_4, which is volatile compound, but Tc(VII) is not distilled in alkali media.

There could be the tiny amount of different salts including Tc in the solution after the distillation.

So we allowed the H^+ ionic concentration of the solution to be $0.1 - 0.5$ mol/L with HNO_3 and extracted the aqueous solution three times with TOA having one-third of this concentration to remove that salts and increase the purity of Tc, and then prepared NH_4TcO_4 by back extracting the loaded organic phase with the $NH_3 \cdot H_2O$ of 1mol/L.

Conclusion

When the sulfuric acid leachate is extracted with TOA at the H^+ ionic concentration from 0.1 to 1mol/L, Tc is extracted more than 98% and Mo and Ru also are extracted together.

When that stripping is extracted with HEDHP at the concentration of H^+ ion over 2 mol/L, Mo is extracted and removed and when the effluent is distilled, Ru is removed.

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