

**Radiation Stability of Benzyl Tributyl Ammonium Chloride towards Technetium-99
Extraction - 13016**

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ABSTRACT

A closed nuclear fuel cycle combining new separation technologies along with generation III and generation IV reactors is a promising way to achieve a sustainable energy supply. But it is important to keep in mind that future recycling processes of used nuclear fuel (UNF) must minimize wastes, improve partitioning processes, and integrate waste considerations into processes. New separation processes are being developed worldwide to complement the actual industrialized PUREX process which selectively separates U(VI) and Pu(IV) from the raffinate. As an example, the UREX process has been developed in the United States to co-extract hexavalent uranium (U) and heptavalent technetium (Tc) by tri-*n*-butyl phosphate (TBP). Tc-99 is recognized to be one of the most abundant, long-lived radiotoxic isotopes in UNF (half-life, $t_{1/2} = 2.13 \times 10^5$ years), and as such, is targeted in UNF separation strategies for isolation and encapsulation in solid waste-forms for final disposal in a nuclear waste repository. Immobilization of Tc-99 by a durable solid waste-form is a challenge, and its fate in new advanced technology processes is of importance. It is essential to be able to quantify and locate 1) its occurrence in any new developed flowsheets, 2) its chemical form in the individual phases of a process, 3) its potential quantitative transfer in any waste streams, and consequently, 4) its quantitative separation for either potential transmutation to Ru-100 or isolation and encapsulation in solid waste-forms for ultimate disposal. In addition, as a result of an U(VI)-Tc(VII) co-extraction in a UREX-based process, Tc(VII) could be found in low level waste (LLW) streams. There is a need for the development of new extraction systems that would selectively extract Tc-99 from LLW streams and concentrate it for feed into high level waste (HLW) for either Tc-99 immobilization in metallic waste-forms (Tc-Zr alloys), and/or borosilicate-based waste glass. Studies have been launched to investigate the suitability of new macrocompounds such as crown-ethers, aza-crown ethers, quaternary ammonium salts, and resorcinarenes for the selective extraction of Tc-99 from nitric acid solutions. The selectivity of the ligand is important in evaluating potential separation processes and also the radiation stability of the molecule is essential for minimization of waste and radiolysis products. In this paper, we are reporting the

extraction of TcO_4^- by benzyl tributyl ammonium chloride (BTBA). Experimental efforts were focused on determining the best extraction conditions by varying the ligand's matrix conditions and concentration, as well as varying the organic phase composition (i.e. diluent variation). Furthermore, the ligand has been investigated for radiation stability. The γ -irradiation was performed on the neat organic phases containing the ligand at different absorbed doses to a maximum of 200 kGy using an external Co-60 source. Post-irradiation solvent extraction measurements will be discussed.

INTRODUCTION

In the industrial PUREX process, Tc (VII) is the most expected stable oxidation state of technetium, and is found as the pertechnetate species (TcO_4^-) because of the presence of oxidizing agents like nitric acid. From the literature [1–3], it is known that technetium can be co-extracted with uranyl ions by tri-*n*-butyl phosphate (TBP) depending on the nitric acid concentration. As an example, the UREX process has been developed at low nitric acid concentration to co-extract U(VI) and Tc(VII) in the first extraction step of the process [4]. As technetium is recognized to be one of the most abundant, long-lived radiotoxic isotopes in used nuclear fuel (UNF) (half-life, $t_{1/2} = 2.13 \times 10^5$ years), its fate in new advanced technology processes is of importance. However, since this radionuclide is a pure beta-emitter, tedious and time-consuming chemical separations are usually performed prior to any measurement in such complex media. Since the discovery of crown-ethers by Pedersen [5], various applications of crown ethers have drawn much attention [6, 8]. The application of crown-ethers on the extraction of Tc-99 has been investigated since the mid 1980's [9-14]. In the US, the focus was on extracting Tc-99 from alkaline tank waste [14] but the research stopped at the demonstration level. Studies have been launched to investigate the suitability of new macrocompounds such as aza-crown ethers, or resorcinarenes [15, 16] for the selective extraction of Tc-99 from nitric acid solutions. In this paper, we are reporting the extraction of TcO_4^- by benzyl tributyl ammonium chloride (BTBA), as well as a newly designed macrocompound: 19-Chloro-3,6,9,12,15-pentaoxa-21-azabicyclo[15.3.1] heneicosa-1(21),17,19-triene-2,16-dione abbreviated as CPAH. The description of the synthesis of CPAH can be found in [16]. The assessment of CPAH's and BTBA's extraction properties toward heptavalent technetium as well as their stability against radiolysis will be discussed.

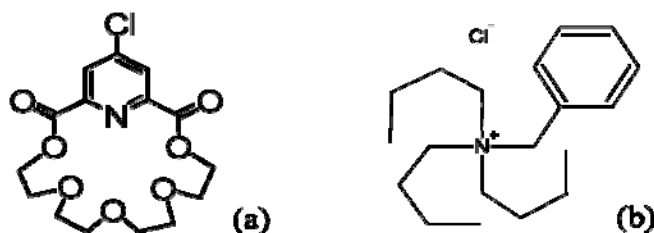


Figure 1: Extractants evaluated in this study for the specific extraction of Tc-99
1a: 9-Chloro-3,6,9,12,15-pentaoxa-21-azabicyclo[15.3.1]heneicosa-1(21),17,19-triene-2,16-dione (CPAH); 1b: Benzyl tributyl ammonium chloride (BTBA).

METHODS

Procedure for Technetium Extraction Study

All chemicals were purchased from Aldrich and were used as received. Ammonium pertechnetate was purchased from Oak Ridge National Laboratory and purified as described elsewhere [17]. Water was purified to $> 18 \text{ M}\Omega$ by a MilliQ system. All samples were run in triplicate. The distribution experiments were carried out in 15 mL test tubes; equal volumes of 1 mL of organic and aqueous phases were emulsified with a vortex for 1 minute at room temperature. After the phases were allowed to coalesce, phase separation was improved by centrifugation for 1 minute at 1500 rpm. The aqueous and organic phases were sampled and the activity of Tc-99 was determined in each phase by liquid scintillation counting (Perkin Elmer Tri-Carb 3100TR Liquid Scintillation Counter) or by ICP-AES analysis (ThermoScientific iCap 6000 Series). Data were collected for 60 minutes or until 2σ was reached. A blank sample was counted for each batch of separations which enabled the subtraction of any background radiation. The window was optimized using the transform Spectral Index of the External Standard in combination with Automatic Efficiency Control (tSIE/AEC). The extraction properties of the ligand are described by the distribution ratio D where $\Sigma[M]_{org}$ and $\Sigma [M]_{aq}$ denote the total concentration of metal species in the organic aqueous phases.

$$D = \frac{\sum [M]_{org}}{\sum [M]_{aq}} \quad (1)$$

Furthermore, this procedure was used to evaluate the extracting efficiency and selectivity of the ligand before and after γ -irradiation.

Stability Studies of the Ligand against Irradiation

The stability studies of the ligand against irradiation have been performed at the Nayade facility at CIEMAT site (Spain), which is a pool 1.2 m^2 by 4.5 m deep (Figure 2). It consists of 60 sources of ^{60}Co distributed in six lots with total activity of $1.14 \cdot 10^{14} \text{ Bq}$ (3000 Ci). There are several irradiation containers, which can provide different radial irradiation flows, depending on the activity of the sources used. To perform the studies described herein the samples were placed inside a container which is placed inside a basket where the ^{60}Co sources are oriented to provide homogeneous irradiation flux.

The samples were prepared at the University of Nevada, Las Vegas (UNLV); BTBA was dissolved in tetrachloroethane, and CPAH was dissolved in cyclohexanone at 2 different molarities (0.005 M and 0.1 M). The solution was frozen; a vacuum was pulled on the tube and was then fire sealed. All labelled samples were shipped to Spain, including a blank 0 sample that was not to be irradiated but tested for travelling conditions. The samples were irradiated at 0, 10, 50, 100, and 200 kGy using external Co-60 sources with a dose rate of $2.5 \text{ kGy}\cdot\text{hr}^{-1}$. For the irradiation tests, all samples were taken out of their original sealed ampoules and placed in vials. After irradiation, the samples were shipped back to UNLV for extraction studies.

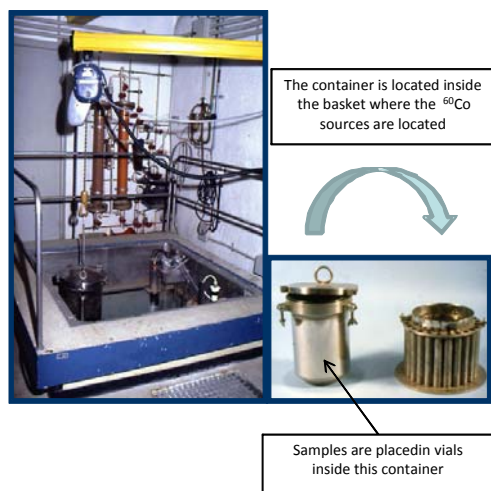


Figure 2. The Nayade facility at CIEMAT site (Spain)—courtesy of CIEMAT

RESULTS and DISCUSSION

Solvent Extraction Tests

Extraction of pertechnetate from acidic solutions by BTBA (Table 1) or CPAH (Table 2) in different diluents was examined to investigate the relationship between diluent properties (such as polarity) and extractability of Tc-99-macrocompound complex. A simple system composed of pertechnetate dissolved in an acidic medium phase was used. The nature of the diluent was examined and was shown to be the most influential variable in controlling the extraction efficiency, encompassing one order of magnitude in the range of observed extraction yield for TcO_4^- . Though some of the diluents tested are not suitable for process applications, this insight provided the means to find a suitable diluent for Tc-99 extraction that would meet process requirements.

Table 1. Distribution ratio D for TcO_4^- extraction with 0.01M BTBA from 0.5N HNO_3

Diluent	Dielectric Constant	Average Distribution Ratio
Toluene (3)/Acetone (2)	2.4/20.7	1.23
Toluene (2.5)/Acetone (2.5)	2.4/20.7	1.17
Dichloromethane	21.2	0.23
Octanol	10.3	1.43
Tetrachloroethane	12.3	23.12
Methyl Isobutyl Ketone	13.1	0.76

The results show here that most of the distribution ratios of Tc-99 extracted by BTBA (Table 1) were higher than the ones obtained with CPAH (Table 2). For example, with a mixture of toluene (2.5)/acetone (2.5), $D_{\text{Tc-99}}$ was found to be 1.171 with BTBA, and 0.004 with CPAH. The highest distribution ratio of Tc-99 extracted by BTBA was obtained with tetrachloroethane, $D_{\text{Tc-99}} = 23.1$. Even though the presence of chlorine atoms is not suitable for engineering-scale extraction processes, tetrachloroethane is the diluent we chose for the subsequent radiolysis experiments.

Table 2. Distribution ratio D for TcO_4^- extraction with 0.01M CPAH from 0.5 N HNO_3

Diluent	Dielectric Constant	Average Distribution Ratio
Toluene (2.5)/Acetone (2.5)	2.4/20.7	0.004
Cyclohexanone	18.2	38.235
Dichloromethane	9.1	0.232
Toluene	2.4	0.002

The distribution ratios of Tc-99 extracted by CPAH were low with non polar solvents such as toluene. With a dipolar aprotic solvent such as cyclohexanone, the distribution ratio reached a value of 38.235. We need to keep in mind though that cyclohexanone is fairly volatile (BP 155.6° C, flashpoint 46° C), and significantly water soluble (50 grams per liter at 30° C), thus making this diluent less suitable for engineering scale demonstration. For the purpose of this investigation, radiation experiments used CPAH dissolved in cyclohexanone.

Irradiation Tests

During an extraction process, the high radioactivity of the feed solution is certainly responsible for the radiation damages on both the organic diluent as well as the ligand. In order to develop a robust process that will stand high radiation dose rates as well as acid hydrolysis, testing the radiolytic stability of a new ligand is imperative. New radiolysis by-products could be created and modify the extracting properties of the original ligand resulting in lower Tc-99 distribution ratios as well as a decrease in the selectivity due to the formation of new complexing agents. For this reason, preliminary irradiation tests by means of an external γ source were performed to evaluate the effect of irradiation on the distribution ratio of Tc-99. Upon receiving the irradiated samples at UNLV, all samples had evaporated to complete dryness. The extracting molecules studied in this paper, BTBA and CPAH do not have any noted characteristics with regard to diluent evaporation, so under this assumption, the amount of extracting molecules should stay consistent even though the solvent evaporated. All dried irradiated and non-irradiated samples were dissolved in either tetrachloroethane or cyclohexanone and tested for the extraction of Tc-99. Triplicate tests on the extraction of Tc-99 were carried out with non-irradiated and irradiated extracting molecules (BTBA or CPAH). Distribution ratios for the irradiated and non-irradiated samples were calculated and are displayed in Tables 3 and 4.

Table 3. Extracting capabilities of BTBA dissolved in tetrachloroethane before and after γ -irradiation at several doses

Dose (kGy)	Avg. distribution ratio	Standard dev.
D_{Tc-99}		
0.1 M BTBA		
0	26.34	2.52
10	24.69	1.38
50	21.68	6.96
100	24.30	2.55
200	22.86	1.55
0.005 M BTBA		
0	22.22	0.72
10	22.26	1.15
50	1.28	0.11
100	1.35	0.07
200	1.16	0.07

Table 4. Extracting capabilities of CPAH dissolved in cyclohexanone before and after γ -irradiation at several doses

Dose (kGy)	Avg. distribution ratio	Standard dev.
D_{Tc-99}		
0.1 M CPAH		
0	75.47	2.29
10	70.88	1.24
50	77.99	2.37
100	60.54	1.71
200	54.15	5.37
0.005 M CPAH		
0	25.95	0.18
10	26.38	0.71
50	24.55	1.61
100	23.98	1.05
200	21.31	1.58

The distribution ratios, as expected, show a decreasing trend, with the exception of the radiation dose at 50 kGy for 0.1 M CPAH and the radiation dose at 10 kGy for 0.005 M CPAH, where the

distribution ratio of Tc-99 is slightly higher than the non-irradiated respective extracting molecules. This may suggest the formation of radiolytic by-products (Figure 3).

We have started a preliminary investigation on the potential formation of radiolysis by-products of CPAH using an Ultimate 3000 HPLC system with a Dionex Acclaim mixed mode wax-1 column. The mobile phase was 25 mM potassium phosphate pH 4.2 and a 50/50 mixture of the phosphate and acetonitrile after five minutes. This ramp was necessary as the sample precipitated in the autosampler. As shown in Figure 4, the HPLC chromatogram indicates at 200 kGy the formation of another species. Due to the properties of the column, we can hypothesise the peak at two minutes is likely to be ketones from the degradation of the solvent. The small peak at 5.6 minutes may be dimethyl 4-chloropyridine-2,6-dicarboxylate but further investigations are necessary to confirm these findings. Other methods for identification of the degradation by-products are necessary due to the precipitation.

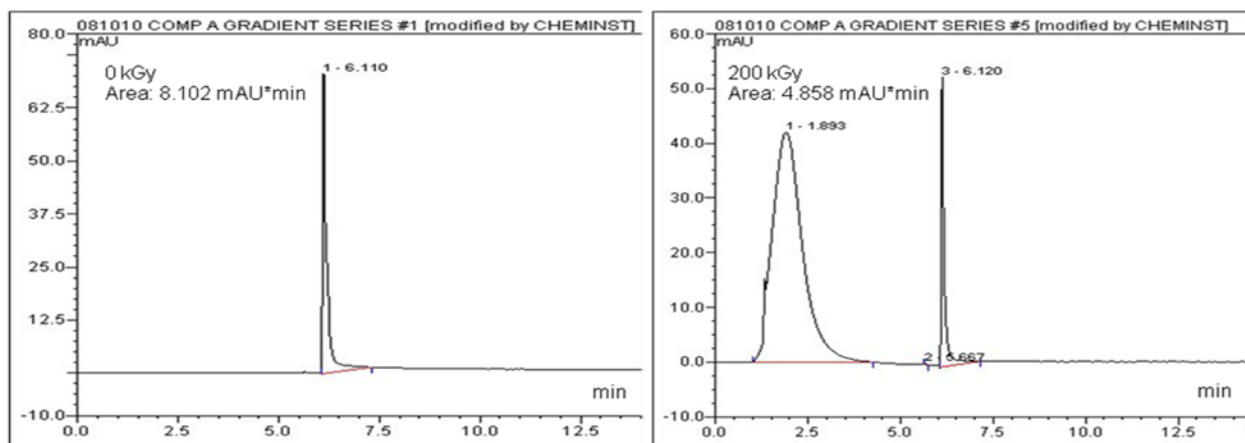


Figure 3. Comparison of HPLC chromatograms of 0.005 M CPAH analysed without any dilution for the respective absorbed doses of 0 kGy and 200 kGy.

CONCLUSION

The results obtained here show the strong potential of BTBA and CPAH to be used for the specific and selective extraction of Tc-99 in different acidic waste-streams. To elucidate the ammonium pertechnetate extraction mechanism with CPAH that is thought to be a co-extraction through a tight ion pair extraction, future studies will involve obtaining a crystal structure of the CPAH-Tc-99 complex. The behavior of both BTBA and CPAH under irradiation conditions are really exceptional and promising. These preliminary results indicate that both BTBA and CPAH show good extracting properties towards Tc-99. It is worth noting that at lower irradiation doses there may be the formation of CPAH γ -radiolysis by-product which may have equal or even better

extracting properties. We are planning to further investigate the radiolysis by-products formation by GC-MS, and to provide a thorough study on their identification and quantification.

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