

Separation of Long-Lived Fission Products Tc-99 and I-129 from Synthetic Effluents by Crown Ethers

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ABSTRACT

To minimize significantly the radiotoxic inventory of nuclear geological repositories to come as well as to reduce the potential of radionuclides migration and to minimize long-term exposure, the concept of partitioning and transmutation (P/T) of nuclear waste is currently discussed. Transmutation offers the possibility to convert radiotoxic radionuclides with long half-lives into radionuclides of shorter half-lives, less toxic isotopes, or even into stable isotopes. Besides the most prominent isotopes of neptunium, plutonium, americium, and curium, the long-lived fission products Tc-99 and I-129 (half-lives of 2.13×10^5 years, and 1.57×10^7 years, respectively) are promising candidates for transmutation in order to prevent their migration from a nuclear repository. Partitioning and transmutation of the most radiotoxic radionuclides will not only minimize the nuclear waste load but most importantly will significantly reduce the long-term radiotoxic hazard of nuclear waste repositories to come. Prior to the deployment of partitioning and transmutation, selective extraction techniques are required to separate the radionuclides of concern.

Since the discovery of crown ethers by C. Pedersen, various applications of crown ethers have drawn much attention. Although liquid-liquid extraction of alkali and alkali earth metals by crown ethers has been extensively studied, little data is available on the extraction of Tc-99 and I-129 by crown ethers. The methods developed herein for the specific extraction of Tc-99 and I-129 provide recommendations in support of their selectively extraction from liquid radioactive waste streams, mainly ILW. We report data on the solvent extraction of Tc-99 and I-129 from synthetic effluents by six crown ethers of varying cavity dimensions and derivatization. To satisfy the needs of new extractant systems we are demonstrating that crown ether (CE) based systems have the potential to serve as selective extractants for the separation of these long lived radionuclides from high level nuclear waste (HLW), intermediate level nuclear waste (ILW), and low level nuclear waste (LLW) streams. The experimental results show that dibenzo-18-crown-6 (DB18C6) is highly selective towards Tc-99, and dicyclohexano-18-crown-6 (DC18C6) is highly selective towards I-129. The nature of the diluent was examined and was shown to be the most influential variable in controlling the extraction coefficients of Tc-99 and I-129. Therefore the addition of polar diluent acetone to non-polar diluent toluene enhanced the distribution

coefficient of Tc-99 (D_{Tc}) was by a factor of 30. For I-129, the best extraction yield was obtained after introducing tetrachloroethane. Through the process, by a single extraction step, 85 % to 95 % of Tc-99 was extracted from synthetic effluents, while 84 % to 88 % of I-129 was extracted from different acidic media. The extraction by crown ether is a fairly rapid process and the total preparation time of the chemical separation takes about 20 minutes for a batch of eight samples.

INTRODUCTION

Tc-99 and I-129 are typically fission products generated in nuclear reactor, and are characterized by long half-lives, and long β -activity decay chains. Regarding the concept of a closed nuclear fuel cycle to be potentially established in the U.S. and the DOE AFCI program, a specific selective fission product separating procedure must be developed. Satisfying the need to develop new extractant systems, the deployment of crown ether (CE) based systems can serve to selectively extract and separate these long lived radionuclides from high-level nuclear waste (HLW) streams and to concentrate it for feed to HLW vitrification. Since the discovery of crown ethers by C. Pedersen [1] and D J. Cram [2] various applications of crown ethers have drawn much attention [3, 4]. Although liquid-liquid extraction of alkali and alkali earth metals by crown ethers has been extensively studied, little data is available on the extraction of Tc-99 [5, 8]. In this paper, we report data on the solvent extraction of heptavalent pertechnetate Tc-99 from synthetic effluents by DB18C6, as well as I-129 from synthetic effluents by DC18C6.

EXPERIMENTAL

Suprapure NaOH (99.99 %), NaCl (99.99 %), HNO₃ (99.99% double distilled, 70 % density), and reagent-grade NaNO₃ (99 %), NaHCO₃ (95 %), and ascorbic acid (99 %) were purchased from Aldrich Chemicals and were used without further purification. The organic diluents toluene, carbon tetrachloride, chloroform, dichloroethane, tetrachloroethane, nitrobenzene, and acetone were obtained from Merck. The crown ethers 12-crown-4 (12C4), 15-crown-5 (15C5), 18-crown-6 (18C6), dicyclohexano-18-crown-6 (DC18C6), dibenzo-18-crown-6 (DB18C6), and dicyclohexano-24-crown-8 (DC24C8) were obtained from Aldrich and Merck. The crown ether tert-butylbenzo-21-crown-7 (tBuB21C7) was kindly gifted by Dr. J.F. Dozol, CEA Cadarache, France. The radionuclides Tc-99, as well as I-129 were obtained from L.M.R.I. CEA/Saclay, France. All the liquid-liquid extractions were performed in 50 mL corning tubes, equal volumes of organic and aqueous phases were contacted automatically by end-over-end rotation for 20 minutes at 25°C. The aqueous and organic phases were subsampled, and analyzed by liquid scintillation counting. The distribution coefficient D_{Rn} was calculated as the ratio $[Rn]_{org} / [Rn]_{aq}$ after reaching chemical equilibrium.

RESULTS AND DISCUSSION

Evaluation of the crown ether

Seven crown ethers with ring sizes of 12-crown-4 to 24-crown-8 (0.0065 M in toluene/acetone mixture) were evaluated for efficiency of pertechnetate (450 Bq.mL⁻¹) extraction from alkaline

synthetic solution (Table I) while six crown ethers from 12-crown-4 to 21-crown-7 in ring size (0.3 M in tetrachloroethane) were evaluated for their specific extraction of iodine (160 Bq.mL^{-1}).

DB18C6 was revealed to be the most efficient crown ether to extract Tc-99 [8, 9]. DB18C6 was chosen because it allows the crown ether ring to be more rigid, and the benzo groups attached to the crown ether tend to increase the extraction coefficient of Tc-99. Moreover the presence of benzo functional groups increases the solubility of the crown ether in the organic phase.

DC18C6 appeared to be the most efficient crown ether to selectively extract I-129 [6].

Table I. Extraction of Tc-99 and I-129 by Selected Crown Ethers

Crown Ether	Cavity Diameter (Å)	$\log D_{\text{Tc-99}}^{\text{a}}$	$\log D_{\text{I-129}}^{\text{b}}$
12C4	1.2 - 2.5	0.82	0.032
15C5	1.7 - 2.2	1.11	0.073
18C6	2.6 - 3.2	1.32	0.17
DC18C6	2.6 - 3.2	1.46	2.37
DB18C6	2.6 - 3.2	1.53	0.06
tBuB21C7	3.4 - 4.3	1.12	$< 10^{-5}$
DC24C8	4.5 - 5.6	1.56	N/A

^a Organic phase: toluene/acetone 1:2 mixture at 25°C , [crown ether] = 0.0065M; Aqueous phase: 4M NaOH, [Tc-99] = 450 Bq.mL^{-1} .

^b Organic phase: Tetrachloroethane at 25°C , [crown ether] = 0.03M; Aqueous phase: 6N HCl, [I-129] = 160 Bq.mL^{-1} .

The extraction of Tc-99 ($1,627 \text{ Bq.mL}^{-1}$) from a 4.0 M NaOH solution was examined at four concentrations of DB18C6 (0.0065 M, 0.0075 M, 0.0085 M, and 0.0095 M) in dichloromethane (Fig. 1). The results reveal a linear relation between the technetium distribution ratio and the crown ether concentration for the diluent dichloromethane. The extraction of I-129 from 4.0 N HCl solution was examined at different concentrations of DC18C6 (the concentration of DC18C6 varied from 10^{-3} M to $5 \cdot 10^{-1} \text{ M}$) in tetrachloroethane (Fig. 1). The results show a linear relation between the iodine distribution ratio and the crown ether concentration for the diluent tetrachloroethane. For both fission products, the dependence of the distribution coefficient on the extractant concentration is characterized by a linear function with a slope close to one. This confirms a Tc-99 to DB18C6 ratio in the extractable compound equal to 1:1, and an I-129 to DC18C6 ratio in the extractable compound equal to 1:1.

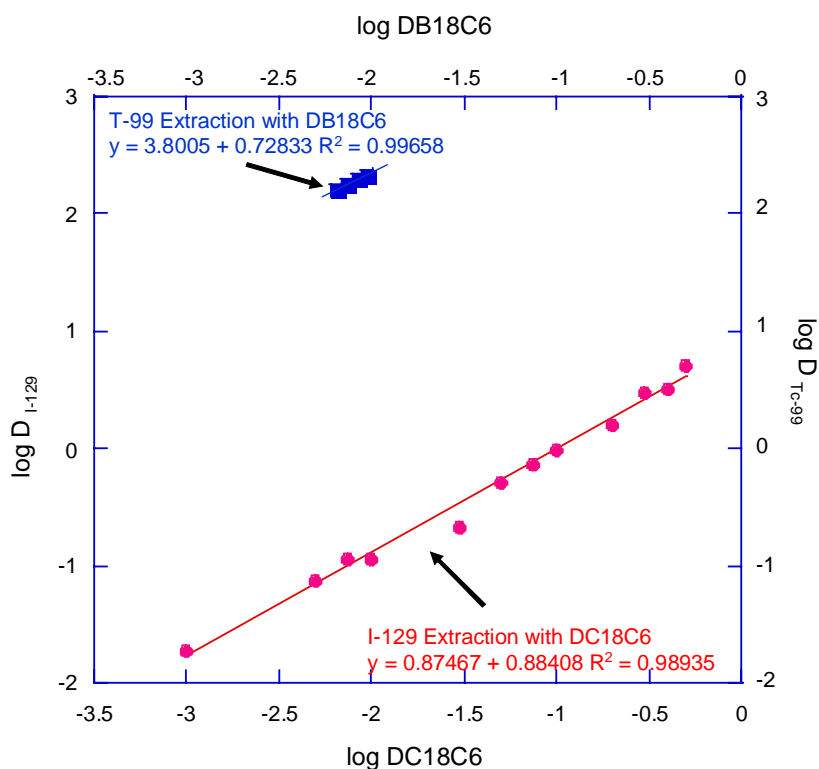


Fig. 1. Extraction of Tc-99: organic phase: DB18C6 in dichloromethane; aqueous phase: $[Tc-99] = 1,627 \text{ Bq.mL}^{-1}$, $[NaOH] = 4 \text{ M}$, ascorbic acid = 0.5 M.
 Extraction of I-129: organic phase: DC18C6 in tetrachloroethane; aqueous phase: $[I-129] = 160 \text{ Bq.mL}^{-1}$, $[HCl] = 4 \text{ N}$.

Evaluation of the solvent

The complex formation with crown compounds complexes a relatively small alkali metal or earth alkaline metal ion to a voluminous organic cation species which, in principle, is more soluble in organic media. If the solvation is a general rule in the case of cations, the anions can be strongly solvated too. As a result, solubilization of inorganic salts in organic diluents of low polarity is observed. Solvation is due to the electrophobic character of the water molecule. The common mineral anions have a low tendency to be co-extracted by the neutral extractants in a “classical” non polar organic diluents such as benzene [10]. This phenomenon is attributed to an insufficient solvation of the anion by the diluent. There are two possibilities to increase the solubilization of the co-extracted anion in the diluent: (1) use of a protic diluent, (2) increase the polarity of the diluent by the addition of a polar diluent (alcohol, phenols, etc.). The nature of the diluent was examined and is shown to be the most influential variable in controlling the extraction coefficients of Tc-99 as well as I-129. The addition of the polar diluent acetone to the non polar diluent toluene enhanced the distribution coefficient D_{Tc} by a factor of 30. For I-129, the best extraction coefficient was obtained with tetrachloroethane. The results are shown in Table II.

Table II. Influence of the Diluent on the Extraction of the Fission Products Tc-99 and I-129

Diluent	Dielectric Constants	D_{Tc-99}^a (4 M NaOH)	D_{I-129}^b (6 N HCl)
Toluene	2.4 (20°C)	$1 * 10^{-3}$	$< 10^{-5}$
Toluene/Acetone 1:2	2.4 - 20.7 (20°C)	34	$< 10^{-5}$
Toluene/Acetone 1:3	2.4 - 20.7 (20°C)	32.2	$< 10^{-5}$
Toluene/Acetone 1:4	2.4 - 20.7 (20°C)	32.5	$< 10^{-5}$
Toluene/Acetone 1:5	2.4 - 20.7 (20°C)	32.9	$< 10^{-5}$
Carbon Tetrachloride	2.2 (25 °)	$1.2 \cdot 10^{-4}$	$< 10^{-5}$
Chloroform	4.8 (20°C)	$7.9 \cdot 10^{-3}$	$< 10^{-5}$
Dichloromethane	8.93 (20°C)		$2 \cdot 10^{-1}$
Dichloroethane	10.4 (25°C)	$3.6 \cdot 10^{-1}$	$7 \cdot 10^{-1}$
Tetrachloroethane	12.3 (20°C)	$7.8 \cdot 10^{-2}$	2.37
Nitrobenzene	34.8 (20°C)	$8 \cdot 10^{-4}$	$6.5 \cdot 10^{-2}$

^a Extraction of Tc-99 ($1,250 \text{ Bq} \cdot \text{mL}^{-1}$) by DB18C6 (0.0065M) from a 4.0 M NaOH solution.

^b Extraction of I-99 ($160 \text{ Bq} \cdot \text{mL}^{-1}$) by DC18C6 (0.25M) from a 6.0N HCl solution.

Simplex optimization

In order to increase the extraction yield of Tc-99 as well as of I-129, a Simplex optimization procedure [11] was applied. The corresponding program was written in C⁺⁺ language for Bull Micral 40 microcomputer [6]. The different experimental conditions, and the parameters involved in the extraction of Tc-99 step such as NaOH concentration, crown ether concentration, and ascorbic acid concentration are displayed in Table III. The three initial experimental conditions were manually established taking into account previous results obtained on the extraction of Tc-99 from a synthetic solution [6, 8, 9].

Table III. Experimental Conditions used for the Simplex Optimization Procedure of Tc-99

Experiment	4 M NaOH (mL)	DB18C6 (* $10^{-3} \text{ Mol} \cdot \text{L}^{-1}$)	Ascorbic acid ($\text{Mol} \cdot \text{L}^{-1}$)	Yield (%)
1	5	6.00	0.30	70
2	6	6.00	0.30	63
3	5	6.00	0.30	63
4	5	6.50	0.30	75
5	5	6.00	0.60	77
6	5	6.00	0.30	73
7	5.4	6.20	0.38	76
8	4.16	6.28	0.41	80
9	3.24	6.42	0.47	71
10	4.82	6.39	0.45	87
11	4.71	6.42	0.55	72
12	4.92	6.18	0.36	88

The final parameters values used for the ⁹⁹Tc extraction are displayed in Table IV.

Table IV. Final Parameter Values for Tc-99 Extraction Determined by Simplex Optimization

Aqueous Phase	Organic Phase
1 mL effluent stream 0.5 M Ascorbic Acid 4 M NaOH	8 mL of 0.0065M DB18C6 in toluene/acetone 1:2

For the Simplex optimization of I-129 extraction, three parameters were selected: HCl concentration, DC18C6 concentration, and the organic phase volume. The experimental results are displayed in Table V. Initial experimental conditions were manually established taking into account previous results obtained on the extraction of I-129 from a synthetic solution [6].

Table V. Experimental Conditions used for Simplex Optimization of I-129

Experiment	[HCl] (Mol.L ⁻¹)	[DC18C6] (Mol.L ⁻¹)	Organic Phase Volume (mL)	D _{I-129}
1	4	0.3	10	5.69
2	4.5	0.3	10	6.19
3	4	0.35	10	7.41
4	4	0.3	11	5.68
5	4.3	0.3	9	7.78
6	4.5	0.35	8	7.88
7	4.6	0.36	8.6	11.50
8	5	0.4	8	13.83
9	4.5	0.43	7	14.60
10	4.5	0.5	6	15.26

The final parameters values used for the I-129 extraction are displayed in Table VI.

Table VI. Final Parameter Values for I-129 Extraction Determined by Simplex Optimization

Aqueous Phase	Organic Phase
1 mL effluent stream diluted in 1N HCl KI (5g/L) Na ₂ S ₂ O ₅ (14g/L)	6 mL of 0.3M DC18C6 in tetrachloroethane

Selectivity of the procedures

To evaluate the influence of Sr-90 and its distribution coefficient while extracting Tc-99, DB18C6 was applied to extract Tc-99 from a synthetic solution composed of a mixture of Sr-90, and Tc-99. The Sr-90 concentration was 25 times the concentration of Tc-99 (Fig. 2). Sr-90 is a major fission product found in nuclear effluents. Fig. 2 displays the liquid scintillation plots of the aqueous and organic phases. Sr-90 remained in the aqueous phase and was not found to be extracted by DB18C6. After a few months, no Y-90 as daughter product of Sr-90 was detected in the organic phase demonstrating that Tc-99 was selectively extracted by DB18C6 crown ether. Actually, the selectivity of DB18C6 is revealed by its spatially rigid skeleton that is in favor of alkali metal ions such as Na⁺. The benzo groups allow the ring to be more rigid which result in lower binding constants for Sr²⁺. From an activity of Sr-90 of 3,400 Bq.mL⁻¹, only 0.2 Bq.mL⁻¹

were extracted and counted in the β -energy window of Tc-99, giving an apparent distribution coefficient as low as 6.10^{-5} .

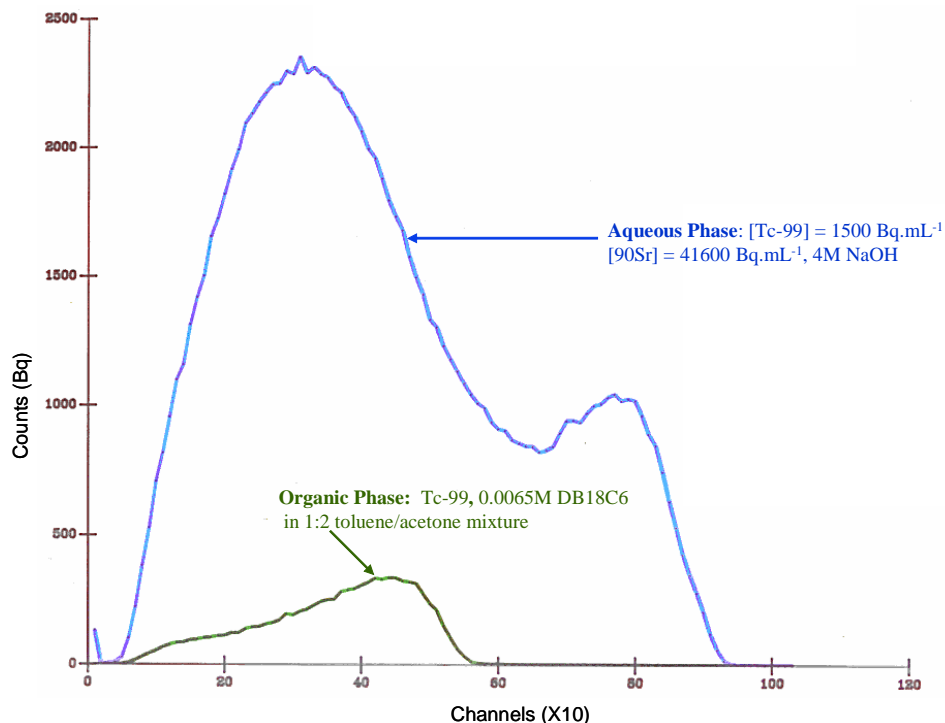


Fig. 2. Liquid scintillation profiles of Tc-99 in the organic and aqueous phases; organic phase: 0.0065 M DB18C6 in toluene/acetone 1:2; aqueous phase: [^{99}Tc]=1,500 Bq.mL $^{-1}$, [^{90}Sr] = 41,600 Bq.mL $^{-1}$, 4M NaOH

This procedure was applied to extract selectively Tc-99 from a synthetic effluent doped with Tc-99. The selectivity of the procedure previously described (see Table IV) was also demonstrated. The results of a gamma-ray spectrometric analysis on both the total waste and the organic phase after Tc-99 extraction from this doped effluent are shown in Table VII along with the corresponding distribution coefficients. These results, when compared to distribution coefficients of over 30 for Tc-99, clearly demonstrate the excellent selectivity of the proposed procedure, taking into account that only one extraction step is necessary in order to extract selectively Tc-99.

Table VII. Distribution Coefficients for Interfering Radionuclides During Tc-99 Extraction

Isotopes	Activity (KBq.L $^{-1}$)		D
	Total waste	Organic phase	
^{60}Co	33.6	0.0124	$3 * 10^{-4}$
^{95}Zr	18.1	0.024	$13 * 10^{-4}$
^{95}Nb	18.1	0.012	$7 * 10^{-4}$
^{106}Ru	130.0	0.12	$9 * 10^{-4}$
^{125}Sb	16.0	0.039	$24 * 10^{-4}$
^{134}Cs	20.9	0.012	$6 * 10^{-4}$
^{137}Cs	120.0	0.014	$1 * 10^{-4}$
^{144}Ce	93.3	0.094	$10 * 10^{-4}$

The selectivity of the I-129 extraction procedure as previously described (see Table VI) has been successfully demonstrated through its analysis. The results of a gamma-ray spectrometric analysis on both the total waste and the organic phase after I-129 extraction from an I-129 doped effluent are shown in Table VIII along with the corresponding distribution coefficients. These results, when compared to I-129 extraction yield of 90%, clearly demonstrate the excellent selectivity of the proposed procedure, taking into account that only one extraction step is necessary to selectively extract I-129.

Table VIII. Distribution Coefficients for Interfering Radionuclides During I-129 Extraction

Isotopes	Activity (KBq.L ⁻¹)		D
	Total waste	Organic phase	
Ru-106	3.10 ⁴	< 6	2.10 ⁻⁴
Sb-125	6.5.10 ²	< 2	3.10 ⁻⁴
Cs-134	4.5.10 ²	< 0.04	8.10 ⁻⁵
Cs-137	2.8.10 ³	5	1.8.10 ⁻³
Eu-154	6.10 ¹	< 10	1.6.10 ⁻¹
Am-241	3.2.10 ¹	< 10	1.75.10 ⁻¹

CONCLUSION

The method presented in this paper for the extraction of Tc-99 and I-129 from synthetic effluents present several features: (1) a considerable time saving over previous procedures since it takes only 20 minutes for the total separation time of a batch of 8 samples, (2) a extraction threshold of 200 Bq.L⁻¹ for Tc-99 and 60 Bq.L⁻¹ for I-129, (3) an excellent selectivity applying a single step extraction procedure.

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