SOLVENT EXTRACTION OF ^{99}Tc FROM RADIOACTIVE INTERMEDIATE LIQUID WASTE BY DIBENZO-18-CROWN-6

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ABSTRACT

Technetium is one of the most prominent problems since its most stable specie in the environment, the pertechnetate ion, is highly mobile and considered as a long-term hazard in nuclear waste disposal. Because of the small activities of ^{99}Tc relative to other fission products ^{137}Cs or ^{90}Sr, and its long half-life time ($t_{1/2} = 2.1 \cdot 10^5$ yrs), ^{99}Tc is one of the key isotopes that should always be analyzed in the radioactive liquid waste streams from the reprocessing industry where the largest concentrations are to be expected. Furthermore, as a pure beta-emitter, ^{99}Tc has to be isolated from the intermediate level waste (ILW) stream prior to any measurement in such complex media. We have developed a method for ^{99}Tc extraction providing recommendations that will be useful for extracting it from acid and basic ILW. The extraction of ^{99}Tc from ILW by dibenzo-18-crown-6 (DB18C6) has been investigated and a simplex optimization of key parameters involved in the procedure has allowed us to set up their best values. Experiments have been carried out on synthetic and real effluents from La Hague reprocessing plant, France, and results show that DB18C6 is highly selective towards ^{99}Tc. The application of this procedure has been successfully demonstrated through the analysis of actual waste streams coming from two reprocessing plants at La Hague and Marcoule, France.

INTRODUCTION

Technetium-99 is one of the fission products produced in a nuclear reactor, having a very long half-life, and a long β-activity decay chain. A concept regarding the nuclear fuel cycle, based on a specific ^{99}Tc separating procedure should be developed. There is a need for the development of new extractant systems, such as systems based on crown ethers (CE) that may serve to selectively extract and separate this long lived radionuclide from high-level nuclear waste (HLW) streams and concentrate it for feed to HLW vitrification. Since the discovery of crown ethers by C. Pedersen and D J. Cram [1,2], 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 is available on the extraction of ^{99}Tc [5-8]. In this paper, we report data on the solvent extraction of ^{99}Tc(VII) from synthetic and real effluents by dibenzo-18-crown-6.

EXPERIMENTAL

The NaOH, NaNO$_3$, NaCl, NaHCO$_3$ and ascorbic acid were purchased from Aldrich Chemicals suprapure (99.99%), 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 donated by Dr. J.F. Dozol, CEA Cadarache, France. The compound NH$_4$^{99}TcO$_4$ in 0.1 M NH$_4$OH was 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 an end-over-end rotation for 20 minutes at 25 °C. The aqueous and organic phases were sampled, and analyzed by liquid scintillation counting. The distribution coefficient D$_{Tc}$ was calculated as the ratio [Tc]$_{org}$/[Tc]$_{aq}$ after reaching the chemical equilibrium.

RESULTS AND DISCUSSION

Seven crown ethers from 12-crown-4 to 24-crown-8 in ring size (0.0065 M in toluene/acetone mixture) were evaluated for efficiency of pertechnetate (450 Bq.mL^{-1}) extraction from alkaline synthetic solution (Table I). DB18C6 was revealed to be the most efficient crown ether [8]. 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 ^{99}Tc. Moreover the presence of these benzo functional groups increase the solubility of the crown ether in the organic phase.

Table I: Extraction of pertechnetate by selected crown ethers; **Organic phase**: toluene/acetone 1:2 mixture at 25°C, [crown ether] = 0.0065M; **Aqueous phase**: 4M NaOH, [^{99}Tc] = 450 Bq.mL^{-1}.

Crown Ether	Cavity Diameter (Å)	log D$_{Tc-99}$
12C4	1.2 - 2.5	0.82
15C5	1.7 - 2.2	1.11
18C6	2.6 - 3.2	1.32
DC18C6	2.6 - 3.2	1.46
DB18C6	2.6 - 3.2	1.53
tBuB21C7	3.4 - 4.3	1.12
DC24C8	4.5 - 5.6	1.56

An intermediate-level nuclear waste (ILW) from La Hague (Table II) containing originally no ^{99}Tc was doped with a known amount of ^{99}Tc (1627 Bq.mL^{-1}) in order to optimize the different parameters, choice of the crown ether, choice of the diluent and influence of NaOH concentration.

Table II: Chemical composition of an ILW stream from La Hague, France.

Radioelement	Concentration (KBq.L^{-1})	Radioelement	Concentration (KBq.L^{-1})
^{60}Co	242	^{144}Ce	670
^{90}Sr	510	^{155}Eu	21
^{95}Zr	130	^{241}Am	72
^{95}Nb	130	^{234}U - ^{237}Np	4
^{106}Ru	932	^{238}Pu - ^{241}Am	110
^{125}Sb	115	^{239}Pu - ^{240}Pu	77
^{137}Cs	860	^{134}Cs	150

Extraction of pertechnetate from La Hague ILW Effluent doped by ^{99}Tc (1627 Bq.mL^{-1}) 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 relationship between the technetium distribution ratio and the crown ether concentration for the diluent dichloromethane. The dependence of the distribution coefficient of Tc on the concentration of the extractant DB18C6 takes the form of a straight line which a slope close to one, which demonstrates a Tc:DB18C6 ratio in the extractable compound equal to 1:1.
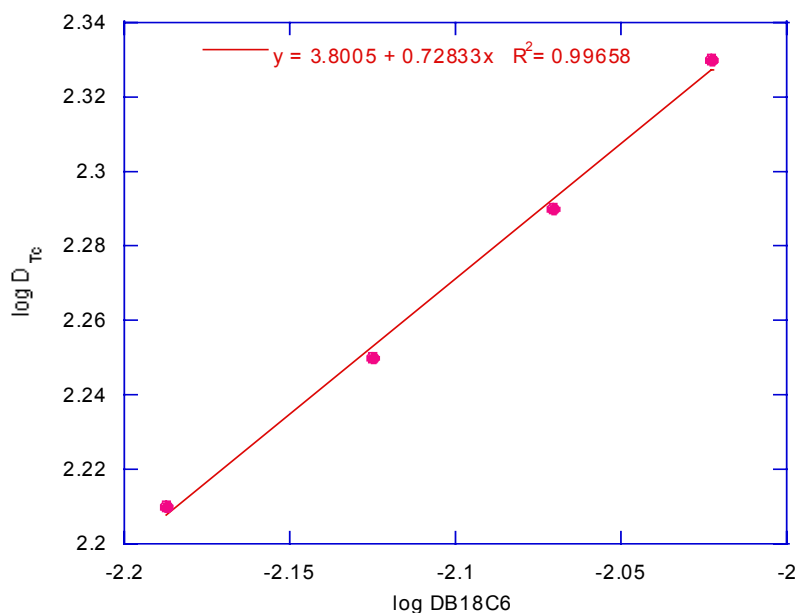

Fig. 1: Extraction of ^{99}TcO$_4^-$, **Organic phase**: DB18C6 in dichloromethane; **Aqueous phase**: La Hague ILW doped by ^{99}Tc (1627 Bq.mL^{-1}), [NaOH]= 4M, 0.5M ascorbic acid.

The influence of alkaline medium on the ^{99}Tc extraction was also investigated. In Fig. 2, the distribution coefficient D_{Tc} is plotted as a function of NaOH concentration in the aqueous phase using DB18C6 in a mixture toluene/acetone 1:2 at ambient temperature. Gradual increase in the extraction of [99]TcO$_4^-$ was obtained up to about 2M NaOH where the slope is 0.25 ± 0.02. This observation reveals that the number of extracted NaOH molecules doesn't vary with the initial concentration of NaOH in the aqueous phase.
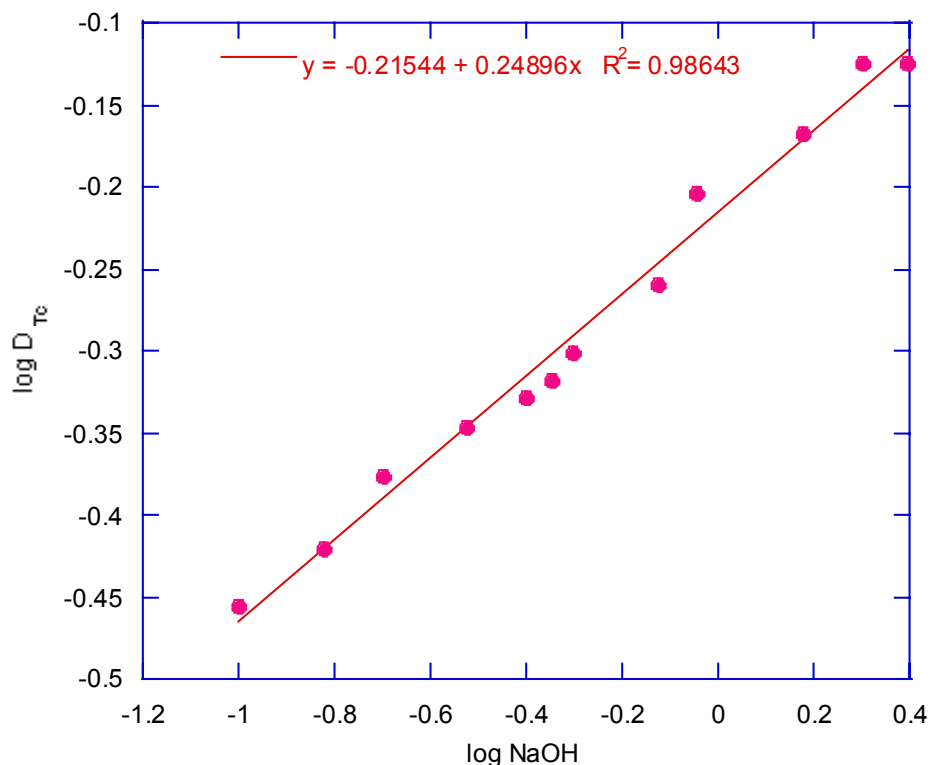

Fig. 2: Extraction of [99]TcO$_4^-$ from a ^{99}Tc doped La Hague ILW; **Organic phase**: 0.0075 M DB18C6 in toluene/acetone 1:2; **Aqueous phase**: [^{99}Tc] = 1120 Bq.mL^{-1}, 0.5 M ascorbic acid, 4 M NaOH.

In order to increase the extraction yield of ^{99}Tc, a SIMPLEX optimization procedure [9] 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 step such as NaOH concentration, DB18C6 concentration, and ascorbic acid concentration applied to the La Hague effluent doped with 1120Bq.mL^{-1} of ^{99}Tc are displayed in Table III. The three initial experimental conditions were manually established taking into account previous results obtained on the extraction of ^{99}Tc from a synthetic solution [6,8].

Table III: Experimental conditions used for the simplex optimization procedure

Experiment	4M NaOH (mL)	DB18C6 ($* 10^{-3}$ Mol.L^{-1})	Ascorbic acid (Mol.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 key parameters values used for the ^{99}Tc extraction from ILW are displayed in Table IV.

Table IV: Final values of key parameters determined by a simplex optimization [6].

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

In order to evaluate the distribution coefficient of ^{90}Sr, DB18C6 was applied to extract ^{99}Tc from a synthetic solution composed of a mixture of ^{90}Sr, and ^{99}Tc, with a 25 fold higher ^{90}Sr concentration than ^{99}Tc (Fig. 3). Fig. 3 displays the liquid scintillation plots of the aqueous and organic phases, and as it is shown, ^{90}Sr remained in the aqueous phase and was not found to be extracted by DB18C6. After a few months, no ^{90}Y presence was detected in ^{99}Tc window, and proved the effective selective extraction of only ^{99}Tc. 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 ^{90}Sr^{2+}. From an activity of ^{90}Sr of 3400 Bq.mL^{-1}, only 0.2 Bq.mL^{-1} were extracted and counted in the ^{99}Tc window, giving an apparent distribution coefficient as low as 6.10^{-5}. Finally, the method presented in this paper for the determination of ^{99}Tc in such complex media as real effluents was tested on four different ILW from the reprocessing industries: La Hague and Marcoule, France (Table V). We observed a simultaneous extraction of ^{99}Tc and ^{3}H as it is shown in Fig. 4. We assumed that ^{3}H was extracted under its cationic form ^{3}H$_3$O^{+} and fitted into the DB18C6 cavity meanwhile, ^{99}Tc was extracted as the counter-anion. Both activities were determined by scintillation counting using a dual label calculation, and the ^{3}H extraction did not interfere in the determination of ^{99}Tc activity in a real effluent.
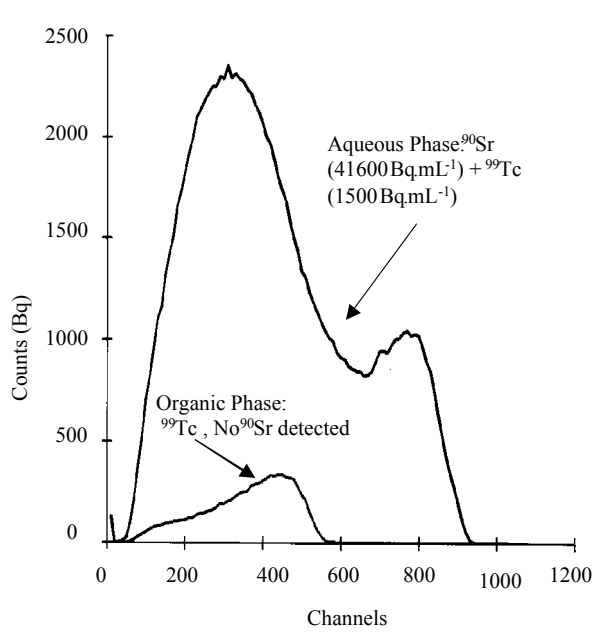
Fig. 3: Liquid scintillation profiles of ^{99}Tc in the organic and aqueous phases;
 Organic Phase:
0.0065 M DB18C6 in toluene/acetone 1:2;
Aqueous Phase: [^{99}Tc]=1500 Bq.mL^{-1}, [^{90}Sr] = 41600 Bq.mL^{-1}, 4M NaOH
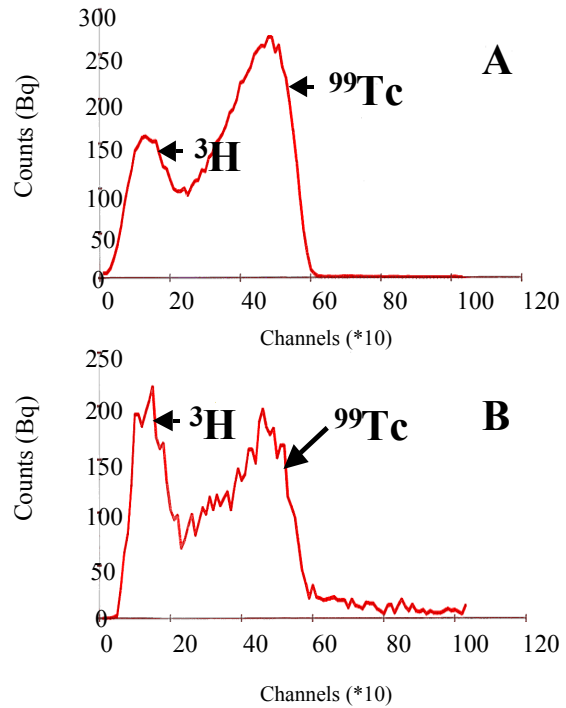
Fig. 4: Liquid scintillation profiles of ^{99}Tc in the organic phase extracted from
A: Synthetic Solution (^{3}H–^{99}Tc, 450 Bq.mL^{-1} and 750 Bq.mL^{-1} respectively),
and B: La Hague Effluent.
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Table V: ^{99}Tc activity and principal radionuclides activities analyzed from different effluents from La Hague and Marcoule reprocessing plants.

	Activities (KBqL^{-1})			
Isotopes	Effluent A	Effluent B	Effluent C	Effluent D
^{22}Na	10	0.0056	7.3	8.4
^{54}Mn	2	--	--	--
^{57}Co	16	2.3	2	3
^{95}Zr	11	--	9.5	11
^{99}Tc	**1750**	**70**	**1100**	**1300**
^{106}Ru	534	4.5	742	1259
^{137}Cs	523	10	1402	2762
^{144}Ce	306	2.5	34	35
^{155}Eu	69	--	765	631
^{241}Am	21	1	126	817

CONCLUSION

The method presented in this paper for the extraction of ^{99}Tc in real effluents from the French reprocessing industry present several features: (1) a considerable saving of time over previous procedures since it takes only 20 minutes for the total separation time of a batch of 8 samples, (2) a detection limit of 200 Bq.L^{-1} in real wastes which is largely sufficient for ILW from the reprocessing industry, (3) an excellent selectivity with only one step extraction.

ACKNOWLEDGMENTS

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