

Stability of Different BTBP and BTPPhen Extracting or Masking Compounds against γ Radiation

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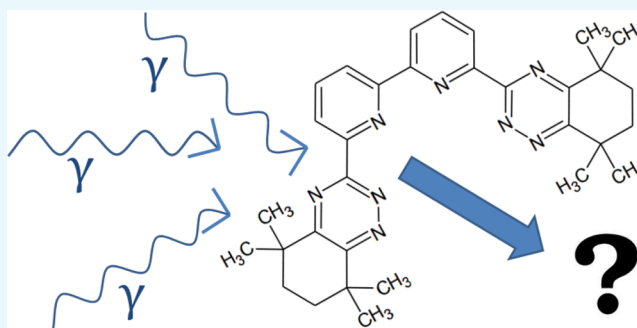
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ABSTRACT: The radiolytic stability of hydrophobic extracting compounds CyMe₄-BTBP and CyMe₄-BTPPhen and a hydrophilic masking agent (PhSO₃H)₂-BTPPhen, widely employed for trivalent minor actinoid and lanthanoid separation, against γ radiation was tested. Even though the solvent with a promising fluorinated diluent BK-1 provides better extraction properties compared to octan-1-ol, its radiation stability is much lower, and no extraction was observed already after an absorbed dose of 150 kGy (CyMe₄-BTBP) or 200 kGy (CyMe₄-BTPPhen). For the (PhSO₃H)₂-BTPPhen hydrophilic masking agent, the results showed that the rate of radiolytic degradation was significantly higher in 0.25 M HNO₃ than in 0.5 M HNO₃. For both the hydrophobic and hydrophilic agents, degradation was slower in the presence of both



organic and aqueous phases during irradiation.

INTRODUCTION

SANEX [selective actinoid (An) extraction] processes are currently studied on a laboratory scale to separate trivalent minor (An's) and lanthanoids (Ln's) during An partitioning from irradiated nuclear fuel for their transmutation. In these processes, different hydrophilic and hydrophobic liquid–liquid extraction systems are used that consist either of An-/Ln-selective hydrophobic extractants in the organic phase or An-/Ln-selective complexants in the aqueous phase. In systems with hydrophobic extractants in the organic phase (also called *r*-SANEX; regular SANEX), CyMe₄-BTBP (Table 1) is currently the European reference extraction molecule. This ligand has promising potential since it is relatively resistant to both the acidic environment and the ionizing radiation.¹ Unfortunately, the kinetics of metal extraction using CyMe₄-BTBP is relatively slow. This disadvantage led to the development of CyMe₄-BTPPhen (Table 1) in which the bipyridine group was replaced by a phenanthroline unit.² This development had a positive effect on extraction kinetics and thermodynamics. The distribution ratios of Am(III) and Eu(III) were found to be higher compared to CyMe₄-BTBP, and the kinetics of extraction was also much faster.³ In the currently considered partitioning schemes, it is preferred that both the extracting molecules and diluents meet the so-called “CHON principle”—they consist of carbon, hydrogen, oxygen, and nitrogen atoms only. Such extractants and diluents can be completely incinerated, releasing only CO₂, nitrogen oxides, and H₂O, thus contributing to the minimization of secondary waste.⁴

Recently, polar diluents containing fluorine (or sulfur) have also been tested as an alternative to hydrocarbon diluents and are considered promising.⁵ As an example, F-3 (*meta*-nitrobenzotrifluoride) or FS-13 (phenyltrifluoromethylsulfone)—aromatic polar diluents with low viscosity, high density, and good chemical stability—may be listed. In addition to other advantages, their high density ensures good phase separation during metal extraction.⁶ A new group of these polar fluorinated diluents includes carbonates of fluorinated alcohols, for example, BK-1 (carbonate of 2,2,3,3-tetrafluoropropan-1-ol; Table 1) or BK-2 (carbonate of 2,2,3,3,4,4,5,5-octafluoropentan-1-ol).⁷ The advantage of these diluents is their chemical stability and high polarity. Polar solvents increase the carrying capacity of the organic phase and reduce the probability of the formation of a third phase.⁸ However, the solubility of CyMe₄-BTBP or CyMe₄-BTPPhen in BK-1 is only approximately 0.004 M, and it is lower than in diluents such as FS-13 or octan-1-ol.⁸ It makes the practical applicability of this diluent in an industrial process questionable.

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Table 1. Structures of Extracting/Masking Agents and Diluents

Structure	Name and abbreviation
	6,6'-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-1,2,4-triazin-3-yl)-2,2'-bipyridine (CyMe ₄ -BTBP)
	2,9-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-1,2,4-triazin-3-yl)-phenanthroline (CyMe ₄ -BTPhen)
	Carbonate of 2,2,3,3-tetrafluoropropan-1-ol (BK-1)
	<i>N,N,N',N'</i> -Tetra(<i>n</i> -octyl)diglycolamide (TODGA)
	3,3',3'',3'''-[3-(1,10-Phenanthroline-2,9-diyl)-1,2,4-triazine-5,5,6,6,-tetrayl] tetrabenzensulfonic acid ((PhSO ₃ H) ₂ -BTPhen)

The radiation stability of different variations of the r-SANEX system has been widely studied in the last 2 decades. This research focused mainly on the molecules CyMe₄-BTP, C5-BTBP, CyMe₄-BTBP, and CyMe₄-BTPhen in different types of diluents, such as octan-1-ol or its mixtures, FS-13, cyclohexanone, or its derivatives.^{5,9–13} Each solvent behaved differently under irradiation. First, a difference was found in the distribution ratio (*D*-values) when only the organic phase was irradiated and when the organic phase was irradiated in contact with the aqueous phase.⁹ For example, in the case of CyMe₄-BTBP dissolved in octan-1-ol, the distribution ratios of both Am(III) and Eu(III) decrease with increasing absorbed dose. Extraction of Am(III) was observed up to 200 kGy (residual concentration of CyMe₄-BTBP was 1%) and for Eu(III) only up to 100 kGy, where the residual concentration was 20%. However, when the system was in contact with 1 M HNO₃ during irradiation, extraction was possible for both radionuclides still at 300 kGy (residual concentration of the molecule was 53%), while the decreasing trend was maintained

as the dose increased.⁹ Second, different extracting molecules display different radiation stabilities in the same diluent. For instance, when the ligands dissolved in octan-1-ol were irradiated in the presence of 1 M HNO₃, the residual concentration of CyMe₄-BTBP was 47% of the initial value at 300 kGy; however, only 7% of CyMe₄-BTPhen remained undegraded at the same dose. Finally, the general trend that *D*-values decrease with increasing dose, observed for most diluents,^{9,14} is reversed for both ligands in the FS-13 diluent. The systems with FS-13 are less prone to degradation than those with octan-1-ol or cyclohexanone (faster degradation of the ligand is observed). However, for CyMe₄-BTBP or CyMe₄-BTPhen in FS-13, both *D*_{Am} and *D*_{Eu} values remain constant or increase with increasing dose, and even the SF_{Am/Eu} (SF = separation factor) values increase. It has been suggested that this behavior is caused by the fact that the products/adducts formed during irradiation in FS-13 are more powerful extractants than CyMe₄-BTPhen itself.¹⁰

The An-selective N-donor BTP, BTBP, and BTPhen ligands are typically used in the organic phase for trivalent An extraction purposes. However, another possibility for making these ligands water-soluble involves functionalization with, for example, sulfonyl groups¹⁵ or other polar groups meeting the CHON principle.^{16–18} Such ligands maintain their coordination properties as they are still capable of forming complexes with trivalent An's selectively. Deployment of hydrophilic An-selective N-donor ligands as masking agents is the key principle of i-SANEX (innovative SANEX) systems.¹⁹

In i-SANEX systems, the aqueous phase usually consists of an acidic medium; in most cases, nitric acid, in which hydrophilic An-selective masking agents are dissolved. Based on numerous factors, such as the acidity of the aqueous medium, concentration of the masking agent, temperature, absorbed dose, and so forth, the extraction results vary broadly.^{20–23} The An(III)/Ln(III) separation is accomplished by the transfer of Ln's to the organic phase, typically as complexes with TODGA (*N,N,N',N'*-tetra(*n*-octyl)-diglycolamide; Table 1), while the majority of An's remains in the aqueous phase in the form of complexes with the masking agent. Numerous compositions of organic phases were investigated, for instance, several modifications of TODGA dissolved in various diluents (kerosene, toluene, *n*-dodecane, *n*-hexane, xylene, and octan-1-ol).²⁴ However, 0.20 M TODGA with 5 v/v % octan-1-ol in an inert diluent such as kerosene or hydrogenated tetrapropylene is used as a reference solvent. Octan-1-ol serves here as a phase modifier preventing the third phase formation.²⁰ In general, the increase in nitric acid concentration suppresses the masking agent's selectivity. It can be explained by the protonation of the coordinating nitrogen atoms resulting in a decrease in the free concentration of ligand and in a drop in selectivity.¹⁵ Consequently, an increase in the distribution ratio values is observed. Because of the steeper increase in the Am(III) distribution ratio values, a steady decrease of the separation factor $SF_{Eu/Am}$ is observed with increasing HNO₃ concentration. It was also observed that with increasing concentration of the masking agent, the extraction of Am(III) is strongly suppressed, whereas the extraction of Eu(III) is not affected to such extent. This leads to an increase in the SF of Am(III)/Eu(III) as it is the product of both TODGA's and masking agent's selectivity.^{21,25}

The performance of some of the i-SANEX systems under irradiation has already been studied. A study of the system with (PhSO₃H)₂-BTP in 0.35 M HNO₃ was performed by Galán et al.²⁶ They found that with increasing dose (up to 300 kGy), the D_{Eu} values increased only slightly, while the observed D_{Am} values increased rapidly (by more than 2 orders of magnitude). After exceeding the dose of 300 kGy, both D -values started to decrease, and this decrease continued up to a dose of 1000 kGy. The authors assumed that 50 and 90% of the masking agent were degraded at 60 and 250 kGy, respectively.²⁶ Even much faster degradation of sulfonated (PhSO₃H)₂-BTP and (PhSO₃H)₂-BTBP was found in another article where 90% of the masking agents are claimed to have been destroyed already after absorbing a dose of 1 kGy.²⁷ This surprisingly high rate of degradation could also have been caused by different conditions during irradiation [masking agents were dissolved only in ultra-pure water and at very low concentrations (not exceeding the value of 0.2 mM)]. Another study of this system was performed under continuous irradiation in an irradiation loop.²⁰ It was observed that the distribution ratios of Am(III) and Eu(III) for an irradiated system consisting of 0.2 M

TODGA with 5 v/v % octan-1-ol in dodecane as the organic phase and 0.018 M (PhSO₃H)₂-BTP in 0.35 M nitric acid as the aqueous phase did not exhibit a significant dependence on the absorbed dose up to a total dose of 174 kGy.

Herein, we focus on the radiation stability of both hydrophobic and hydrophilic ligands. The first aim has been to obtain data on the radiation stability of solvents containing CyMe₄-BTBP or CyMe₄-BTPhen (dissolved in BK-1 diluent). A decrease in the D 's for Am(III), Eu(III), and Cm(III) from 1 M HNO₃ in these solvents after irradiation by ⁶⁰Co γ radiation up to 300 kGy along with the concentrations of the undestroyed ligand were studied as the main factors relevant for further considerations about the use of BK-1. The second objective has been to study the influence of γ radiation on the ability of the hydrophilic masking agent (PhSO₃H)₂-BTPhen (Table 1) to selectively suppress the extraction of Am(III) and/or Cm(III) in the presence of Eu(III) from HNO₃ solutions into a TODGA-based solvent. This promising masking agent has been widely studied.^{22,28,29} However—to the best of our knowledge—the radiation stability of (PhSO₃H)₂-BTPhen or the impact of irradiation on the separation of An(III) from Ln(III) in systems with (PhSO₃H)₂-BTPhen has not yet been reported.⁹ The structure of all used diluents and extracting/masking compounds is shown in Table 1.

RESULTS AND DISCUSSION

Radiation Stability of the Solvents Containing CyMe₄-BTBP or CyMe₄-BTPhen in BK-1 Diluent. The behavior of i-SANEX solvents based on carbonates of fluorinated alcohols was investigated under γ irradiation. The extraction system consisted of two immiscible phases, the organic phase consisted of a 0.001 M solution of CyMe₄-BTBP or 0.001 M CyMe₄-BTPhen dissolved in the fluorinated diluent BK-1, and the aqueous phase was represented by 1 M HNO₃. Extraction properties of the solvents were determined for two different experimental setups—irradiation of the neat solvent or irradiation of the solvent in contact with 1 M HNO₃. The residual concentration of the extracting compounds was determined by HPLC in all the irradiated solvents.

Fast degradation was observed in all samples measured. Complete degradation was observed in both series without contact with acid even after a dose of 50 kGy. The highest stability was observed for the CyMe₄-BTBP series in contact with 1.0 M HNO₃ in which the concentration of the ligand decreased gradually up to 150 kGy. The concentrations found for this series are summarized in Table 2. Surprisingly enough, the concentrations of the original ligand in the irradiated samples of CyMe₄-BPhen showed a much steeper decrease, and no protective effect of contact with 1 M HNO₃ could be seen. Only approximately 1% of undestroyed ligand could be detected after a dose of 50 kGy (data not shown).

Table 2. Residual Concentrations of CyMe₄-BTBP in BK-1 Irradiated in Contact with 1 M HNO₃

dose [kGy]	remaining CyMe ₄ -BTBP [%]	r.s.d. [%]
50	35.5	1.2
100	25.7	0.6
150	6.1	1.8
200	0	

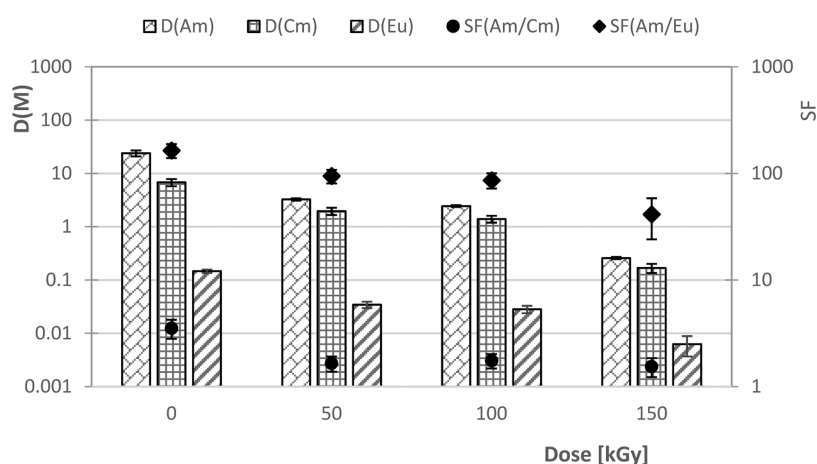


Figure 1. Extraction of Am(III), Cm(III), and Eu(III) by 0.001 M CyMe₄-BTBP in BK-1 from 1 M HNO₃ solution as a function of absorbed dose. Organic phase irradiated in contact with the aqueous phase. Mixing time: 60 min/1800 min⁻¹ and temperature: 22 ± 1 °C.

When examining the extraction properties of the solvents, in the first group of samples, where only the solvent was irradiated, the activity of Am(III), Eu(III), and Cm(III) in the organic phase after shaking was below the detection limit for both the solvents with CyMe₄-BTBP or CyMe₄-BTPhen, indicating that there were no extracting molecules, or their extracting adducts remained in the system after the absorbed dose of 50 kGy. This correlates well with the result of residual concentrations of the extracting molecules tested where no initial compound was found even after a dose of 50 kGy. In a reference system with octan-1-ol,⁹ when only the organic phase was irradiated, Am(III) extraction also decreased faster as the absorbed dose increased compared to conditions when the organic phase was irradiated in contact with the aqueous phase. In this case, the solvent with CyMe₄-BTBP extracted Am(III) up to 150 kGy, and the solvent with CyMe₄-BTPhen was able to extract Am(III) up to 300 kGy.⁹

Next, the radiation stability of the solvents in contact with 1 M HNO₃ during irradiation was investigated. For the solvent with CyMe₄-BTBP, the individual distribution ratios and SFs found are shown in Figure 1. The results show that CyMe₄-BTBP was able to extract, at least to some extent up to a dose of 150 kGy, where the values of the distribution ratios fell below 1. The HPLC analysis revealed that ca. 94% of the ligand was degraded at this dose (cf. Table 2). At a dose of 200 kGy, the ligand was already completely degraded and, in accordance with this, the solvent was not capable of being extracted. The values of D_{Am} , D_{Eu} , and $SF_{Am/Eu}$ decreased monotonously with increasing dose and decreasing residual concentration of the ligand. In the non-irradiated sample, $D_{Am} = 24 \pm 3$, $D_{Eu} = 0.15 \pm 0.01$, and $SF_{Am/Eu} = 164 \pm 24$. These values drop to $D_{Am} = 0.26 \pm 0.01$, $D_{Eu} = 0.006 \pm 0.003$, and $SF_{Am/Eu} = 41 \pm 17$, respectively, at an absorbed dose of 150 kGy. When comparing the Am(III) and Cm(III) separation, the system behavior was similar; the highest observed SF was found in the non-irradiated sample ($SF_{Am/Cm} = 2.6 \pm 0.9$), and the values after irradiation dropped to around $SF_{Am/Cm} = 1.8 \pm 0.3$. Compared to the system containing the octan-1-ol diluent, the studied solvent based on the fluorinated diluent BK-1 was less resistant to radiation. Indeed, the CyMe₄-BTBP molecule in octan-1-ol was still able to be extracted at doses of 300 kGy (if irradiated in contact with aqueous phase), where $D_{Am} = 1$ and $D_{Eu} = 0.05$.⁹

To assess the extracting properties of the CyMe₄-BTBP radiolysis products, theoretical D -values were calculated based on the D -values in the non-irradiated sample and the residual CyMe₄-BTBP concentrations in the irradiated samples; 1 metal/2 CyMe₄-BTBP stoichiometry was assumed. As can be seen from the results shown in Table 3, all the theoretical D -

Table 3. Comparison of Experimental D_{exp} and Theoretical D_{theo} Values of Am(III), Eu(III), and Cm(III) Extraction for the Irradiated Solvent with 0.001 M CyMe₄-BTBP in BK-1 Diluent (Solvent Irradiated in Contact with 1 M HNO₃ Aqueous Phase; 1:2 Stoichiometry Assumed in the Calculation)

dose (kGy)	Am(III)		Eu(III)		Cm(III)	
	D_{exp}	D_{theo}	D_{exp}	D_{theo}	D_{exp}	D_{theo}
0	24.0		0.15		7.0	
50	3.2	3.1	0.034	0.019	2.0	0.91
100	2.4	1.6	0.028	0.010	1.4	0.47
150	0.3	0.09	0.006	0.001	0.17	0.025

values are lower than the respective experimentally observed values. The most plausible explanation for this effect is that the primary radiolytic products are also, to some extent, able to extract the target radionuclides. This conclusion is in agreement with the earlier observations made for the solvent with the octan-1-ol diluent.⁹

According to the HPLC–MS results, the peaks corresponding to the main products originating from the reactions of CyMe₄-BTBP ($m/z = 535$) with solvent molecules and the degradation products were detected across the series up to total decomposition, around 200 kGy. In the following text, M represents CyMe₄-BTBP, X represents BK-1, and Y means 1,1,2,2-tetrafluoroethane. The pattern observed throughout the spectra of irradiated samples measured (50–150 kGy) was quite uniform and consisted of well distinguishable peaks corresponding to the addition of either one or two molecules of the diluent $[M + X]^+$ or its degradation product, such as 1,1,2,2-tetrafluoroethane $[M + Y]^+$, to the CyMe₄-BTBP scaffold with loss of two protons to form a covalent bond. Adducts with both variants can also be found in high representation $[M + Y + X]^+$ with increasing dose (Figure 2). Also, along with this dose trend used, the relative abundance of the peaks was found to clearly move to higher

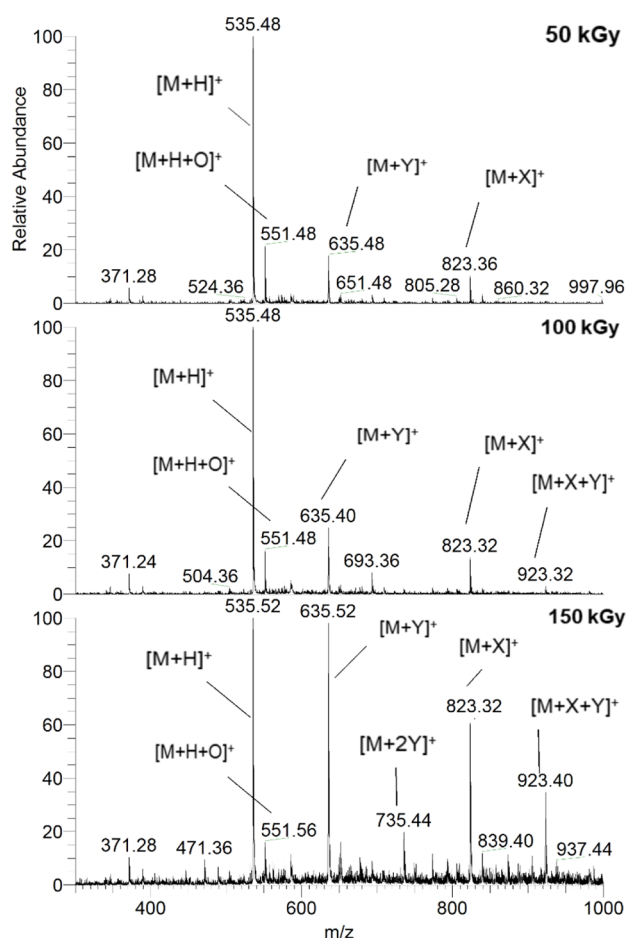


Figure 2. Mass spectra of CyMe₄-BTBP irradiated in BK-1 by a dose of 50–150 kGy in contact with 1 M HNO₃ (M = CyMe₄-BTBP, X = BK-1, and Y = 1,1,2,2-tetrafluoroethane).

mass adducts with the solvent and its part, together with a declining trend in the concentration of CyMe₄-BTBP. Other peaks in the spectra of the irradiated samples were found to be accompanied by smaller peaks with a mass increase of 16 mass units ($m/z = 551$ and 651), which probably corresponds to the addition of an OH group. The relative abundance of the peaks corresponding to higher mass products increased depending on the absorbed dose. Furthermore, the presence of several isomers of same mass (e.g., m/z 551 and 635) at different ratios was observed by the HPLC–MS measurements; an example is given in Figure 3.

For the solvent with CyMe₄-BTPhen, the distribution ratios and SFs are shown in Figure 4. In contrast to CyMe₄-BTBP, it is possible to extract Am(III), Eu(III), and Cm(III) up to 200 kGy with this solvent. The values for D_{Am} , D_{Eu} , and $SF_{Am/Eu}$ decreased with increasing doses, similar to CyMe₄-BTBP. In the non-irradiated sample, $D_{Am} = 142 \pm 42$, $D_{Eu} = 0.60 \pm 0.03$, and $SF_{Am/Eu} = 237 \pm 71$. These values dropped to $D_{Am} = 0.126 \pm 0.007$, $D_{Eu} = 0.006 \pm 0.003$, and $SF_{Am/Eu} = 21 \pm 12$ at the dose of 200 kGy. This behavior seems to contradict the results from the HPLC assay of CyMe₄-BTPhen concentration since no original CyMe₄-BTPhen ligand could be observed in the solvent already after an absorbed dose of 50 kGy. The most probable explanation for this discrepancy is that the CyMe₄-BTPhen radiolysis products are also able to extract the target radionuclides. Based on this assumption, it can be further hypothesized on the basis of the data obtained that the

radiolysis proceeds through primary product(s) with an extraction ability similar to or slightly lower than that of the parent molecule (no parent molecule was present at 50 kGy, while the D -values dropped only about twice) to the secondary non-extracting products of deeper radiolysis (steady decrease of D -values beyond 50 kGy). When correlated with the HPLC–MS analysis shown above, we can further anticipate that these primary (extracting) products are adducts corresponding to $[M + X]^+$ and $[M + Y]^+$, while the products of deeper radiolysis that do not extract would be the BK-1 adducts with two molecules of the diluent $[M + 2X]^+$, its degradation product 1,1,2,2-tetrafluoroethane $[M + 2Y]^+$ or both $[M + Y + X]^+$ (M represents CyMe₄-BTBP, X represents BK-1, and Y represents 1,1,2,2-tetrafluoroethane).

Considering the Am(III)/Cm(III) separation, the values of the SF remain similar for the non-irradiated and irradiated samples; $SF_{Am/Cm}$ was between 2.4 ± 1.1 and 2.9 ± 0.4 . When we compared the stability of the system consisting of CyMe₄-BTPhen in BK-1 and that in octan-1-ol, the former solvent was found to be more prone to radiolysis. This is similar to the behavior of CyMe₄-BTBP in BK-1 diluent. In octan-1-ol, the extraction by CyMe₄-BTPhen was still feasible up to the absorbed dose of 300 kGy, where the measured distribution ratios of Am(III) and Eu(III) were approximately $D_{Am} = 100$ and $D_{Eu} = 1$.

On comparing the results shown above for the solvents with BK-1 diluent with earlier data obtained with octan-1-ol, it can be concluded that the systems behave in a similar way, even though the radiation stability of the systems with BK-1 was inferior to those with octan-1-ol. In both diluents, a decreasing trend for the distribution ratios as the absorbed dose increased was observed. This differs from the behavior observed in an analogous system containing another fluorinated solvent FS-13, where the distribution ratios showed an increase upon increasing the absorbed dose. This curious observation may be explained in terms of the higher extraction efficiency of CyMe₄-BTPhen radiolysis products when compared with that of the parent molecule. In addition, the degradation products appeared to possess a better selectivity for the separation of Am(III) from Eu(III).¹⁰ This diluent-dependent behavior is depicted in more detail in Table 4, where changes in the D -values measured with CyMe₄-BTPhen systems are compared for five different diluents after irradiation by a dose of 100 kGy in contact with 1 M HNO₃. As can be seen, BK-1 behaves in a similar way as the previously studied cyclohexanone-based diluents—after irradiation, D_{Am} and D_{Eu} decreased to values close to 10% of the original value measured for non-irradiated solvents.¹⁴ This dramatically differs from the behavior of the system with FS-13 diluent where multiple increases of D -values were observed.¹⁰

Masking Properties and Radiation Stability of (PhSO₃H)₂-BTPhen. The results presented in Figure 5 compare systems with 0.2 M TODGA in the organic phase for four different HNO₃ concentrations, either without (B = blank) or with the presence of 0.01 M (PhSO₃H)₂-BTPhen as the masking (complexing) agent. The results showed increasing trends in distribution ratios of both Am(III) and Eu(III) with increasing HNO₃ concentration. For the blanks (in the absence of the masking agent), both D_{Eu} and D_{Am} were higher than 1 (D_{Am} increased from 9.4 ± 0.4 in 0.25 M HNO₃ to 175 ± 31 in 1 M HNO₃; D_{Eu} followed the same trend, but the values were slightly higher) and the $SF_{Eu/Am}$ slowly decreased with increasing acidity from 6.2 ± 0.8 at 0.25 M

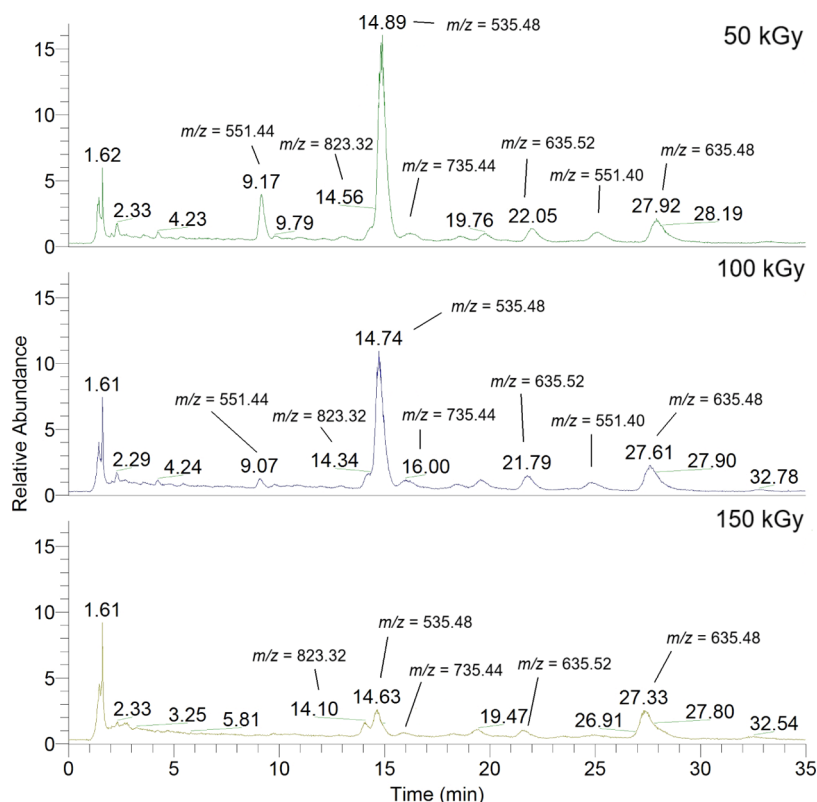


Figure 3. HPLC–MS chromatograms showing separation of the CyMe₄-BTBP samples irradiated in BK-1 in contact with 1 M HNO₃ by various doses in the range 50–150 kGy. The peak with $m/z = 535.48$ corresponds to residual CyMe₄-BTBP, and other peaks can be attributed to degradation products. Conditions: MS detection flow rate, 0.5 mL/min; column, Gemini-NX C18 110 Å (3 μ m, 150 \times 3.00 mm I.D.); mobile phase, 0.010 M DEAO (pH: 8.2) with 78% ACN.

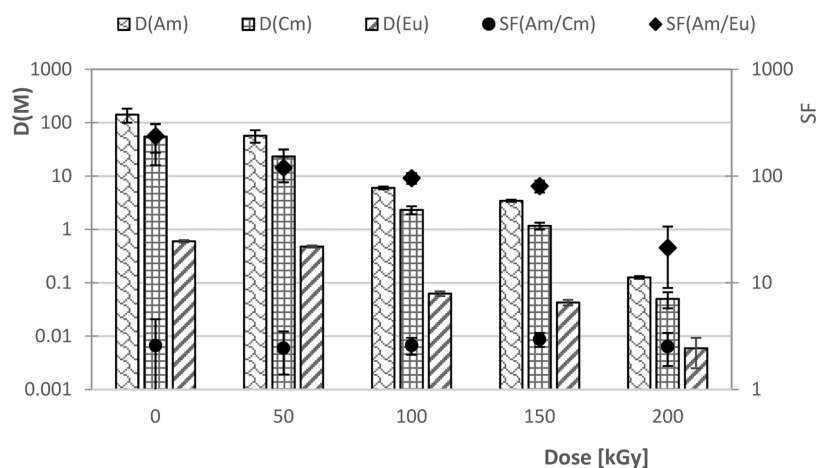


Figure 4. Extraction of Am(III), Cm(III), and Eu(III) by 0.001 M CyMe₄-BTPhen dissolved in BK-1 from 1 M HNO₃ solution as a function of absorbed dose. Organic phase is irradiated in contact with the aqueous phase. Mixing time: 60 min/1800 min⁻¹; temperature: 22 \pm 1 $^{\circ}$ C.

Table 4. D_{Am} and D_{Eu} (D_{irr}) Values Measured for CyMe₄-BTPhen in Selected Diluents after Irradiation with a Dose of 100 kGy Expressed Relative to Those of Non-Irradiated Samples (D_0)^a

diluent	D_{irr}/D_0 [%]				
	BK-1 ^b	cyclohexanone ¹⁴	3-methyl cyclohexanone ¹⁴	2,6-dimethyl cyclohexanone ¹⁴	FS-13 ¹⁰
Am	3	15	4	11	4200
Eu	10	5	6	50	380

^aThe aqueous phase was 1 M HNO₃. During irradiation, the solvent was in contact with 1 M HNO₃. ^bThis work.

HNO₃ down to 2.2 \pm 1.4 at 1 M HNO₃. For samples with (PhSO₃H)₂-BTPhen, D_{Eu} increased from 0.69 \pm 0.02 in 0.25

M HNO₃ to $D_{\text{Eu}} = 175 \pm 44$ in 1 M HNO₃. The dependence of the extraction of Am(III) on the HNO₃ concentration was

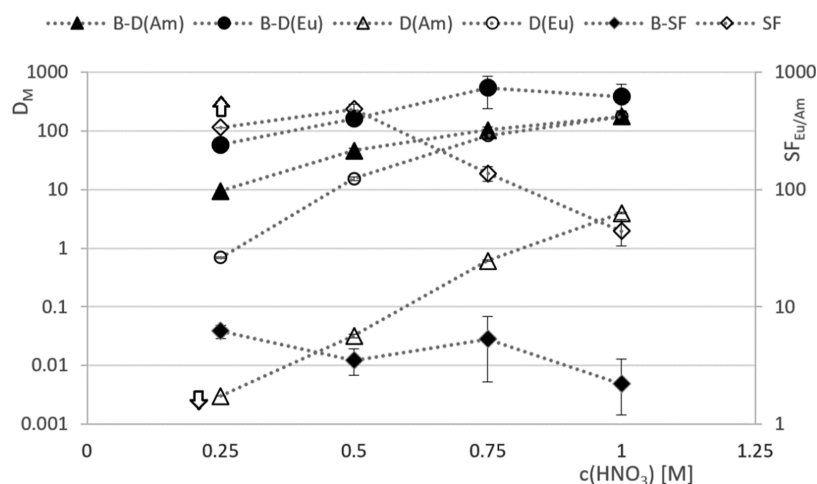


Figure 5. Extraction of Am(III) and Eu(III) from HNO₃ by TODGA (0.2 M dissolved in 5 vol % octan-1-ol in kerosene) in the absence (blank = B samples) or presence of (PhSO₃H)₂-BTPhen (0.01 M) in the aqueous phase as a function of initial HNO₃ concentration. Contact time: 360 min/250 min⁻¹; temperature: 22 ± 1 °C. The arrow means that the value was higher/lower than the corresponding limit of detection shown.

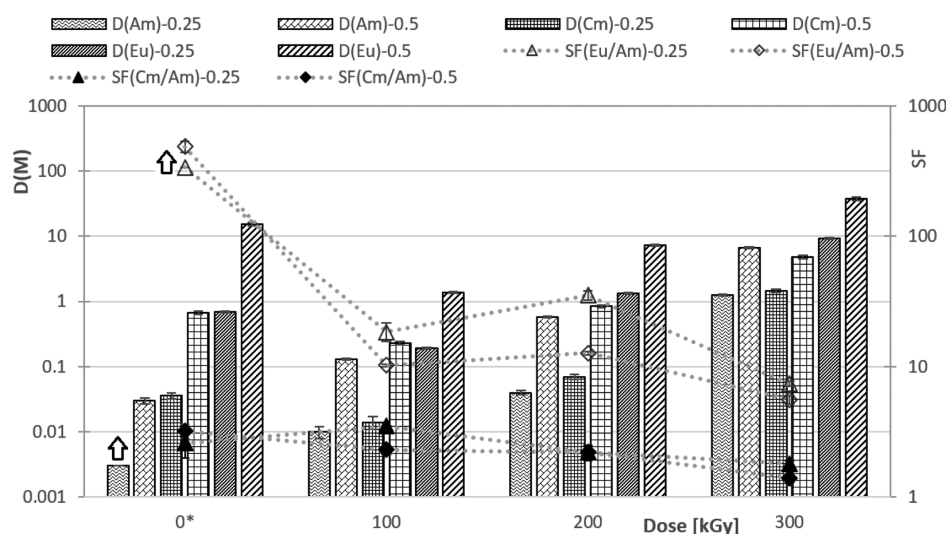


Figure 6. Extraction of Am(III), Cm(III), and Eu(III) from 0.25 M or 0.5 M HNO₃ by TODGA (0.2 M dissolved in 5 vol % octan-1-ol in kerosene) in the presence of (PhSO₃H)₂-BTPhen (0.01 M) in the aqueous phase as a function of the absorbed dose; neat aqueous phase irradiated, mixing time: 60 min/1800 min⁻¹; temperature: 22 ± 1 °C. * Data for non-irradiated Cm(III) extraction are taken from our publication.¹⁵ The arrow means that the value was higher/lower than the corresponding limit of detection shown.

found to be more steep; D_{Am} increased from <0.003 (the distribution ratio is below the detection limit) in 0.25 M HNO₃ to 4.0 ± 0.1 in 1 M HNO₃. This effect was caused by an increased formation of the $([M(\text{TODGA})_3](\text{NO}_3)_3)_{\text{org}}$ complex, which depended on the cubic of the HNO₃ concentration.²⁹ The extraction of Am(III) was strongly suppressed by the presence of (PhSO₃H)₂-BTPhen in the aqueous phase, especially at low HNO₃ concentrations (e.g., 0.25 and 0.5 M). The decreasing selectivity of (PhSO₃H)₂-BTPhen can be explained by the protonation of coordinating nitrogen atoms, which was earlier described as occurring for both hydrophilic (PhSO₃H)₂-BTP and (PhSO₃H)₂-BTBP ligands.²¹ The protonation results in a lower concentration of free (PhSO₃H)₂-BTPhen at higher HNO₃ concentrations and, consequently, leads to a decrease in the observed SFs. For the system studied, $\text{SF}_{\text{Eu}/\text{Am}}$ decreased from >230 in 0.25 M HNO₃ solution to 44.3 ± 11.2 in 1 M HNO₃. The observed dependencies of the distribution ratios on the acidity are in agreement with the values reported in refs 21 and 22. Based on

these results, systems in 0.25 and 0.5 M HNO₃ were chosen to be studied in detail for their radiation stability against γ irradiation.

Subsequently, the dependence of Am(III), Cm(III), and Eu(III) extraction from 0.25 and 0.5 M HNO₃ on the irradiation dose in the presence of 0.01 M (PhSO₃H)₂-BTPhen was determined for the samples irradiated in the absence of the organic phase (only the aqueous phase was irradiated); the results are shown in Figure 6. For the irradiated samples, the D -values increased for all metals as doses increased. In all cases, distribution ratios of tested metals (D_M) was higher in 0.5 M HNO₃ than in 0.25 M HNO₃, which agrees with the discussion above. Even after an absorbed dose of 300 kGy, the D -values were much smaller than those observed for an analogous system without the masking agent, indicating that some (PhSO₃H)₂-BTPhen was still present. Finally, on comparing the D -values at 100 and 300 kGy at different HNO₃ concentrations, the increase in D -values as the dose increased was found to be approximately 3 times higher

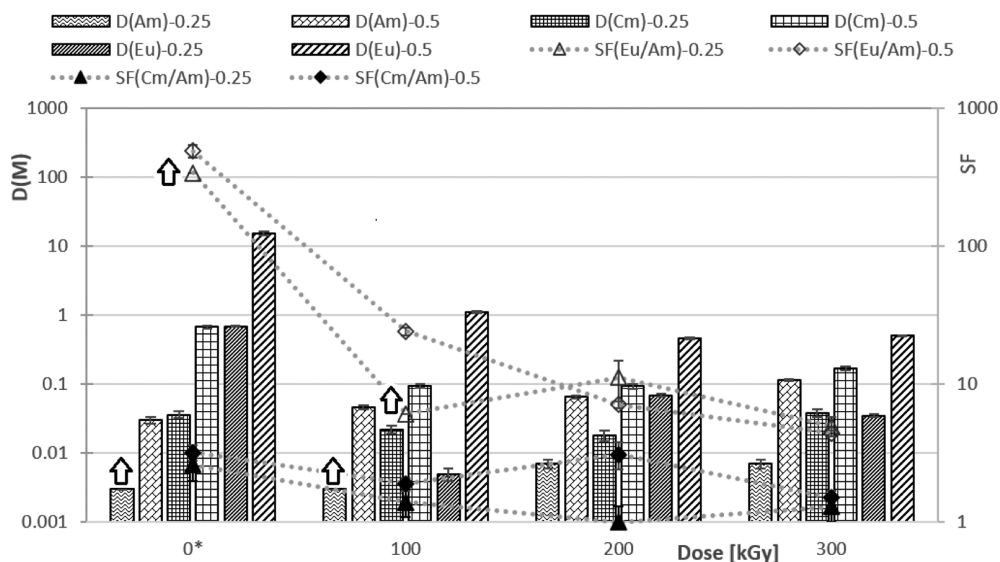


Figure 7. Extraction of Am(III), Cm(III), and Eu(III) from 0.25 or 0.5 M HNO₃ by TODGA (0.2 M dissolved in 5 vol % octan-1-ol in kerosene) in the presence of (PhSO₃H)₂-BTPhen (0.01 M) in the aqueous phase as a function of absorbed dose; the aqueous phase irradiated in the presence of an organic phase, mixing time: 60 min/1800 min⁻¹; temperature: 22 ± 1 °C. * Data for non-irradiated Cm(III) extraction are taken from our publication.¹⁵ The arrow means that the value was higher/lower than the corresponding limit of detection shown.

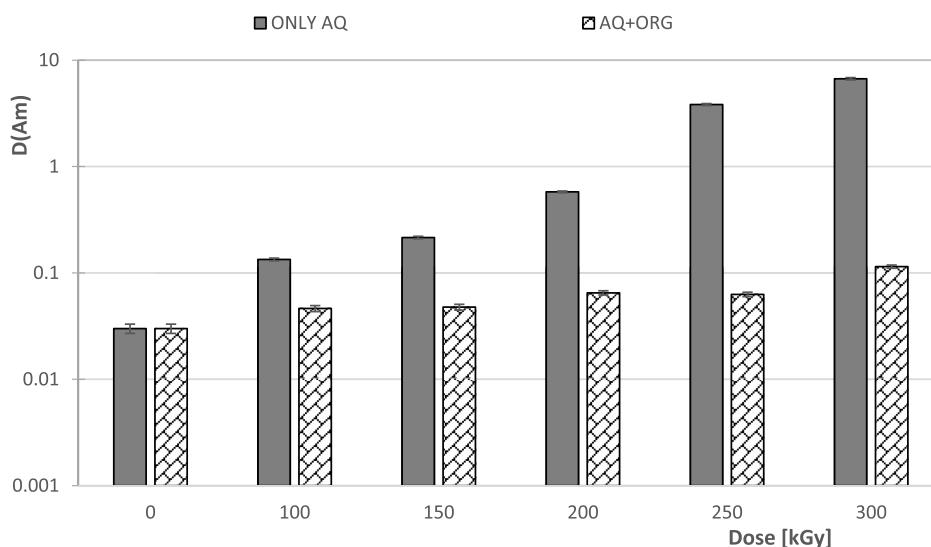


Figure 8. Extraction of Am(III) from 0.5 M HNO₃ with 0.01 M (PhSO₃H)₂-BTPhen solution by TODGA (0.2 M dissolved in 5 vol % octan-1-ol in kerosene) in the absence (ONLY AQ) or the presence (AQ + ORG) of the organic phase during irradiation as a function of absorbed dose; mixing time: 60 min/1800 min⁻¹; temperature: 22 ± 1 °C.

in 0.25 M HNO₃, indicating a higher rate of radiolysis than in 0.5 M HNO₃. This is in agreement with the conclusions of a similar study on radiolysis of water-soluble BTP and BTBP in 0.1 or 1 M HNO₃.³⁰ The distribution ratios increased faster for the minor An's Am(III) and Cm(III) than for Eu(III), which can be explained by the lower complexation constant of the Ln and the gradual decomposition of the masking agent with the absorbed dose. A similar trend in D_{Eu} values (a decrease followed by an increase with increasing doses) was also observed by Sánchez-García.³¹ It may be caused by the initial degradation of TODGA and a follow-up formation of adducts/degradation products in the organic phase that were able to extract Eu(III).

The $SF_{Eu/Am}$ values dropped from a value higher than 337 for the non-irradiated system in 0.25 M HNO₃ to 7.4 ± 0.3 after a dose of 300 kGy and from 486 ± 49 to 5.6 ± 0.4 in 0.5

M HNO₃ (again, non-irradiated vs 300 kGy). The values of $SF_{Cm/Am}$ were between 2.2 ± 0.3 and 1.4 ± 0.1 in a range from 200 to 300 kGy, indicating a smaller selectivity toward the two elements than in non-irradiated systems, where the $SF_{Cm/Am}$ were between 2.4 ± 0.2 and 3.4 ± 0.3 in a range from 0.25 to 1 M HNO₃.¹⁵ Unfortunately, due to the instrumental setup, the analytical procedure described in the Methods section could be applied to the organic phases only. Thus, getting further support from the determination of residual concentrations of (PhSO₃H)₂-BTPhen in the aqueous phase was not possible.

In the last i-SANEX experiment, the (PhSO₃H)₂-BTPhen containing aqueous phase was irradiated in contact with the TODGA organic phase, and the results obtained were compared with those of irradiation of only the aqueous phase. Our goal here was to investigate whether the presence of an organic phase during irradiation might increase the

radiolytic stability of the studied system toward γ irradiation. Comparing Figures 6 and 7, describing the behavior of the same systems irradiated under different conditions, it can be seen that irradiation has a significantly smaller effect on the system when the organic phase is present during irradiation—the trends of the D -values shown in Figure 7 are not clear—the D_{Eu} -values in 0.5 M HNO_3 even monotonously decreased with the absorbed dose. Even though the D -values were less clearly affected by the radiation, the trends in the SF values were similar to those of the system irradiated in the absence of the organic phase. $\text{SF}_{\text{Eu}/\text{Am}}$ dropped from a value higher than 337 for the non-irradiated system with 0.25 M HNO_3 to $\text{SF}_{\text{Eu}/\text{Am}} = 5.0 \pm 0.8$ after a dose of 300 kGy and from $\text{SF}_{\text{Eu}/\text{Am}} = 486 \pm 49$ to 4.4 ± 0.2 in 0.5 M HNO_3 (again, non-irradiated vs 300 kGy). The values of $\text{SF}_{\text{Cm}/\text{Am}}$ were between 1.4 ± 0.3 and 1.9 ± 0.2 for both HNO_3 concentrations, with a probable outlier of $\text{SF}_{\text{Cm}/\text{Am}} = 3.1 \pm 0.7$ after 200 kGy in 0.5 M HNO_3 . Therefore, again, the values of $\text{SF}_{\text{Cm}/\text{Am}}$ dropped at higher absorbed doses.

More detailed data on the dependency of D_{Am} on dose are shown in Figure 8. The steep increase in the D_{Am} values, observed in particular for irradiation of the aqueous phase only, can be probably ascribed to the radiolytic degradation of the $(\text{PhSO}_3\text{H})_2$ -BTPhen hold-back reagent. However, this assumption could not be fully confirmed experimentally due to the lack of an analytical technique for $(\text{PhSO}_3\text{H})_2$ -BTPhen determination in the aqueous phase. As can be seen, the extraction of Am(III) remained significantly more suppressed when the aqueous phase was irradiated in the presence of the organic phase. At the extreme, the D_{Am} -value in the sample irradiated in contact with the organic phase by a dose of 300 kGy was more than 1 order of magnitude lower compared to that obtained after irradiation in the absence of the organic phase ($D_{\text{Am}} = 0.115 \pm 0.004$ vs $D_{\text{Am}} = 6.7 \pm 0.2$). The increasing D_{Am} and D_{Eu} values and the resulting drop of $\text{SF}_{\text{Eu}/\text{Am}}$ illustrate the loss of selectivity toward Eu(III) extraction. However, this loss of selectivity was efficiently suppressed when the irradiation was carried out in contact with the organic phase. These findings agree with the results published in ref 20 (where the distribution ratios for Am(III) and Eu(III) stayed almost constant for an absorbed dose in the range from 0 to 174 kGy). Hence, it can be assumed that $(\text{PhSO}_3\text{H})_2$ -BTPhen is similarly stable under irradiation in the presence of an organic phase as the $(\text{PhSO}_3\text{H})_2$ -BTP and $(\text{PhSO}_3\text{H})_2$ -BTBP hold-back reagents.^{20,26,27} Also, it demonstrated the radioprotective action of the presence of an organic phase during irradiation. This is a similar phenomenon to the radioprotective action of the presence of nitric acid aqueous phases on the radiolytic stability of hydrophobic extractants in organic phases.⁹

Simultaneously, the mutual separation of Am(III) and Cm(III) in the studied system was investigated. The distribution ratios of Cm(III) shown in Figure 6 closely follow the increase of D_{Am} values with the absorbed dose. Similar to the Am(III) behavior shown in Figure 8, the D_{Cm} values stayed almost constant when the aqueous phase was irradiated in contact with the organic phase (cf. also Figure 7). As a result; there was quite a small difference in $\text{SF}_{\text{Cm}/\text{Am}}$ values under different conditions. For the non-irradiated system, the $\text{SF}_{\text{Cm}/\text{Am}}$ was 3.2 ± 0.4 . With increasing doses, the $\text{SF}_{\text{Cm}/\text{Am}}$ got closer to 1; at a dose of 300 kGy, the $\text{SF}_{\text{Cm}/\text{Am}}$ values were 1.3 ± 0.3 and 1.5 ± 0.2 for 0.25 M and 0.5 M HNO_3 , respectively, for the systems irradiated in the presence of the

organic phase. Again, this can be attributed to the decrease in the $(\text{PhSO}_3\text{H})_2$ -BTPhen concentration during irradiation.

CONCLUSIONS

The radiolytic stabilities of two r-SANEX systems based either on hydrophobic CyMe_4 -BTBP or CyMe_4 -BTPhen extractant dissolved in BK-1 diluent (carbonate of fluorinated alcohol) and one i-SANEX system with the $(\text{PhSO}_3\text{H})_2$ -BTPhen hydrophilic masking agent were tested under γ radiation.

From the results obtained with the r-SANEX systems, it can be concluded that the radiolytic stability of the solvents with BK-1 diluent is significantly inferior to that of an analogous solvent that contains octan-1-ol as a diluent. Similar to other systems studied earlier, the systems were found to be significantly more radiation stable when the organic phase was irradiated in contact with the nitric acid-based aqueous phase. Based on the comparison of the experimental and calculated theoretical values of the metal distribution ratios, it has been hypothesized that the radiolysis of both CyMe_4 -BTBP and CyMe_4 -BTPhen in BK-1 proceeds through primary product(s) with an extraction ability similar to or slightly lower than the parent molecules to the non-extracting products of deeper radiolysis. The adducts formed during irradiation of CyMe_4 -BTBP (M) in BK-1 (X) consisted of one molecule of the diluent $[\text{M} + \text{X}]^+$ or its degradation product, such as 1,1,2,2-tetrafluoroethane (Y), $[\text{M} + \text{Y}]^+$, attached to the CyMe_4 -BTBP scaffold with the loss of two protons to form a covalent bond. Adducts with both variants $[\text{M} + \text{Y} + \text{X}]^+$ were highly represented at higher doses. In contrast with FS-13, a system with another fluorinated diluent, the distribution ratios of all metals and the SFs rapidly decrease upon increasing the absorbed dose. The Am/Cm separation trends mimicked those observed for Am/Eu separation.

From the results obtained for the i-SANEX systems, it can be concluded that the rate of $(\text{PhSO}_3\text{H})_2$ -BTPhen radiolysis depends significantly on the HNO_3 concentration (3-fold increase of degradation observed in 0.25 M HNO_3 relative to 0.5 M HNO_3). Further, the results revealed a clear positive influence (radioprotective effect) of the presence of an organic phase (0.2 M TODGA in 5 vol % octan-1-ol in kerosene) on the radiation stability of $(\text{PhSO}_3\text{H})_2$ -BTPhen in the aqueous phase. In such systems, not only do the D_{Am} values decreased slowly but also the Am/Eu selectivity was suppressed to a much lesser extent. The trends in the Am/Cm separation followed those observed for the Am/Eu separation.

To complete the characterization of all the main representatives of the family of N -donor bis-triazinyl hydrophilic masking agents (BTP, BTBP, and BTPhen), the radiation stability of the remaining two masking agents, $(\text{PhSO}_3\text{H})_2$ -BTP and $(\text{PhSO}_3\text{H})_2$ -BTBP, will be studied in detail in the next step. To support the hypothesis about the extraction properties of various products formed successively upon irradiation of the solvents with CyMe_4 -BTPhen or CyMe_4 -BTBP in BK-1, the synthesis and determination of the extraction properties of these products could provide more insight into the chemistry of these systems. Also, performing a similar r-SANEX study with CyMe_4 -BTBP and CyMe_4 -BTPhen in the BK-2 diluent could yield information about the influence of the length of the fluorinated alcohol chain in the molecule of the diluent on the behavior of the solvent under irradiation.

METHODS

r-SANEX System. The organic phase consisted of a 0.001 M solution of CyMe₄-BTBP or CyMe₄-BTPhen dissolved in the fluorinated diluent BK-1, and the aqueous phase was represented by 1 M HNO₃. Four different samples were sealed in glass vials: a neat organic phase containing (i) CyMe₄-BTBP or (ii) CyMe₄-BTPhen (1.5 mL each); or an aqueous phase (1 M HNO₃) together with an organic phase (iii) CyMe₄-BTBP or (iv) CyMe₄-BTPhen (1.5 mL organic + 1.5 mL aqueous phase each). After irradiation, 500 μL from the organic phases was used to determine the residual concentration of the ligand and identify the adducts/degradation products in the samples. Another 800 μL of irradiated organic phase was used for liquid–liquid extraction. Each irradiated organic phase was contacted with 800 μL of freshly diluted 1 M HNO₃ ($V_{\text{aq}}/V_{\text{org}} = 1$) spiked with trivalent radionuclide tracers (²⁴¹Am, ¹⁵²Eu, and ²⁴⁴Cm). The solutions were shaken for 1 h at 1800 min⁻¹ (Heidolph, Multi Reax Shaker, ca 22 °C, unthermostatted) without any pre-equilibration (solvent or acidic medium). After shaking, the organic and aqueous phases were separated by centrifugation (1 min at 6000 rpm). For the measurements by an alpha spectrometer, 2 × 10 μL was sampled on steel planchets, and for the measurements with a γ-ray spectrometer, 2 × 150 μL was transferred into plastic ampules. Walls of the ampules were washed with 1 mL of distilled water or octan-1-ol, respectively, to remove any radioactivity from them and to guarantee constant geometry for γ counting.

i-SANEX System. First, distribution ratio and separation factor dependencies on the HNO₃ concentration were studied. In 0.25, 0.50, 0.75, and 1.00 M HNO₃ solutions, the concentration of (PhSO₃H)₂-BTPhen was adjusted to 0.01 M, and the solutions were spiked with Am(III) and Eu(III) tracers. These aqueous phases were then contacted with an equal volume of the organic phase ($V_{\text{aq}}/V_{\text{org}} = 1$) containing 0.2 M TODGA in kerosene with 5 v/v % octan-1-ol for 6 h at ambient temperature (ca 22 °C, non-thermostatted) using a GFL 3005 Orbital Shaker (250 min⁻¹). After phase separation by centrifugation (1 min at 6,000 rpm), the two aliquots of each phase (150 μL) were withdrawn into ampules for Am(III) and Eu(III) analyses. Similar to the r-SANEX system, the walls of the ampules were washed with an additional 1 mL of distilled water or kerosene. Next, the two different extractions systems were irradiated. The first system represented only the aqueous phase, consisting of 0.01 M (PhSO₃H)₂-BTPhen in 0.25 M or 0.5 M HNO₃ solution in glass ampules. The second system consisted of the same aqueous phase in the presence of the organic phase consisting of 0.2 M TODGA in kerosene with 5 v/v % octan-1-ol. After irradiation, the aqueous phases from both systems were transferred to new ampules, spiked with ²⁴¹Am, ¹⁵²Eu, and ²⁴⁴Cm tracers, and contacted with an equal volume of a fresh organic solution ($V_{\text{aq}}/V_{\text{org}} = 1$; $V = 400 \mu\text{L}$). The extraction systems were then shaken for 1 h at ambient temperature (ca 22 °C, non-thermostatted) using a Heidolph, Multi Reax Shaker (1800 min⁻¹) without any pre-equilibration of the fresh solvent. Phase separation and preparation of samples for γ measurement were done in the same manner as described above. For alpha measurements, 2 × 10 μL aliquots were deposited on stainless-steel planchets and heated in a burner flame until the sample glowed to dull red heat.

Activity Measurements. Activity measurements of ¹⁵²Eu and ²⁴¹Am were performed with a γ-ray spectrometer EG&G

Ortec 919 MCB using a PGT HPGe detector and evaluated by Maestro for Windows (EG&G Ortec, USA). The γ-lines at 59.5 keV and 121.8 keV were examined for ²⁴¹Am and ¹⁵²Eu determination, respectively. Alpha activity measurements of ²⁴¹Am and ²⁴⁴Cm were performed with an ORTEC OCTETE Plus Integrated Alpha-Spectroscopy System equipped with an ion-implanted-silicon ULTRA Alpha Detector, model BU-020-450-AS. The ²⁴¹Am and ²⁴⁴Cm peaks were evaluated by AlphaVision-32 Alpha Analysis Software (EG&G ORTEC, USA). The doublets at 5443 + 5486 and 5763 + 5805 keV in the alpha spectra were evaluated for ²⁴¹Am and ²⁴⁴Cm determinations, respectively.

HPLC Analysis. Analytical HPLC was used to quantitatively determine the concentration of undestroyed ligand in the organic phase after irradiation. The chromatographic system consisted of a Merck-Hitachi HPLC system (LaChrom 7000 series) equipped with a Pump L7100, a DAD 7450 detector, an Intelligent Injector L7250, and an interface. Chromatographic conditions were as follows. For CyMe₄-BTBP: column, Merck Purospher STAR RP-C 8e endcapped (5 μm, 250 × 2 mm I.D.); isocratic elution with 20 mM aqueous triethylamine citrate (TEAC, pH 8.2; the pH was adjusted with aqueous buffer before mixing with CH₃CN) in 78% aqueous CH₃CN (CHROMASOLV for HPLC, gradient grade, Aldrich); flow rate, 0.3 mL/min; detection, DAD (220–350 nm); fixed wavelengths 237, 239, 242, and 287 nm; and the selected wavelength, 237 nm. For CyMe₄-BTPhen: column, Phenomenex Gemini NX RP-C18 110 Å (3 μm, 150 × 3 mm I.D.); isocratic elution with 20 mM aqueous TEAC (pH: 9.8, which was adjusted in aqueous buffer before mixing with CH₃CN) in 85% aqueous CH₃CN (CHROMASOLV for HPLC, gradient grade, Aldrich); flow rate, 0.6 mL/min; detection, DAD (220–350 nm); fixed wavelengths, 245, 259, 262, and 287 nm; and the selected wavelength, 259 nm. The samples with a volume of 250 μL were syringed into vials, and the volume was adjusted to 1.0 mL by adding acetonitrile (ACN). The injection volumes were 3 μL. The data represent mean values from five injections made from two vials. The calibration curve was constructed using nonirradiated reference samples with concentrations of 0.001 M CyMe₄-BTBP or CyMe₄-BTPhen and data from four injections of volumes between 1 and 4 μL for each vial ($R^2 = 0.9996$ for the CyMe₄-BTBP calibration curve).

HPLC–MS Analysis. All r-SANEX samples were analyzed in parallel for the presence of degradation products on a Thermo Finnigan Surveyor HPLC system equipped with a photodiode array detector and further connected to a Thermo LCQ Fleet Ion Trap MS detector. Chromatographic conditions: column, Gemini-NX C18 110 Å (3 μm, 150 × 2.00 mm I.D.). Mobile phase preparation: 20 mL of 0.5 M stock solution of diethylamine oxalate (DEAO) was diluted with water (HPLC grade) to 220 mL (pH was adjusted to 8.2). This buffer was mixed with 780 mL of ACN (HPLC gradient grade). Flow rate, 0.3 mL/min; detection, PDA (190–800 nm); and fixed wavelengths: 237, 285, and 290 nm. All samples of concentration 0.050 M or 0.010 M were diluted with CH₃CN to a final concentration of 0.00025 M. The injection volume was 5 μL. MS measurements were performed with an APCI probe (atmospheric pressure chemical ionization) in a positive enhanced mode using helium (5.0 Messer) as a collision gas in the ion trap. Conditions used for the APCI interface: vaporizer temperature, 350 °C; N₂ (isolated from air in NitroGen N1118LA, Peak Scientific) as

a nebulizing sheath gas and an auxiliary gas; flow, 38 and 7 arb, respectively; discharge current, 5.0 μ A; capillary temperature, 250 $^{\circ}$ C; capillary voltage, 26 V; and mass range, from 200 to 1200.

γ Irradiation. The systems were irradiated up to six different doses: 50, 100, 150, 200, 250, and 300 kGy. γ radiation from a cobalt source (^{60}Co) in the Central Bohemian Museum in Roztoky u Prahy—Conservation Irradiation Workplace—was used. The γ -ray source was placed in the middle of the irradiation room, while the extraction systems were located at specified distances. The γ -ray dose rate at the time of the experiments varied from 100 to 300 Gy/h based on the distance. The samples were not shaken during irradiation.

Evaluation of Extraction Quantities. Distribution ratios and separation factors of individual radionuclides were calculated from the measured count rates. The distribution ratios D_M of the metals were calculated as

$$D_M = \frac{I_{\text{org}}}{I_{\text{aq}}}$$

where I_{org} and I_{aq} are the count rates in the organic and aqueous phases, respectively. The separation factor SF_{M_1/M_2} is given by

$$SF_{M_1/M_2} = \frac{D_{M_1}}{D_{M_2}}$$

where D_{M_1} and D_{M_2} are the distribution ratios of two different metals. The errors given in the figures are 1σ and are based on the counting statistics only.

For the r-SANEX system, the theoretical distribution ratio values (D_{theo}) were calculated taking into account the stoichiometry between the metal ion and the $\text{CyMe}_4\text{-BTBP}$ molecule¹ as 1:2 according to the formula

$$D_{\text{theo}} = D_{\text{exp}} \cdot \left(\frac{c_{\text{res}}}{c_0} \right)^2$$

where D_{exp} is the experimental value of the distribution ratio, c_{res} is the residual concentration of the extracting compound, and c_0 is the initial concentration of the extracting compound.

Extracting Compounds and Diluents. BK-1 diluent was synthesized at the Laboratory of Sensors, ITMO University, Russian Federation (V. A. Babain). TODGA was synthesized at the Laboratory of Molecular Nanofabrication, University of Twente, the Netherlands (R. J. M. Egberink and W. Verboom) according to ref 32. $\text{CyMe}_4\text{-BTBP}$, $\text{CyMe}_4\text{-BTPPhen}$, and $(\text{PhSO}_3\text{H})_2\text{-BTPPhen}$ were purchased from Technocomm Limited, U.K.

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Notes

The authors declare no competing financial interest.

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