



Development of experimental irradiation strategies to evaluate the robustness of TODGA and water-soluble BTP extraction systems for advanced nuclear fuel recycling

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ABSTRACT

More sustainable nuclear fuel cycle options will entail the implementation of efficient separation processes of actinides from lanthanides, which currently continues being a critical milestone. One of the limiting points to ensure a safe and stable long-term operation is the resistance against radiation of the extraction systems under development. During the latest years, processes like i-SANEX and EURO-GANEX have been developed and tested to separate actinides from lanthanides, addressing the heterogeneous and the homogeneous recycling strategy respectively. Both of them are the result of the combination of an organic phase containing TODGA, and an aqueous phase containing the sulfonated 2,6-bis(5,6-di(sulphophenyl)-1,2,4-triazin-3-yl)pyridine. In this work, we report an extended stability study of the water-soluble SO₃-Ph-BTP as part of the full system considering both phases, the organic and aqueous phase. A systematic set of gamma irradiation experiments were carried out in order to explore the effects of each phase and the influence of the experimental irradiation methodology chosen in the global system resistance. For that, different phase composition, oxygen content and contact between phases have been considered to achieve a better simulation of the most relevant process conditions. The current results corroborate not only that the stability of SO₃-Ph-BTP has been sub-estimated, but also that the experimental irradiations test for process demonstration should involve the contact between both phases, the corresponding organic and aqueous phase.

1. Introduction

Used nuclear fuel from nuclear power plants is managed by interim storage, to reduce the radioactivity and heat generated, followed by final disposal in a deep geological repository or recycling of valuable materials to produce new fuel, with final disposal of the residual high level waste (HLW) from reprocessing. The composition of used nuclear fuel from a typical light water reactor (burn-up of 40 GWd/t) is ~96% of the initial uranium (U), ~3–4% fission products (FPs) and approximately 1% transuranium elements (TRU: neptunium (Np), plutonium (Pu), americium (Am) and curium (Cm)). Accordingly, nowadays recycling improves the conservation of natural resources, optimize the waste management and disposal conditions and minimizes the environmental impact (Taylor, 2015). Other way, decay heat and radiotoxic loading of nuclear waste is initially governed by FPs, but after approximately 60 years plutonium and the main minor actinides (MAS:

Np, Am, and Cm) are the mayor contributors to the long-lived heat and radiotoxic. Therefore, after the recovering of the useful components (U and Pu) by the known PUREX process (Lanham and Runion, 1949), an additional recycling of MAS would significantly reduce the burden of HLW long term management and optimize the utilisation of a final deep geological repository (OECD-NEA, 2011).

Two possible concepts of MAS recycling have been addressed, the heterogeneous or homogeneous recycling (Warin, 2010; Poinssot et al., 2012). In the first one, a sequential separation of elements is needed starting from already implemented U and Pu recovering, to finally isolate MAS from the previous raffinate; by contrast, the homogeneous recycling lies on the separation of all the TRU together after the previous recovering of U, the so-called GANEX concept (*Grouped Actinide Extraction*) (Adnet et al., 2005; Miguiditchian et al., 2007).

Two of the most successful families of extractants developed so far and used for that purpose are the diglycolamides (DGAs) (Ansari et al.,

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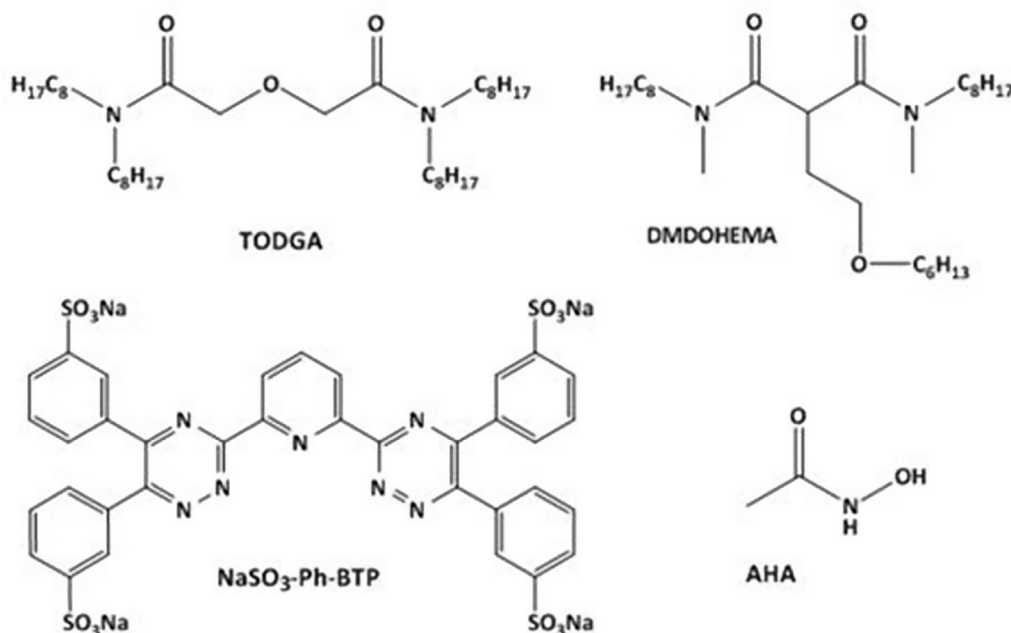


Fig. 1. Structures of the molecules involved in the stripping step of An in the *i*-SANEX process: TODGA and NaSO₃-Ph-BTP; and in the EURO-GANEX process: TODGA, DMDOHEMA, NaSO₃-Ph-BTP and AHA.

2012; Whittaker et al., 2018), particularly the well-known DGA TODGA (*N,N,N',N'*-tetraoctyldiglycolamide) (Sasaki et al., 2001; Ansari et al., 2005), and the bistriazinylbipyridines (BTBPs) and bistriazinylpyridines (BTPs) (Foreman et al., 2005; Hudson et al., 2006; Panak and Geist, 2013) (see Fig. 1). TODGA is an efficient co-extractant of actinides (An) and lanthanides (Ln), and BTBPs or BTPs separate the An(III) from Ln due to its selectivity towards An over Ln elements. Both families of compounds were initially developed as extractants used in the organic phase, and later extended as their hydrophobic derivatives. Particularly, the functionalization of a BTP with sulfonyl groups to make it soluble in the aqueous phase gave place to the successful combination between the properties of TODGA and the SO₃-Ph-BTP (2,6-bis(5,6-di(sulphophenyl)-1,2,4-triazin-3-yl)pyridine) (Geist et al., 2012). This combination of selective extraction properties has allowed developing different routes to achieve the separation of MAs, such as the promising *i*-SANEX (Geist et al., 2012; Wilden et al., 2012, 2015) and EURO-GANEX (Taylor et al., 2016; Carrott et al., 2014; Malmbeck et al., 2019) processes.

Following an heterogeneous recycling strategy, after the direct co-extraction of Ln and An from PUREX raffinate by a TODGA-based solvent (0.2 mol/L TODGA in kerosene with a 5% of 1-octanol), the *i*-SANEX (*Innovative Selective Actinide Extraction*) process aims a selective stripping of An(III) into the aqueous phase using SO₃-Ph-BTP in nitric acid (Wilden et al., 2012). By contrast, the EURO-GANEX process is one of the possible options to be chosen for the second cycle of GANEX process (Malmbeck et al., 2019; Miguiditchian et al., 2009; Halleröd et al., 2015). During the first cycle (GANEX-1) U(VI) is selectively extracted leaving TRU, Ln(III) and the other fission products (FPs) in the aqueous phase (Miguiditchian et al., 2009b). Then, EURO-GANEX solvent consisting in TODGA and the malonamide DMDOHEMA (*N,N'*-dimethyl-*N,N'*-dioctylhexyloxyethyl malonamide) co-extracts An and Ln from GANEX-1 raffinate; after that, all TRU are stripped using a mixture of SO₃-Ph-BTP and AHA (acetohydroxamic acid) (Fig. 1) (Malmbeck et al., 2019). DMDOHEMA is used in EURO-GANEX solvent to increase the Pu loading capacity of the organic solvent (Malmbeck et al., 2019) and AHA to strip Pu(IV), Np(VI), and Np(VI) into aqueous phase (Taylor et al., 1998; Carrott et al., 2007).

One of the limiting points for the development of these extraction processes is their resistance to the highly radioactive field where they

must be used. In general, it can be said that the stability to radiation of main molecules involved in both processes mentioned before, *i*-SANEX and EURO-GANEX, has already been studied, particularly TODGA and SO₃-Ph-BTP (Sugo et al., 2002; Galán et al., 2012, 2014, 2020; Modolo et al., 2007; Zarzana et al., 2015; Peterman et al., 2016; Horne et al., 2019). However, the chemical composition of the solvent studied is very important. In general, it can be said that under fuel cycle conditions the direct radiolysis of the aqueous and alkane diluents used produces a known suite of transient species capable of reacting with ligands producing their degradation (Mincher et al., 2009). Therefore, factors such as the presence of nitric acid during the irradiation, oxygen content, the composition of diluents, etc. could lead a scavenger process that may act as radio-protection agent for ligands. In consequence, results published in literature are not always comparable due to the different experimental conditions chosen. For example, stability of TODGA has been studied by different authors, concluding that TODGA shows a high resistance against radiolysis until relevant absorbed doses, but it is still discussed the effect of different parameters such as the presence of nitric acid over degradation compounds or the degradation pathways (Sugo et al., 2002; Galán et al., 2012; Modolo et al., 2007; Zarzana et al., 2015). Other way, BTBP and BTP compounds have shown more susceptibility to degradation under radiation conditions (Aneheim et al., 2011; Galán et al., 2014, 2020; Peterman et al., 2016; Horne et al., 2019) than DGA ligands, especially when they are part of the aqueous phase such as the SO₃-Ph-BTP. In spite of this, again conflicting results have been found from different resistance experiments against γ -radiation (Galán et al., 2014, 2020; Peterman et al., 2016; Horne et al., 2019). For example, we reported an estimated loss of 90% of the initial SO₃-Ph-BTP concentration after 250 kGy when 10 mmol/L SO₃-Ph-BTP dissolved in 0.5 mol/L HNO₃ is irradiated up to 1000 kGy (Galán et al., 2014, 2020); on the contrary, Peterman et al. (2016) concluded that no significant effects of degradation are observed up to doses of 175 kGy when the irradiation of SO₃-Ph-BTP, as part *i*-SANEX system, is carried out using a solvent irradiation loop where the organic and aqueous phases are irradiated in contact (organic: 0.2 mol/L TODGA in (95:5)_{vol} n-dodecane/1-octanol; aqueous: 18 mmol/L SO₃-Ph-BTP in 0.35 mol/L HNO₃). Recently, Horne et al. (2019) have reported a higher radiolytic degradation (over 90% for the concentrations studied in that work, 145 μ mol/L) of the sulphonated BTP and BTBP derivatives

in aerated water solution within 1 kGy. Unfortunately, none of these stability studies are comparable; in consequence, the most important conclusion that can be drawn from all of them is the strong dependence of the results with the experimental conditions chosen for the irradiation experiments.

Since the final goal of these stability studies is to understand, simulate and predict what would happen along a real separation process, the cornerstone to ensure a safe and stable operation is to develop simple but also reliable strategies of simulation. For that reason, relevant process conditions affecting to the stability and behaviour of process steps must be carefully explored to select the most suitable irradiation patterns for each extraction system.

Recently, we have published the first part of this work (Sánchez-García et al., 2019), where the study of how and why the different experimental conditions applied to the irradiation of a TODGA-based solvent affect to the system stability was carried out. Particularly, TODGA solvent stability was evaluated against γ -radiation when it was irradiated in contact with an aqueous phase containing 0.5 mol/L HNO_3 . In order to clarify the effect of parameters such as the contact between phases or the oxygen content during the irradiation process, air or argon atmosphere and air sparging flow were used. From those experiments, we concluded that until 500 kGy the system maintains perfectly the extraction properties of Ln and An, in agreement with the literature; however, the different irradiation conditions applied revealed changes in the degradation pathways of the main molecule TODGA.

In this work, we have extended that methodology of study to the corresponding full extraction systems, focusing now on the effects over the aqueous phase. Considering that the key step of *i*-SANEX and EURO-GANEX processes are based on TODGA and SO_3 -Ph-BTP molecules, TODGA/ SO_3 -Ph-BTP system could be considered as a good starting point for the development of an irradiation pattern where factors affecting to the global stability can be isolated. For that reason, other molecules or phase modifiers involved in EURO-GANEX solvent such as DMDOHEMA or AHA are not considered in this first study. The result of submitting to γ -irradiation SO_3 -Ph-BTP samples in nitric acid individually, in contact with odourless kerosene (OK) and in contact with TODGA solvent is reported herein. Moreover, following the same methodology of our previous work, conditions leading to increase the contact between phases and the content of oxygen have also been considered (air and argon atmosphere and an air sparging flow). The extraction behaviour and composition of all systems studied have been analysed after γ -irradiation by gamma spectrometry and LC-MS, respectively.

2. Experimental

2.1. Chemicals, solutions and isotopes

N,N,N',N'-tetraoctyldiglycolamide (TODGA) was synthesised at CIEMAT modifying an existing literature procedure under air atmosphere and without drying solvent (de Mendoza et al., 2009; Horwitz et al., 2005). The raw product was then purified by column chromatography (silica gel, 98:2 $\text{CH}_2\text{Cl}_2/\text{MeOH}$) to give TODGA as oil. ^1H RMN spectrum agrees with published data (de Mendoza et al., 2009; Horwitz et al., 2005) and the purity of compound was determined by HPLC-MS (see HPLC-MS measurements subsection) as 98%. 2,6-bis(5,6-di(sulphophenyl)-1,2,4-triazin-3-yl)pyridine (SO_3 -Ph-BTP) with a purity of 98% by HPLC-MS was purchased from Technochem Ltd. The organic diluent was odourless kerosene (OK), purity 98%, from Alfa Aesar. Nitric acid used as the aqueous diluent was purchased from VWR Chemical as nitric acid (HNO_3) 65% with the grade AnalaR NORMA-PUR for analysis; it was additionally purified twice by a Quartz sub-boiling distillation system (MLS-Milestone) and used in a short period of time. The solutions of HNO_3 used as the aqueous diluent were prepared by diluting concentrated nitric acid with ultrapure water

(18 $\text{M}\Omega/\text{cm}$). All others reagents were used from commercially available sources without further purification. The radioactive tracer solutions of $^{241}\text{Am}(\text{III})$ and $^{152}\text{Eu}(\text{III})$, were obtained as MCl_3 , in HCl 1 mol/L, from Isotope Products Laboratories, California (USA).

2.2. Irradiation procedure

Irradiation experiments were performed at the Náyade irradiation facility (CIEMAT) (Náyade facility, 2020). This facility consists of a pool of a 1.2 m^2 by 4.5 m deep that uses water as the biological shield. At the bottom of the pool, 60 sources of ^{60}Co (15 mm diam. x 135 mm long each) with a total activity of $1.1 \cdot 10^{14}$ Bq can be distributed in six lots. The cylindrical irradiation container used provides homogeneous irradiation flux within a 60 mm diam. x 100 mm high volume. Samples of this work were submitted to doses of 200 and 500 kGy at a dose rate of 4.02 ± 0.2 kGy/h determined by Fricke dosimetry (Fricke and Hart, 1935). Although the absorbed dose in the organic phase should be corrected based on solution density, for the sake of an easy understanding of the experiments in this work absorbed doses of phases irradiated together were considered the same. All samples were irradiated in glass vessels. Samples under air and argon atmosphere were irradiated in sealed vessels of 2 mL and for aerated samples an air sparging flow was employed.

Extraction experiments (see below) using the irradiated samples were performed immediately after the last step of irradiation. Reference samples were kept in the laboratory during the irradiation process for control.

After irradiation experiments, the proton concentration in the aqueous phases has been determined by using the potentiometrically acid-base titration with KOH and an automatic titrator Metrohm 798 MP titrino with an Unitrode as electrode purchased from Metrohm. A dynamic equivalence point of titration was employed for the determination, where the KOH was added in variable volume steps. The electrode was calibrated employing buffer solutions of pH 4.00 and 7.00 supplied by Metrohm.

2.3. Extraction experiments

Extraction experiments were performed by mixing for 30 min each 0.5 mL of organic (0.2 mol/L TODGA in kerosene) and aqueous (18 mmol/L SO_3 -Ph-BTP in 0.5 mol/L HNO_3) phases, spiked with 10 μL of $^{241}\text{Am}(\text{III})$ and $^{152}\text{Eu}(\text{III})$ (100 kBq/mL each). After centrifugation (at 5000 rpm), phases were separated and aliquots of each organic and aqueous phases (0.3 mL each) were taken and analysed by gamma spectrometry. Canberra High Purity-Germanium detector with a 20% of intrinsic efficiency was used for gamma spectrometry measurements, using Genie-2000 software from Canberra and gamma characteristic photopeak at 59.5 keV and 121.8 keV for ^{241}Am and ^{152}Eu , respectively. The results are reported as distribution ratios D ($D_M = [\text{M}^{3+}]_{\text{org}}/[\text{M}^{3+}]_{\text{aq}}$). These experimental conditions show a LID of 2 and 6 Bq for Am and Eu respectively. Distribution ratios between 0.01 and 100 exhibit a maximum error of $\pm 5\%$.

2.4. HPLC-MS measurements

The chemical composition of the irradiated organic samples was characterised by HPLC-MS. These measurements were performed by using an HPLC-MS Bruker EVOQTM (Triple Quadrupole detector) with an ACE 3 C18-PFP column (50 mm x 2.1 mm) at 40 °C, using a gradient mode and a mobile phase composed by: Solvent A (0.1% HCOOH in H_2O); solvent B (0.1% HCOOH in CH_3CN). The ionisation modes APCI⁺ and ESI⁺ were used for the quantification of TODGA and its degradation compounds (DC's) respectively. Samples for HPLC studies were analysed without pre-evaporation and diluted 1:30000 in HPLC grade MeOH + 0.1% HCOOH. Calibration curves were obtained by HPLC-MS for TODGA (10–1000 ppb) and each TODGA DC (1–250 ppb)

with correlation coefficients in the range of 0.993–0.999 in all cases. All measurements were repeated twice in order to have uncertainty analysis where results show a maximum error of $\pm 3\%$.

3. Results and discussion

Irradiation reference systems consisting in TODGA in OK (odourless kerosene) as organic phase and $\text{SO}_3\text{-Ph-BTP}$ in nitric acid as aqueous phase could be considered as a starting point to study the robustness of *i*-SANEX and EURO-GANEX full systems (organic + aqueous phase), where main possible factors affecting to the stability can be easily isolated. Until now the effects of radiation over $\text{SO}_3\text{-Ph-BTP}$ in nitric acid have been evaluated comparing the An stripping efficiency from an *i*-SANEX solvent (Galán et al., 2014, 2020; Peterman et al., 2016), which involves a small proportion of 1-octanol as phase modifier in its formulation. Different irradiation experiments have revealed repercussions of the presence of 1-octanol on the stability of some TODGA-based solvents (Galán et al., 2012); therefore, first of all it was checked if similar results from the chosen reference system could be extracted. For that purpose, aqueous phase containing $\text{SO}_3\text{-Ph-BTP}$ in nitric acid have been irradiated with ^{60}Co sources individually in the initial conditions studied (0.010 mol/L $\text{SO}_3\text{-Ph-BTP}$ in 0.5 mol/L HNO_3) (Galán et al., 2020) and in those chosen for the irradiation reference system (0.018 mol/L $\text{SO}_3\text{-Ph-BTP}$ in 0.5 mol/L HNO_3); and then, the An stripping efficiency was evaluated by the corresponding *i*-SANEX solvent (0.2 mol/L TODGA in 5% 1-octanol in kerosene) and the simplified TODGA solvent as reference pattern (0.2 mol/L TODGA in OK). Additionally, to compare with data obtained from the irradiation loop reported by Peterman et al. (2016), where both phases were irradiated together, TODGA and $\text{SO}_3\text{-Ph-BTP}$ solvents have been irradiated in contact as full irradiation reference pattern. Although it is not expected that these aqueous phases will receive a high dose, since they will not recycle (Malmbeck et al., 2019), 200 and 500 kGy at 3.95 kGy/h were chosen for a better comparison with previous irradiation studies (Galán et al., 2014, 2020; Peterman et al., 2016).

Over the course of the irradiation, the aqueous samples darkened considerably from green in unirradiated samples to dark colours (orange at 200 kGy and dark brown at 500 kGy). This significant darkening of the aqueous phase was initially related to the radiolytic degradation of the $\text{SO}_3\text{-Ph-BTP}$ molecule. No sulphur odour was noted after irradiation, as it could be expected from the results of our previous irradiation experiments (Galán et al. 2014, 2020). After irradiation, in order to assess the efficiency to strip An(III) from Ln(III), all samples were spiked with ^{241}Am and ^{152}Eu and those samples irradiated alone were also contacted with the corresponding fresh organic phase. On the

one hand, Fig. 2 shows distribution ratios obtained for Am(III) and Eu(III) as a function of the dose using the original *i*-SANEX solvent and the chosen reference irradiation system when only the aqueous phase is irradiated (Exp. 1.1 and Exp. 1.2 respectively). On the other hand, Fig. 2 also shows the $D_{\text{M(III)}}$ values obtained when the organic and aqueous phases of *i*-SANEX and the reference system have been irradiated together (Exp. 1.3 (Peterman et al., 2016) and Exp. 1.4, respectively).

After 200 kGy, for Exp. 1.1 and 1.2 a significant increase in $D_{\text{Am(III)}}$ ($D_{\text{Am(III)}} > 1$) is observed, producing a reduction of the separation factor between Eu(III) and Am(III) ($\text{SF}_{\text{Eu(III)/Am(III)}}$). This reduction in $\text{SF}_{\text{Eu(III)/Am(III)}}$ can be attributed to a total loss of the ability to keep An in the aqueous phase due to $\text{SO}_3\text{-Ph-BTP}$ degradation. Consequently, it can be said that when aqueous phases are irradiated individually the system almost completely loses its efficiency for separating An(III) from Ln(III) at 200 kGy. By contrast, $D_{\text{Am(III)}}$ values obtained when the full reference system was remained in contact during the irradiation (Exp.1.4) agree with those obtained by Peterman et al. (2016) which have been represented as Exp.1.3 in Fig. 2. These results point out to a sub-estimation of the resistance TODGA/ $\text{SO}_3\text{-Ph-BTP}$ systems when $\text{SO}_3\text{-Ph-BTP}$ aqueous phase is irradiated individually. Moreover, it seems that neither the presence of 1-octanol nor a higher concentration of $\text{SO}_3\text{-Ph-BTP}$ nor nitric acid modify the conclusion extracted. Therefore, all those conclusions can be extended from the initial *i*-SANEX systems studied to the simplified pattern chosen for *i*-SANEX and EURO-GANEX systems.

The contrasting results obtained for the irradiation of the aqueous phase individually or in contact with the corresponding organic phase could be explained due to different reasons: the presence of an organic diluent, the presence of an extractant such as TODGA, the presence of more oxygen in the irradiation loop conditions or a combination of all these factors. Therefore, to isolate, study and know if these factors are relevant or not in the simulation of the global resistance different irradiation experiments have been designed. On the one hand, the influence of the contact during the irradiation process between an aqueous phase containing $\text{SO}_3\text{-Ph-BTP}$ with an organic diluent has been studied (Exp. 2), as well as when that organic diluent also contains TODGA (Exp. 3). Table 1 summarises the composition of the aqueous and organic phases employed during the irradiation performed for Exp. 2 and 3. On the other hand, it is possible to find in literature several studies highlighting the relevance of the oxygen presence or radicals coming from water radiolysis in the mechanism of the degradation (Mincher et al., 2009; Mincher, 2018). For that reason, all systems shown in Table 1 were also irradiated in three different ways: (1) in presence of air, (2) in presence of an inert atmosphere such as argon

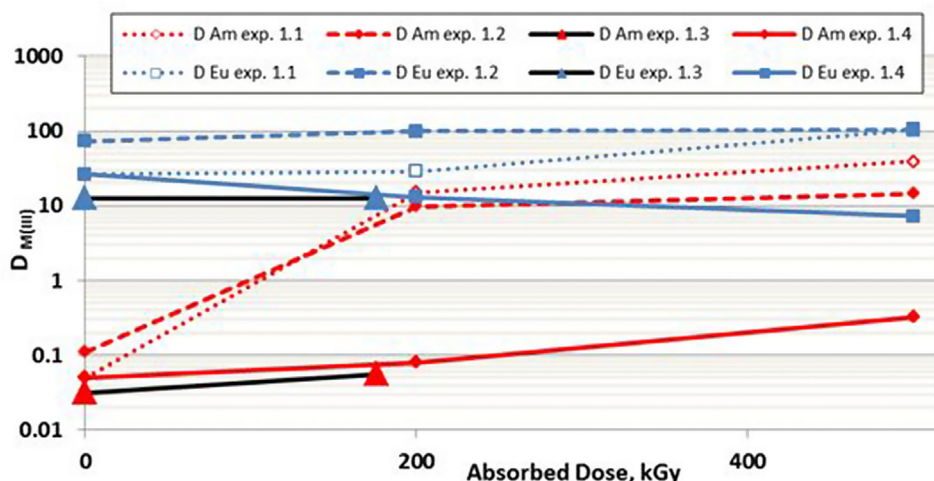


Fig. 2. Am(III) and Eu(III) distribution ratios of fresh and irradiated $\text{SO}_3\text{-Ph-BTP}$ samples at different doses (200 and 500 kGy) and irradiation conditions.

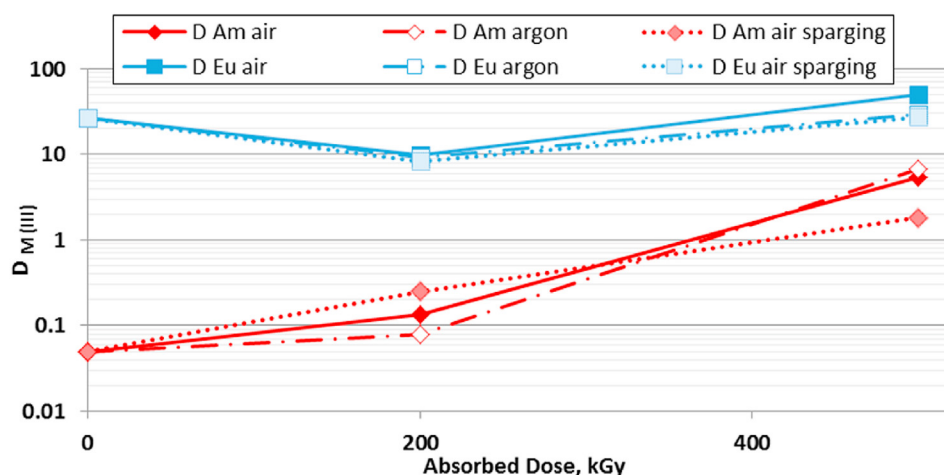


Fig. 3. Distribution ratios of Am(III) and Eu(III) as a function of dose for the Exp. 2 by a fresh organic phase of 0.2 mol/L TODGA in OK and irradiated aqueous phase. The corresponding aqueous phase (18 mmol SO₃-Ph-BTP in 0.5 mol/L HNO₃) was previously irradiated in the presence of OK under different irradiation conditions: air, argon and air sparging.

and (3) using an air sparging flux. The argon atmosphere was chosen to check the system stability in the absence of oxygen, while the air sparging flux simulates a better contact between phases and the presence of higher oxygen content during the irradiation process.

After the irradiation, An(III) and Ln(III) extraction were measured and compared for all solvent compositions and conditions explored. For a rightful comparison of the D_M values obtained, the organic phases consisting of OK during the irradiation in Exp. 2 were replaced by fresh TODGA solvent. Table 1 also shows the composition of the organic and aqueous phases for the extraction experiments carried out, where all Exp. 2 and Exp. 3 samples were spiked with ²⁴¹Am and ¹⁵²Eu.

$D_{Am(III)}$ and $D_{Eu(III)}$ values obtained after the irradiation of the Exp. 2, SO₃-Ph-BTP aq. phase in contact with OK and under the three different atmospheres employed, are shown in Fig. 3. The extraction experiments show a slight increase in $D_{Am(III)}$ until 200 kGy. However, after 500 kGy the distribution ratios of Am increase until values higher than 1, indicating Am is not kept in the aqueous phase under any conditions studied in this experiment. This means that, despite the contact with kerosene during the irradiation, the system loses the ability to keep An in the aqueous phase. However, if these results are compared with those shown in Fig. 2 for Exp.1.2, where SO₃-Ph-BTP was irradiated without any organic phase, it can be seen that $D_{Am(III)}$ values are lower after each studied dose. In consequence, the presence of an organic phase like kerosene during the irradiation process could be providing such protection over SO₃-Ph-BTP solvent. These results point out that when two phases are irradiated together the system could keep better the performance. Furthermore, effects observed for $D_{Eu(III)}$ in Fig. 2 can only be attributed to the degradation of the aqueous phase since fresh TODGA solvent was used in these extraction experiments. Moreover, although a similar trend was observed for the three different atmospheres used, slight differences in $D_{Am(III)}$ values are found when air sparging was used.

The $D_{Am(III)}$ and $D_{Eu(III)}$ values obtained for Exp. 3 are shown in Fig. 4. Now, both phases containing SO₃-Ph-BTP as well as TODGA have been irradiated in contact and under the three different atmospheres chosen. The evaluation of results is now more complicated since

TODGA solvent is also degraded, affecting the extractability of An/Ln into organic phase. Fig. 4 shows that when two solvents are irradiated together up to 200 kGy, not significant changes in $D_{Am(III)}$ and $D_{Eu(III)}$ are observed, showing a better resistance compared with Exp. 1.1 and Exp. 1.2, and in agreement with data represented in Exp.1.3 and Exp.1.4. At 500 kGy, higher effects are observed not only in $D_{Am(III)}$ but also in $D_{Eu(III)}$. After 500 kGy, TODGA concentration is expected to halve (Galán et al., 2012; Sánchez-García et al., 2019) reducing the extractability of An/Ln into the organic phase, which explains the important reduction in $D_{Eu(III)}$ values and why despite the degradation of SO₃-Ph-BTP the $D_{Am(III)}$ values do not increase too much. In fact, using air and argon atmosphere, $D_{Am(III)}$ values are still lower than 1, indicating that Am is still mainly kept in the aqueous phase. Only when the air sparging conditions are used, a total loss of the ability to separate An from Ln is observed, $D_{Am(III)}$ is higher than 1. Again, the different behaviour observed by using air sparging flow points out to changes in degradation pathways, probably because of a better phase mixture or a higher oxygen content. Taking into account these results, it can be concluded that the resistance against radiation of the full TODGA/SO₃-Ph-BTP system is much better than it could be expected from the individually stability studies of each solvent. Besides, these results corroborate that different studies reported until now are correct, but also highlight the importance to choose the experimental conditions for a rightful simulation of the degradation of each system.

Although distribution ratios give us a lot of information about the systems and allow predicting their behaviours, themselves should not be used as the only metric for ligand degradation. For that reason, a further understanding of the factors affecting the extraction properties of the full system after irradiation implies to explore the composition of the organic and the aqueous phase. For example, it is known that TODGA systems are able to keep the An/Ln extraction even after a moderate dose (500 kGy), because some of the degradation products also show extraction properties (Galán et al., 2012). Thus, the composition of all TODGA and SO₃-Ph-BTP solvents under study were investigated.

Following the same methodology of our recent stability studies

Table 1

Composition of the org. and aq. phases that have been irradiated together (up to 200 and 500 kGy) and those used for the extraction experiments.

Experiments		Solvent formulation	
		Organic phase	Aqueous phase
Exp. 2	1) Irradiation	OK	0.018 mol/L SO ₃ -Ph-BTP in 0.5 mol/L HNO ₃
	2) Extraction	0.2 mol/L TODGA in OK FRESH	0.018 mol/L SO ₃ -Ph-BTP in 0.5 mol/L HNO ₃ IRR
Exp. 3	1) Irradiation	0.2 mol/L TODGA in OK	0.018 mol/L SO ₃ -Ph-BTP in 0.5 mol/L HNO ₃
	2) Extraction	0.2 mol/L TODGA in OK IRR	0.018 mol/L SO ₃ -Ph-BTP in 0.5 mol/L HNO ₃ IRR

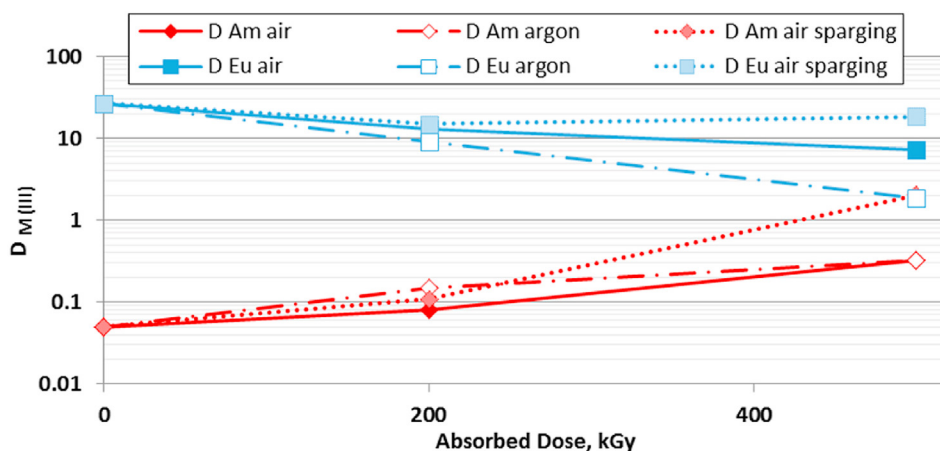


Fig. 4. Distribution ratios of Am(III) and Eu(III) as a function of dose for the Exp. 3 by an irradiated organic phase (0.2 mol/L TODGA in OK) and an irradiated aqueous phase (18 mmol $\text{SO}_3\text{-Ph-BTP}$ in 0.5 mol/L HNO_3) under different irradiation conditions: air, argon and air sparging.

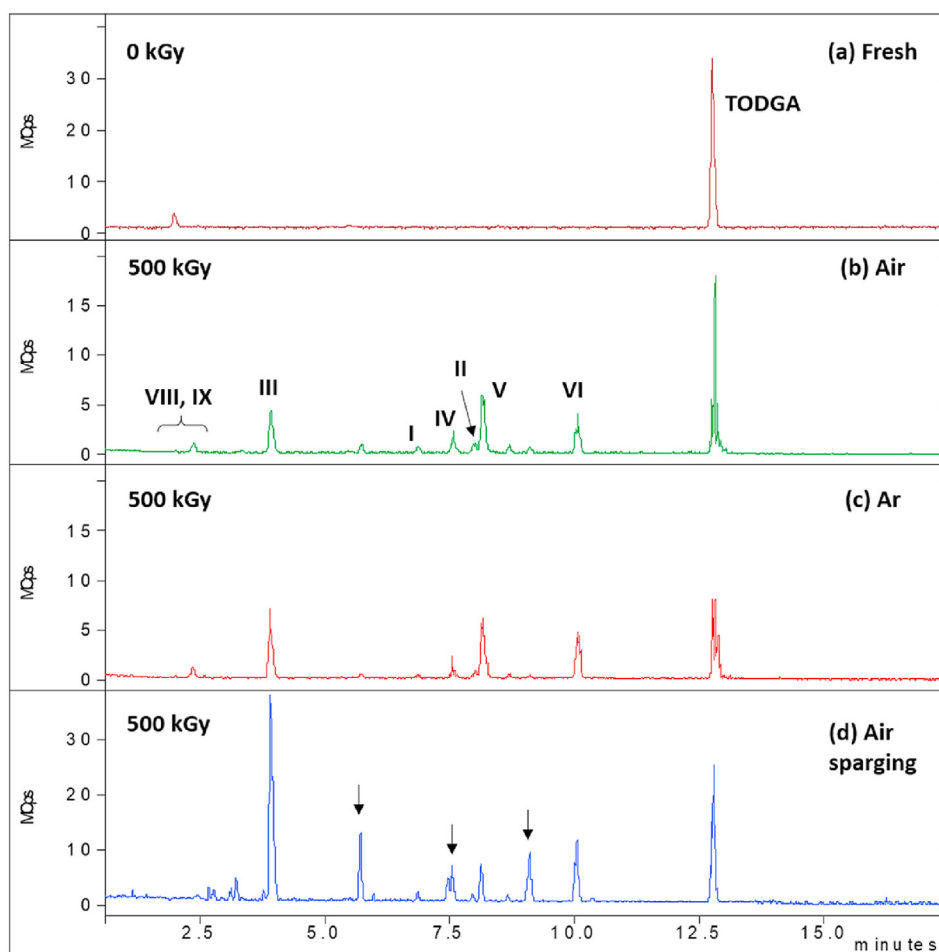


Fig. 5. HPLC-MS chromatograms of TODGA solvents of Exp. 3, where TODGA solvent is irradiated in contact with 18 mmol/L $\text{SO}_3\text{-Ph-BTP}$ in 0.5 mol/L HNO_3 : a) fresh TODGA as reference material; b) irradiated in presence of air up to 500 kGy; c) irradiated in presence of argon up to 500 kGy; d) irradiated up to 500 kGy using air sparging flow.

about TODGA-based solvents (Sánchez-García et al., 2019), the remaining TODGA concentration and all their identified degradation compounds in the media have been quantified by HPLC-MS. Fig. 5 shows the qualitative analysis by HPLC-MS of the reference and irradiated (500 kGy) TODGA-solvents under the three different irradiation conditions chosen, where eight of the main DCs have always been identified after irradiation. The structure of the common TODGA

degradation compounds (DCs) is shown in Fig. 6. The DCs found after the irradiation experiments with air (Fig. 5b) or argon (Fig. 5c) atmosphere are in perfect agreement with known TODGA DCs shown in Fig. 6 (Sugo et al., 2002; Galán et al., 2012; Modolo et al., 2007; Zarzana et al., 2015; Sánchez-García et al., 2019). Furthermore, as it was found in our previous work (Sánchez-García et al., 2019), when air sparging is used three new signals identified as possible undescribed

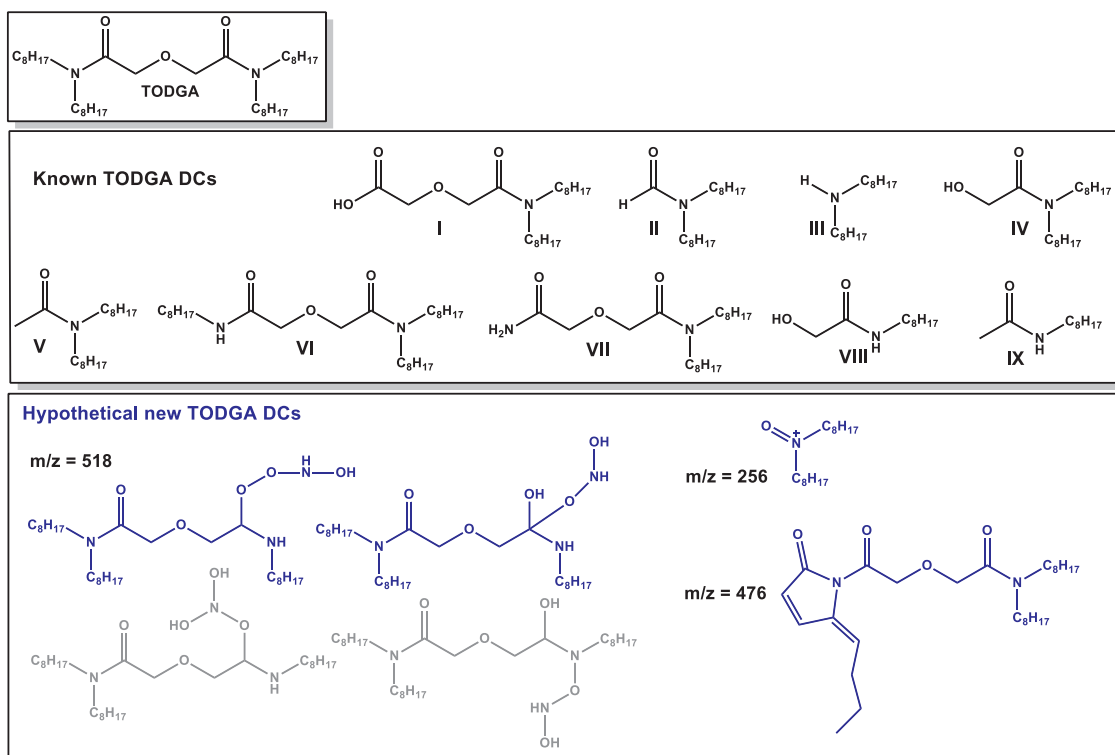


Fig. 6. Structures of TODGA and its known degradation compounds and some hypothetical structures for new signal found by HPLC-MS.

TODGA DCs have been detected ($m/z = 256.1$, $r.t = 5.70$ min; $m/z = 476.1$, $r.t = 7.66$ min; and $m/z = 518.1$, $r.t = 9.11$ min). Two of them ($m/z = 476.1$ and $m/z = 518.1$) agree perfectly with the previous work and the peak corresponding to $m/z = 256.1$ could be attributed to an oxidation of the DC III (Fig. 6). Although this last signal appears in all HPLC-MS chromatograms of Exp.3, the increase of its intensity when air flow is used, support the same conclusions.

Fig. 7 shows the quantification of remaining TODGA concentration after the irradiations of Exp.3 (Table 1), using an air or argon atmosphere or mixing by air sparging flow respectively. TODGA concentration decreases as a function of the dose in the same way when two phases were just contacted (samples without sparging), reducing its concentration around 50% after 500 kGy, in agreement with our previous published data. However, when an air sparging flow is applied, i.e. increasing the oxygen content and mixing between phases, higher reduction of the concentration is found (65%, after 500 kGy),

coinciding again with data obtained before (Sánchez-García et al., 2019) where the decrease in TODGA concentration reached 70%. Moreover, all these results remark that the presence of $\text{SO}_3\text{-Ph-BTP}$ in the aqueous phase during the irradiation has no obvious effect over the degradation of the TODGA-based solvent, in agreement with conclusions extracted by Peterman et al. (2016).

In order to evaluate the different proportions of TODGA DCs identified in qualitative HPLC-MS chromatograms of Exp. 3, the 6 main TODGA DCs observed (I-VI) were quantified by HPLC-MS after 200 and 500 kGy. Fig. 8 shows the quantification of TODGA DCs in the three irradiation conditions. It is well known that the weakest bonds of TODGA due to the effect of radiation are C-O_{ether} and C_{carbonyl}-N (Galán et al., 2012; Modolo et al., 2007; Zarzana et al., 2015), producing mainly DCs IV, V and VI. After 200 kGy, the variations in the concentration of DCs formed are negligible because TODGA degradation is still not relevant. However, after 500 kGy, different results are obtained

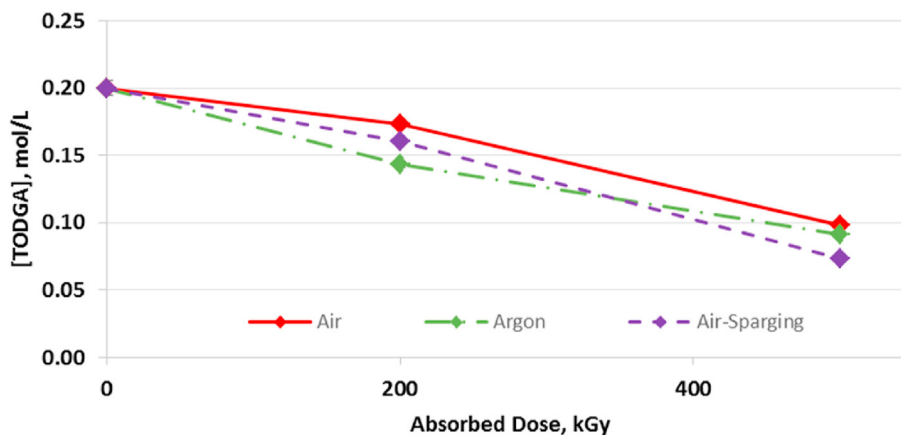


Fig. 7. Concentration of TODGA as a function of the dose in Exp. 3, where 0.2 mol/L TODGA is irradiated in contact with 0.018 mol/L $\text{SO}_3\text{-Ph-BTP}$ in 0.5 mol/L HNO_3 under the different experimental conditions.

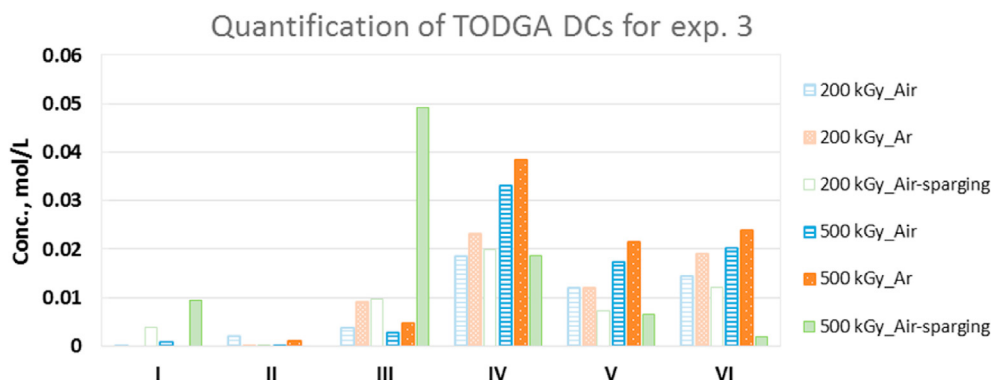


Fig. 8. HPLC-MS quantitative analysis of different TODGA DCs in Exp. 3 (Table 1) under different experimental conditions: air, argon and air sparging.

between samples irradiated in contact (air and argon atmosphere) and samples mixed by air sparging flow. When air and argon atmosphere conditions are employed, the main DCs formed are the expected ones: DC IV, V and VI (Fig. 6). However, when air sparging condition is used, the concentration of DC I and III increase, meanwhile, there is a reduction in the concentration of DCs V and VI (Fig. 8). These data indicate an increase of $C_{\text{carbonyl-N}}$ bond ruptures. The radiolytic degradation of TODGA typically produces DC IV and V in approximately the same proportion (Galán et al., 2012), but in this case, the proportion of both of them is different and particularly lower when air sparging condition is employed. This reduction of the final concentration of DCs IV and V could be attributed to oxidations or recombination not identified yet. A similar behaviour was observed when TODGA was irradiated in contact with HNO_3 under the same conditions (Sánchez-García et al., 2019). Therefore, again air sparging flow is producing a different proportion of the TODGA DCs and all is pointing out to a modification of the predominant degradation pathway under these conditions.

Considering that this work is more focused on the radiation effects over the aqueous phase, the development of an optimal methodology to quantify the degradation of $\text{SO}_3\text{-Ph-BTP}$ would also be desirable, as well as the identification of the possible degradation compounds. In the literature it can be found examples of the identification by LC-MS of the hypothetical degradation compounds of lipophilic BTBPs, such as reported by A. Fermvik et al. (2009). However, due to the tetrasulfonated nature of the $\text{SO}_3\text{-Ph-BTP}$ this kind of analysis are more complicated. Until now, only one work has reported the quantification of $\text{SO}_3\text{-Ph-BTP}$ samples after irradiation by LC-MS (Horne et al., 2019); and we have proposed hypothetical structures of its degradation compounds (Galán et al., 2020) based on mass analysis of irradiated samples at a low dose (50 kGy). In the current experiments, it was possible to follow three of the main MS signals of $\text{SO}_3\text{-Ph-BTP}$ (di, tri and tetra charged compounds by mass spectroscopy, $m/z = 214.3, 286.3$ and 429.9 , respectively, for samples treated with $\text{H}_2\text{SO}_4/\text{H}_2\text{O}/\text{MeOH}$), but calibrations curves obtained by HPLC-MS were not reproducible. Therefore, assuming that its possible degradation compounds do not interfere in the extraction efficiency of Am (Galán et al., 2020), and taking into account the dependence of $D_{\text{Am(III)}}$ distribution ratios on the concentration of $\text{SO}_3\text{-Ph-BTP}$ as reported in the literature (Geist et al., 2012), the decrease in $\text{SO}_3\text{-Ph-BTP}$ concentration with increasing dose was estimated for the different solvent formulation studied. Fig. 9 shows a linear dependence of $D_{\text{Am(III)}}$ as a function of $\text{SO}_3\text{-Ph-BTP}$ concentration in the aqueous phase by the corresponding organic solvent composition, which has been used for estimating the remaining $\text{SO}_3\text{-Ph-BTP}$ concentration after irradiation experiments. As expected, when the $\text{SO}_3\text{-Ph-BTP}$ concentration increases, the D_{Am} is reduced following a linear function ($r^2 = 1.00$) which slope of is -1.87 , in agreement with Geist et al. (2012).

It is also known that the extraction efficiency could be affected by

different parameters such as extractant concentration, nitric acid concentration and temperature. The nitric acid concentration of the samples could be affected due to the radiolytic degradation too, and thus it could affect the D values obtained. Therefore, before estimating the $\text{SO}_3\text{-Ph-BTP}$ concentration as function of the $D_{\text{Am(III)}}$ dependence, the measurement of proton concentration after irradiation was carried out for each sample and is summarized in Table 2. When $\text{SO}_3\text{-Ph-BTP}$ aqueous phase is irradiated alone (Exp 1.2), the proton concentration increases significantly after 200 kGy, in agreement with the first $\text{SO}_3\text{-Ph-BTP}$ stability studies (Galán et al., 2020). However, when the aqueous phase is irradiated in contact with an organic phase, the proton concentration hardly decreases even at 500 kGy, indicating a higher resistance or a different degradation pathway than in the previous case. It can also be observed a slight difference between air sparging and the other atmosphere conditions employed, which could be related to a higher degradation of $\text{SO}_3\text{-Ph-BTP}$ in that condition. In consequence, as no relevant changes were observed in proton concentration after 200 kGy in Exp. 2 and TODGA-solvent was not irradiated in this case, the reduction in $D_{\text{Am(III)}}$ observed in Exp. 2 (Fig. 3) can only be attributed to changes in $\text{SO}_3\text{-Ph-BTP}$ concentration.

Having in mind all factors mentioned before, Fig. 10 shows the estimated concentration of $\text{SO}_3\text{-Ph-BTP}$ for Exp. 1.2, Exp.2 and Exp. 3. As can be seen in Fig. 10a Exp. 1.2, $\text{SO}_3\text{-Ph-BTP}$ concentration in the aqueous phase is reduced from 18 to 1 mmol after 200 kGy when the aqueous phase is irradiated alone. On the contrary, after 200 kGy in contact with kerosene (Fig. 10b, Exp. 2), the worst results were only a halved reduction of $\text{SO}_3\text{-Ph-BTP}$ concentration. As we mentioned before, these data highlight that the resistance of the aqueous phase increases when it is irradiated in the presence of an organic phase. In addition, from Exp. 2 it can be extracted that the highest $\text{SO}_3\text{-Ph-BTP}$ degradation is produced when air sparging flux is used (8 mmol/L after 200 kGy). Therefore, although the contact between phases improves the performance resistance along the irradiation procedure, the air sparging flux increases the degradation of $\text{SO}_3\text{-Ph-BTP}$, probably due to the presence of a higher proportion of oxygen.

Nevertheless, to extract conclusions from Exp. 3 (Fig. 10c) is not so simple since in this case both phases are degraded by radiation. Thus, changes observed in D_{Am} as a function of the dose (Fig. 4) could not only be attributed to the decrease in $\text{SO}_3\text{-Ph-BTP}$ concentration but also to the decrease of TODGA concentration. However, if TODGA remaining concentration after 200 and 500 kGy is compared (see Fig. 7), it can be assumed that TODGA degradation at 200 kGy is no so high. Presumably, the changes observed in the extraction results of Exp. 3 at 200 kGy could be better related to the degradation of $\text{SO}_3\text{-Ph-BTP}$. Therefore, the data obtained at 200 kGy for Exp. 2 and Exp. 3 (see Figs. 3 and 4) are compared, the $D_{\text{Am(III)}}$ values are slightly lower when the full system is irradiated, suggesting that the $\text{SO}_3\text{-Ph-BTP}$ remaining concentration could be higher in Exp. 3 than in Exp. 2.

Although the development of a methodology to characterize the

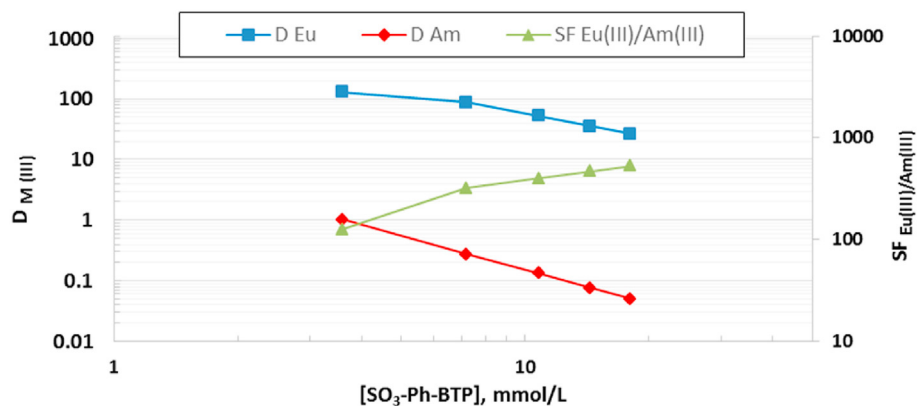


Fig. 9. Influence of SO₃-Ph-BTP concentration in the extraction of Am(III) and Eu(III) into TODGA solvent. Organic phase, 0.2 mol/L TODGA in OK. Aqueous phase, increasing concentration of SO₃-Ph-BTP in 0.5 mol/L HNO₃.

Table 2

Proton concentrations obtained in the SO₃-Ph-BTP aqueous phase as a function of dose and the experimental conditions of experiments.

Sample	[H ⁺] concentration mol/L		
	0 kGy	200 kGy	500 kGy
Aq. Phase _ Exp. 1.2	0.5	0.89	0.98
Aq. Phase _ Exp. 2_Air	0.5	0.45	0.37
Aq. Phase _ Exp. 2_Argon	0.5	0.45	0.37
Aq. Phase _ Exp. 2_Air sparging	0.5	0.46	0.58
Aq. Phase _ Exp. 3_Air	0.5	0.41	0.34
Aq. Phase _ Exp. 3_Argon	0.5	0.37	0.29
Aq. Phase _ Exp. 3_Air sparging	0.5	0.45	0.47

composition of the aqueous phase after irradiation is still needed, the results obtained in this work are very interesting because they do not only corroborate that when two phases of the TODGA/SO₃-PhBTP system are irradiated together the degradation is not so dramatic, but they also give answers to the disagreeing previous studies and help to design the future pattern tests and irradiation strategies.

4. Conclusions

In this research, controversial results between some fundamental stability studies of extraction systems against γ -radiation have been collected and compared. These studies highlight the importance of the adequate experimental strategy of simulation to evaluate the resistance of extraction systems against radiation, which is fundamental for their application in nuclear fuel recycling.

This work is particularly focused on the evaluation of the most relevant conditions to simulate the degradation of extraction systems involved *i*-SANEX and EURO-GANEX processes, two of the most promising processes to achieve the separation of actinides from lanthanides. The possible factors affecting to the organic solvent have previously addressed considering TODGA as the main molecule. The present study deals with the full system with the main attention point on the stability of the aqueous phase and its interaction with the corresponding organic phase. For that purpose, a new set of γ -irradiation experiments focused on the stability of the SO₃-Ph-BTP aqueous phase were carried out, covering different factors such as the presence of one or two phases during irradiation, the mixture between phases and the oxygen content.

All current results considering the full TODGA/SO₃-Ph-BTP system corroborated our previous conclusions about TODGA-based solvents: TODGA molecule is more degraded when the organic and aqueous phases are irradiated together and using an air sparging flow; but also, air sparging flow could modify the predominant degradation pathway

since new possible signals of degradation compounds have been identified and different proportions of known degradation compounds have been quantified.

In addition, it can be concluded that the viability of SO₃-Ph-BTP to be employed for nuclear fuel recycling by irradiating the aqueous phase alone had been underestimated. The irradiation of the full TODGA/SO₃-Ph-BTP system keeps better the performance for longer operational periods, in agreement with the study done by [Peterman et al. \(2016\)](#). In fact, it has been checked that when the aqueous phase is irradiated in the presence of TODGA solvent, the system keeps better the performance to separate actinides from lanthanides, rather than when it was irradiated only in the presence of an organic diluent such as kerosene. Furthermore, the data obtained demonstrate that the resistance of SO₃-Ph-BTP in nitric acid also depends on the irradiation conditions employed, being similar in the case of air and argon atmosphere; but different when air sparging flow is used, probably because of higher oxygen content or the higher contact between phases.

Considering all these results, the suitability of the extractants as well as the general performance of the solvents submitted to radiation should always be evaluated as a full system irradiating the corresponding organic and aqueous phases together. It is still not clear if oxygen content or the higher contact between phases is the responsible of the modifications in the degradation pathways observed, therefore, extended studies addressing these two factors individually are needed.

CRediT authorship contribution statement

I. Sánchez-García: Investigation, Methodology, Formal analysis, Writing - original draft, Writing - review & editing. **H. Galán:** Supervision, Methodology, Conceptualization, Validation, Writing - review & editing. **J.M. Perlado:** Validation, Funding acquisition. **J. Cobos:** Supervision, Validation, Funding acquisition.

Declaration of competing interest

None.

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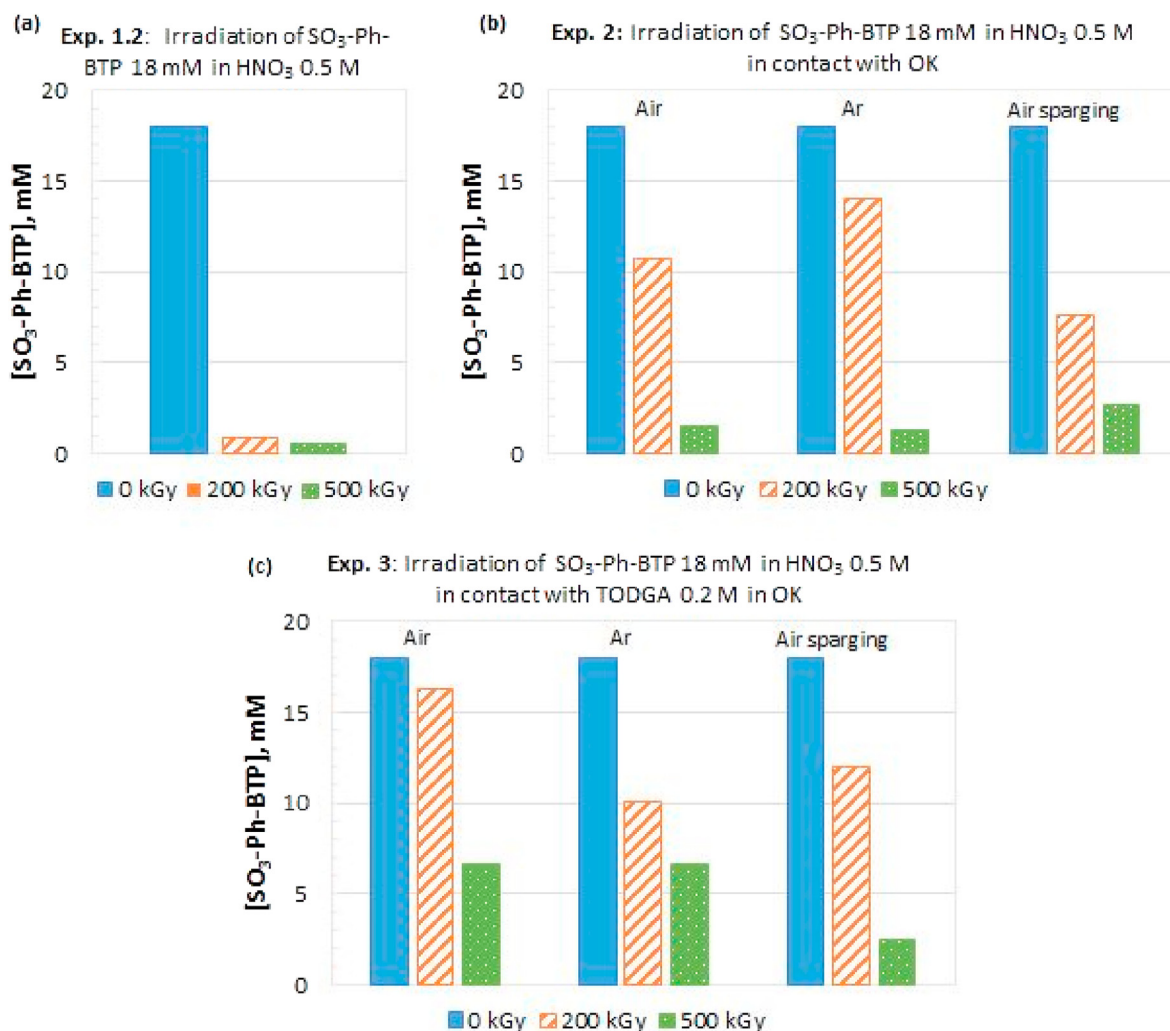


Fig. 10. Estimated $\text{SO}_3\text{-Ph-BTP}$ concentration as a function of dose (0–500 kGy) for the different experiments performed: a) Exp. 1.2: irradiation of 18 mmol/L $\text{SO}_3\text{-Ph-BTP}$ in 0.5 mol/L HNO_3 without organic phase; b) Exp. 2: irradiation of 18 mmol/L $\text{SO}_3\text{-Ph-BTP}$ in 0.5 mol/L HNO_3 in contact with OK under air, argon and air sparging conditions; c) Exp.3: irradiation of 18 mmol/L $\text{SO}_3\text{-Ph-BTP}$ in 0.5 mol/L HNO_3 in contact with 0.2 mol/L TODGA in OK under air, argon and air sparging conditions.

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