

Stability studies of GANEX system under different irradiation conditions

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Abstract. To demonstrate the robustness of extraction systems against radiolytic degradation is nowadays one of the limiting points to ensure a safe and stable operation for advanced nuclear fuel strategies. In this paper, is addressed the stability of one of most promising extractants (TODGA, *N,N,N',N'*-tetraoctyldiglycolamide) but also the importance of designing realistic model to simulate and study the degradation of the systems. For that, new irradiations experiments were carried out where mixture between phases and the oxygen content have been taken into account. Extraction behaviour and composition of the organic phases after γ -irradiation have been measured and compared. Although TODGA studies are applicable to many processes currently under development, this work is focus on Grouped Actinides Extraction (GANEX) process development.

1 Introduction

In the development of more sustainable nuclear fuel cycle options, a future potential scenario involves the transition from thermal reactors to fast reactors with a closed fuel cycle to recycle actinide elements. Due to that, currently two actinides recycling scenarios are considered: the heterogeneous recycling of using a modified version of the PUREX process [1] followed by SANEX type process (*Selective Actinides Extraction*) [2]; and the homogeneous recycling of all actinides together, the named as GANEX concept (*Grouped Actinide Extraction*) [3].

The development and applicability of these extraction processes are limited by safety issues related to the resistance to radiation because they must work in continue operation in the recycling plant. For that reason, extractants like the diglycolamide TODGA (*N,N,N',N'*-tetraoctyldiglycolamide), which shows promising extraction properties and a good resistant to radiation, are being used widely for these applications [1–7].

GANEX concept involves an initial U recovering (using the monoamide DEHiBA in total petroleum hydrocarbons (TPH) diluent) followed by the separation of all transuranium elements (TRU) [5]. One of the candidate options for the second step of GANEX concept is the so called EuroGANEX process, where actinides and lanthanides are co-extracted from the first raffinate into an organic phase

containing TODGA (*N,N,N',N'*-tetraoctyldiglycolamide) and the malonamide DMDOHEMA (*N,N'*-dimethyl-*N,N'*-dioctylhexyloxyethyl malonamide) as phase modifier to increase the Pu loading capacity. From this loaded organic phase, all TRU are stripped by using a mixture of SO_3 -Ph-BTP (2,6-bis(5,6-di(sulphophenyl)-1,2,4-triazin-3-yl)pyridine) and AHA (aceto-hydroxamic acid) [6].

Many efforts have been done in the last years to study the stability of the most relevant molecules involved in this promising process (TODGA, DMDOHEMA, SO_3 -Ph-BTP, etc) [7–8]; and particularly those that are in the organic phase, expected to be recycled, like TODGA and DMDOHEMA. Nevertheless, the results are not always consistent neither comparable due to the different experimental conditions chosen. e.g., TODGA has been studied by many authors [7–11] but some authors are still discussing about the effect of nitric acid, degradation compounds formed or degradation pathways.

Sugo et al. [9] performed quantitative and qualitative studies on the radiolytic degradation of TODGA in different conditions of diluents but always irradiating only the organic phase, and they found that the G value was strongly dependent on both initial concentration and also on the solvent. Galán et al. [7] studied the radiolytic stability of TODGA solvents pre-equilibrated with 3 mol/L HNO_3 varying the composition of diluents with octanol, and they found an important decrease of its concentration, especially when TODGA is not pre-equilibrated with HNO_3 . From their results, they reported that HNO_3 has a protective role of TODGA during the irradiation. However,

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others authors such as Modolo et al. [10] and Zarzana et al. [11] concluded that the presence of the acidic aqueous phase has no obvious effect on the dose rate (d) when irradiation is performed in kerosene or dodecane. Moreover, Mincher [13] explains also that TODGA dose rate seems to be insensitive to the presence or absence of aqueous phases, by varying acidity and/or oxygen concentration flow during irradiation in dodecane. However must be highlighted that all experiments performed by Modolo et al. [10], Zarzana et al. [11] and Mincher et al. [13] were performed in non-polar diluents, such as kerosene or dodecane where nitric acid is minimum extracted.

In addition to these studies, Peterman et al. [12] performed quantitative studies of TODGA samples irradiated in contact with HNO_3 but also in contact with $\text{SO}_3\text{-Ph-BTP}$ aqueous phase, in static and in dynamic conditions. They concluded that the stability of TODGA and $\text{SO}_3\text{-Ph-BTP}$, and the general performance of the system depends strongly on the simulation of irradiation process conditions. Under their conditions the TODGA/ $\text{SO}_3\text{-Ph-BTP}$ system kept the original performance; in contrast with results observed by Galán et al. [8], where the irradiation of $\text{SO}_3\text{-Ph-BTP}$ in HNO_3 gave place to a degradation of 90% after 200 kGy.

Given the differences found in the literature about the radiolytic degradation of main molecules involved in Euro-GANEX process, the aim of this work is looking for the process-relevant conditions, which should be simulated to achieve reliable degradation models to ensure a safe and stable operation in nuclear fuel reprocessing plants. And for that, it has been explored how and why the experimental conditions affect to the ligand stability and proportions of by-products formed during irradiation. Particularly, this work shows the first studies to determinate the conditions to simulate the degradation of the organic phase from the point of view of the key step of Euro-GANEX process, the TRU stripping step. In that sense, it has been submitted to γ -irradiation samples of 0.2 mol/L TODGA in OK (odourless Kerosene) in contact with 0.5 mol/L nitric acid under different conditions. For an easy understanding of the parameters involved and a first approach to Euro-GANEX solvent, the phase modifier DMDOHEMA has been removed from the solvent. Both phases have been irradiated under (a) normal air atmosphere; (b) argon atmosphere; and (c) using an air sparging flow (to increase the contact between phases and the content of oxygen) conditions. After irradiation, the performance and composition of the systems have been analysed by gamma spectrometry and LC-MS respectively.

2 Experimental

2.1 Chemicals, solutions and isotopes

TODGA was synthesised at CIEMAT modifying an existing literature procedure under air and without drying solvent and glassware [14,15]. $\text{SO}_3\text{-Ph-BTP}$ was purchased in Technocomm Ltd. Degradation compounds I-VI have been obtained as described in previous studies [7]. The diluents were odourless kerosene (OK), purity 98%, from Alfa Aesar. All reagents were used from commercially

available sources without further purification. Nitric acid, HNO_3 , purchased from VWR Chemical was purified by Quartz sub-boiling distillation system (MLS-Milestone) and solutions were prepared by diluting concentrated nitric acid (65%) with ultrapure water (18 M Ω /cm). The radioactive tracer solutions of $^{241}\text{Am(III)}$ and $^{152}\text{Eu(III)}$, were obtained as MCl_3 , in HCl 1 mol/L, by Isotope Products Laboratories, California (USA).

2.2 Irradiation procedure

Irradiation experiments of the different samples were performed in the Náyade irradiation facility (CIEMAT) described in detail elsewhere (Náyade facility¹). This facility consists in a 1.2 m² by 4.5 m pool with 60 sources of ^{60}Co , distributed in six lots with a total activity of 1.1×10^{14} Bq. The irradiation container used provides homogeneous irradiation flux.

Different samples of TODGA (0.2 mol/L in OK) in contact with 0.5 mol/L HNO_3 were irradiated in glass vessels up to doses of 200 and 500 kGy at dose rates of 4.02 kGy/h, as determined by Fricke dosimetry. Samples under air atmosphere and Argon were irradiated in sealed glass vessels and for aerated samples an air sparging flow was employed. Extraction experiments (see below) using the irradiated organic phases were performed immediately after the last step of irradiation. Reference samples were kept in the laboratory during the irradiation process for control.

2.3 Extraction experiments

Extraction experiments were performed using 0.5 mL of fresh and irradiated organic phases (0.2 mol/L TODGA + in kerosene) and 0.5 mL of fresh aqueous phase (18 mmol/L $\text{SO}_3\text{-Ph-BTP}$ in 0.5 mol/L HNO_3), spiked with 10 μL of $^{241}\text{Am(III)}$ and $^{152}\text{Eu(III)}$ in 0.5 mol/L HNO_3 (1 kBq/mL each). The phases are mixed 30 min, and after centrifugation, 0.3 mL of organic and aqueous phases were taken to for analysis of ^{241}Am and ^{152}Eu activities by gamma spectrometry. Canberra HPGe detector were used for high energy gamma spectrometry measurements, using Genie-2000 as gamma analysis software from Canberra, and gamma characteristic photopeak at 59.5 keV and 121.8 keV were analyzed for ^{241}Am and ^{152}Eu , respectively. The results are reported as distribution ratios D ($D_M = \frac{[\text{M}^{3+}]_{\text{org}}}{[\text{M}^{3+}]_{\text{aq}}}$).

2.4 HPLC measurements

The chemical composition of the irradiated organic samples was characterised by HPLC-MS. HPLC measurements were performed by using an HPLC-MS Bruker EVOQTM (Triple Quadrupole detector) with a ACE 3 C18-PFP column (50 mm \times 2.1 mm) at 40°C, using a gradient of mobile phase [(A: 0.1% HCOOH in H_2O), (B: 0.1% HCOOH in CH_3CN)]. The ionisation modes

¹ http://fusionwiki.ciemat.es/wiki/LNF:Technology#NAYADE_Co-60_irradiation_facility

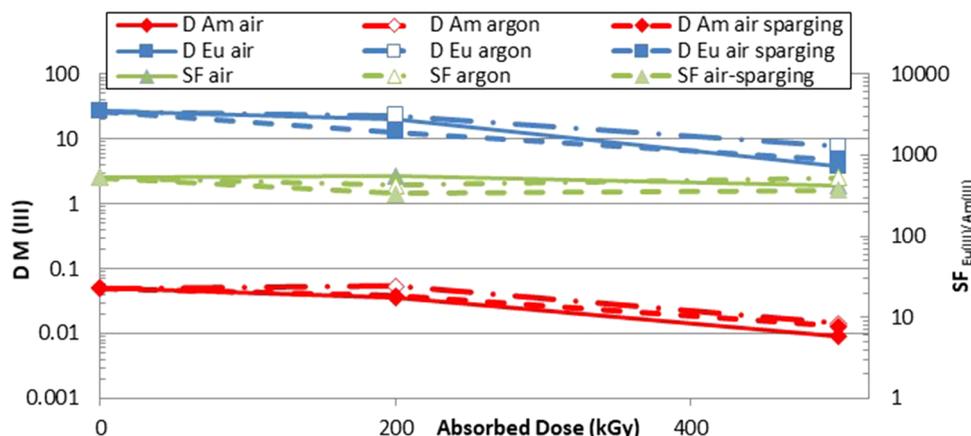


Fig. 1. Distribution ratios of Am(III) and Eu(III) as function of dose and the different irradiation conditions of the organic phase: air, Argon and air sparging. Organic phases: fresh or irradiated 0.2 mol/L TODGA in OK. Aqueous phases: fresh 18 mmol $\text{SO}_3\text{-Ph-BTP}$ in 0.5 mol/L HNO_3 . Spiked with $^{241}\text{Am(III)}$ and $^{152}\text{Eu(III)}$ (1 kBq/mL each).

APCI⁺ and ESI⁺ were used for TODGA and TODGA degradation compounds (DC's) quantification, respectively. Samples for HPLC studies were analysed without pre-evaporation and diluted 1:30000 in HPLC grade MeOH. Calibration curves were performed by HPLC-MS for TODGA (10-1000 ppb) and each degradation compound of TODGA (1-250 ppb) and the correlation coefficient in all cases were in the range of 0.993-0.999. All measurements were repeated twice.

3 Results and discussion

The organic solvent selected as a simplified Euro-GANEX solvent (0.2 mol/L of TODGA in OK) in contact with 0.5 mol/L HNO_3 were irradiated up to 200 and 500 kGy with external ^{60}Co sources as described above. After irradiation, the An stripping efficiency of the different irradiation models designed was analysed by the Ln/An distribution ratio measurements. Fresh and irradiated organic phases were contacted with the corresponding aqueous phase of Euro-GANEX system (18 mmol/L of $\text{SO}_3\text{-Ph-BTP}$ in 0.5 mol/L HNO_3) and spiked with Am(III) and Eu(III). The evolution of the distribution ratio versus dose (Fig. 1) shows a slightly reduction of $D_{\text{Am(III)}}$ and $D_{\text{Eu(III)}}$ for all samples when the dose was higher than 500 kGy as could be expected from the previous TODGA stability studies [10]. In these experiments, aqueous phases containing $\text{SO}_3\text{-Ph-BTP}$ were not irradiated, therefore their ability to keep An in the aqueous phases ($D_{\text{Am}} \ll 1$) is not affected and the reduction of D_{Am} as function of the dose is only attributed to the degradation of TODGA in the organic phase. Even so, the separation factor between Am(III) and Eu(III) is kept invariable in all chosen experimental conditions.

Regarding the different proposed irradiation experiments (air, Argon atmosphere and air sparging), only small differences in the distribution ratio of both metals were observed. These results pointed out that the different irradiation conditions could not affect considerably to the extraction properties of the studied system.

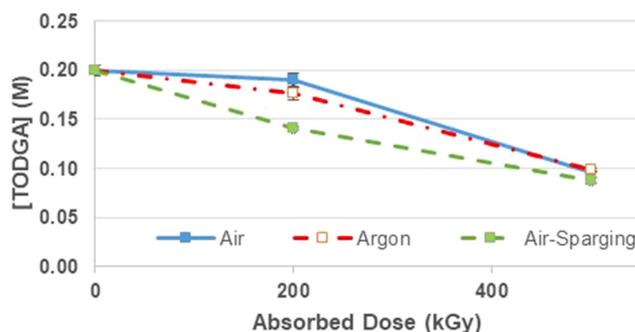


Fig. 2. Concentration of TODGA as function of the dose for 0.2 mol/L TODGA irradiated in contact 0.5 mol/L HNO_3 .

These results are in a good agreement with TODGA stability studies [7,9,10] where no significant changes in the Am and Eu distribution ratio at high irradiation dose were observed. According to these results, TODGA is hardly degraded by the radiation effect. However, TODGA systems are able to keep the An/Ln distribution ratio even after a high degradation due to some degradation products have good extraction properties maintaining the good extraction properties of the system until higher doses. Therefore, distribution ratios themselves should not be used as the only metric for ligand degradation.

Quantitative HPLC-MS measurements of TODGA have been carried out for a better understanding of results. Figure 2 shows concentrations of TODGA as function of the dose for the three experimental conditions used: air, Argon and air sparging. TODGA concentration decreases as function of doses in the same way when two phases were not mixed, just contacted (samples without sparging), they halved after 500 kGy. However, applying an air flow sparging, it means increasing the oxygen content and mixing between phases, there was a higher reduction of the concentration, 70% loss after 500 kGy. The small differences in the distributions ratios observed in Figure 1 could be now explained by the higher TODGA degradation in samples irradiated with air sparging. However, a complete characterization of the organic phases

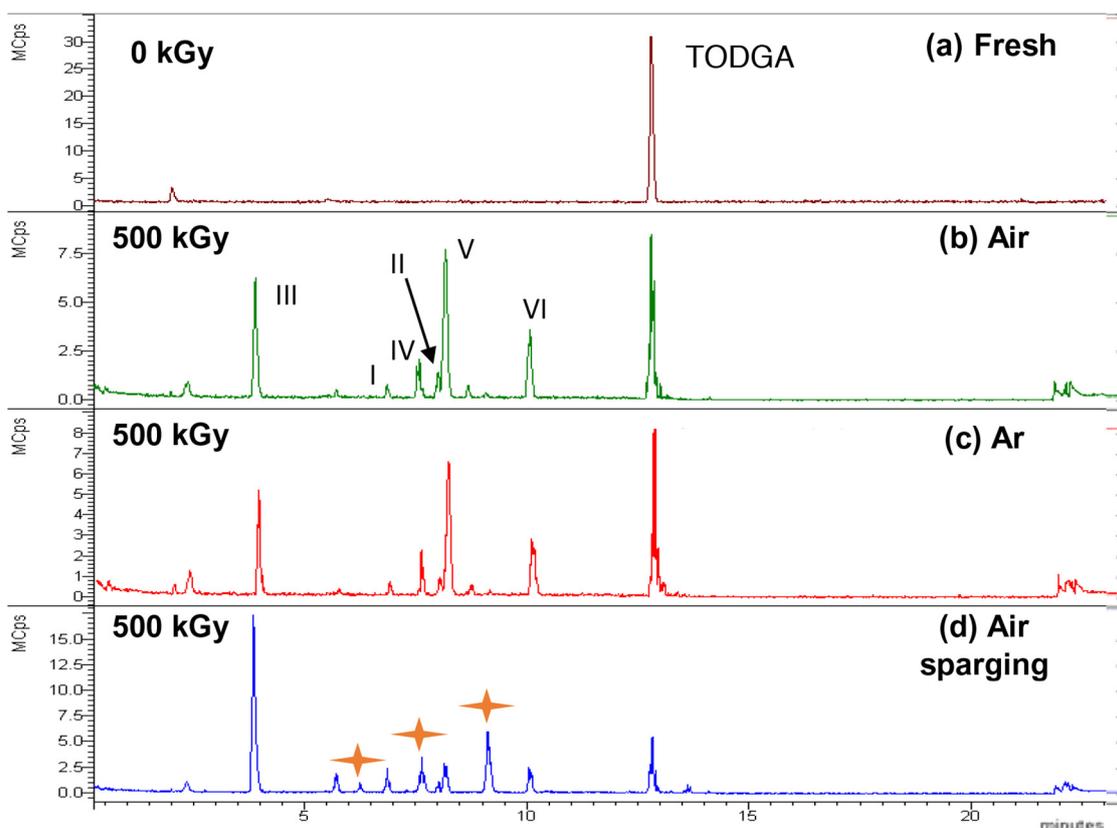


Fig. 3. HPLC-MS chromatograms of TODGA solvents (a) fresh as reference material, (b) in presence of air irradiated up to 500 kGy, (c) in presence of Argon irradiated up to 500 kGy and (d) air flow sparging irradiated up to 500 kGy all of them in contact with 0.5 mol/L HNO_3 .

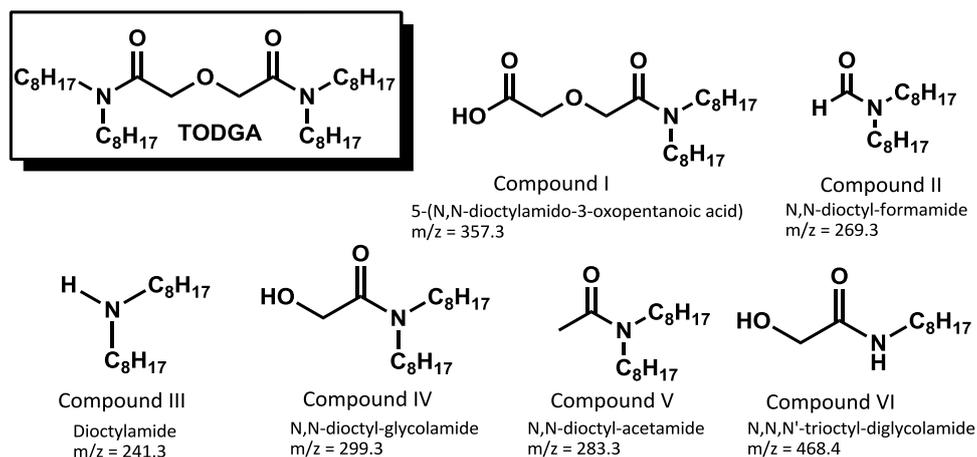


Fig. 4. Structures of TODGA and its main radiolytic degradation products.

implies the identification and quantification of all those new species formed due to radiation. For that reason, to identify the degradation products formed during the irradiation, the composition of samples has been qualitative and quantitatively analysed and compared by HPLC-MS.

Figure 3 shows qualitative HPLC-MS chromatograms of a fresh TODGA solvent and irradiated solvents up to 500 kGy in contact with HNO_3 under different experimental conditions. In TODGA reference system (0 kGy), DCs

have not been observed (Fig. 3a). Results observed for TODGA systems irradiated up to 500 kGy in presence of air and Argon atmosphere (Figs. 3b and 3c) are in agreement with the literature [7,9,16], 9 typical TODGA DCs and in the expected proportion were identified (Fig. 4). However, in the irradiated system using an air flow sparging (Fig. 3d) different proportions of TODGA DCs and new signals corresponding to three possible unidentified TODGA DCs ($m/z = 434.1$, $r.t. = 6.26$ min; $m/z = 476.1$, $r.t. = 7.66$ min; and $m/z = 518.1$, $r.t. = 9.13$ min)

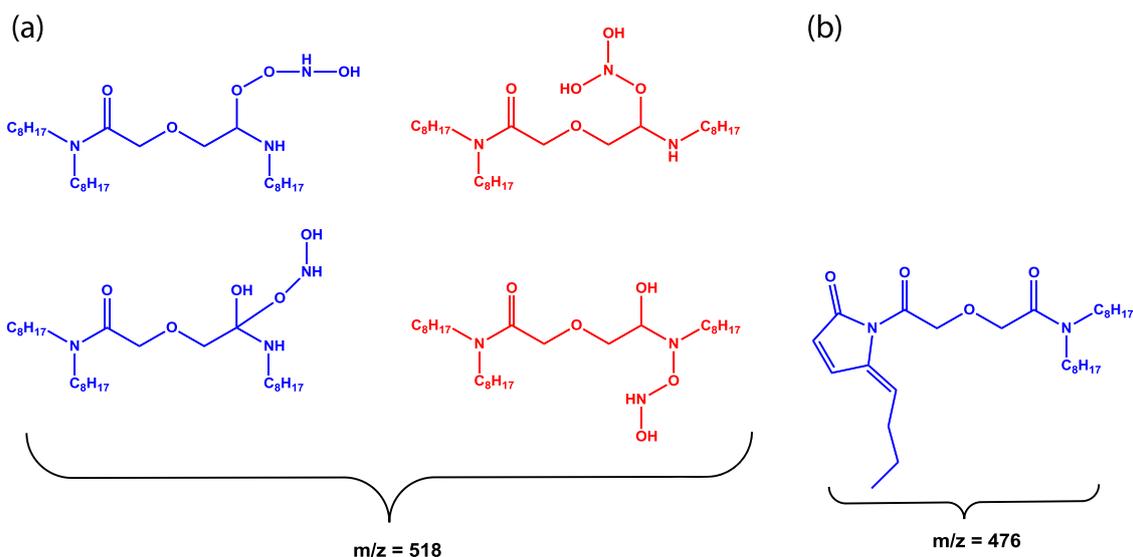


Fig. 5. Hypothetical structure of new possible TODGA degradation compounds corresponding to (a) m/z 518 and (b) m/z 476.

have been detected. Therefore, air sparging flow changes the dominant degradation pathway due to different proportion of DCs and new possible unidentified TODGA DCs are observed. This fact should be taken into account in future stability studies for process development.

Figure 5 shows the plausible structures assigned to the signals analysed by HPLC-MS for the new possible TODGA DCs, corresponding to m/z 518 and 476 respectively. Anyhow, deepest studies are needed to corroborate these hypothetical structures as TODGA degradation compounds.

To assess the different proportions of TODGA DCs identified in Figure 3, the quantification of the 6 main known DCs (I-VI) observed by HPLC-MS was carried out. Calibration curves were performed by HPLC-MS for each TODGA DCs and the concentration of all of them was calculated.

It is known that the weakest bonds of TODGA due to the radiation effect are C–O and N–C [7,9,11,16], giving place to DC IV, V and VI. As it can be expected, after 200 kGy the TODGA degradation is not relevant and therefore the difference in DCs formed are negligible. However, after 500 kGy, where 50% of the initial TODGA concentration has been degraded, it can be observed different results between samples irradiated in contact (air and Argon atmosphere) and those mixed by air flow sparging. Data show that the concentration of DCs I and III increased, it means the rupture of N–CO bonds is higher; meanwhile there is a reduction in the concentration of DCs V and VI (Fig. 4). When TODGA is degraded by C–O bond, the concentration of DCs IV and V should be similar, but DC IV can be also broken into DC V due to the effect of radiolysis. Therefore, the reduction observed for DC V could be attributed to oxidations or recombination that it has not been identified yet. The new proposed degradation compounds are identified when there is a higher oxygen content in the system, and it could be formed by oxidative conditions. This oxidative condition could explain why it has been observed a reduction in the

concentration of DC VI to favour the formation of compounds I and III, but also, they are in good agreement with a higher oxidation of DC III when air sparging condition is used (Fig. 6).

As can be seen in Figure 2, air flow increases TODGA degradation after 500 kGy, although differences are not too important to the performance of the system it is compared with the other conditions employed. In fact, those differences are not reflected in the behaviour of the system since samples irradiated with air sparging shows a similar $D_{Eu(III)}$ for the three model of irradiation tested at 500 kGy (Fig. 1), continue showing an excellent separation of actinides and lanthanides in the conditions employed. However, the different proportion of DCs formed using air sparging condition is a very important observation because the different DCs and their accumulations could affect the extraction properties of the system in the long term, due to its individual extraction properties.

4 Conclusions

The effects of ^{60}Co γ -radiation on TODGA-based solvents under different irradiation conditions to reach realistic model of radiolysis simulations by experiments as simple as possible have been investigated. Direct radiolysis of extractants is much less statistically probable than its indirect radiolysis through diluents, which are more abundant in solution. For that reason, the oxygen content and the present of radicals from water radiolysis have been selected as the experimental conditions to explore the degradation of TODGA in contact with HNO_3 . For that, experiments under air or Argon atmosphere, and using an air sparging flow to increase the mixture between phases have been analysed. The results for a simplify GANEX system after a moderate dose, 500 kGy, show that organic TODGA-solvent maintained the separation between actinides and lanthanides in all cases. However, in the case of experiments performed in presence of air flow

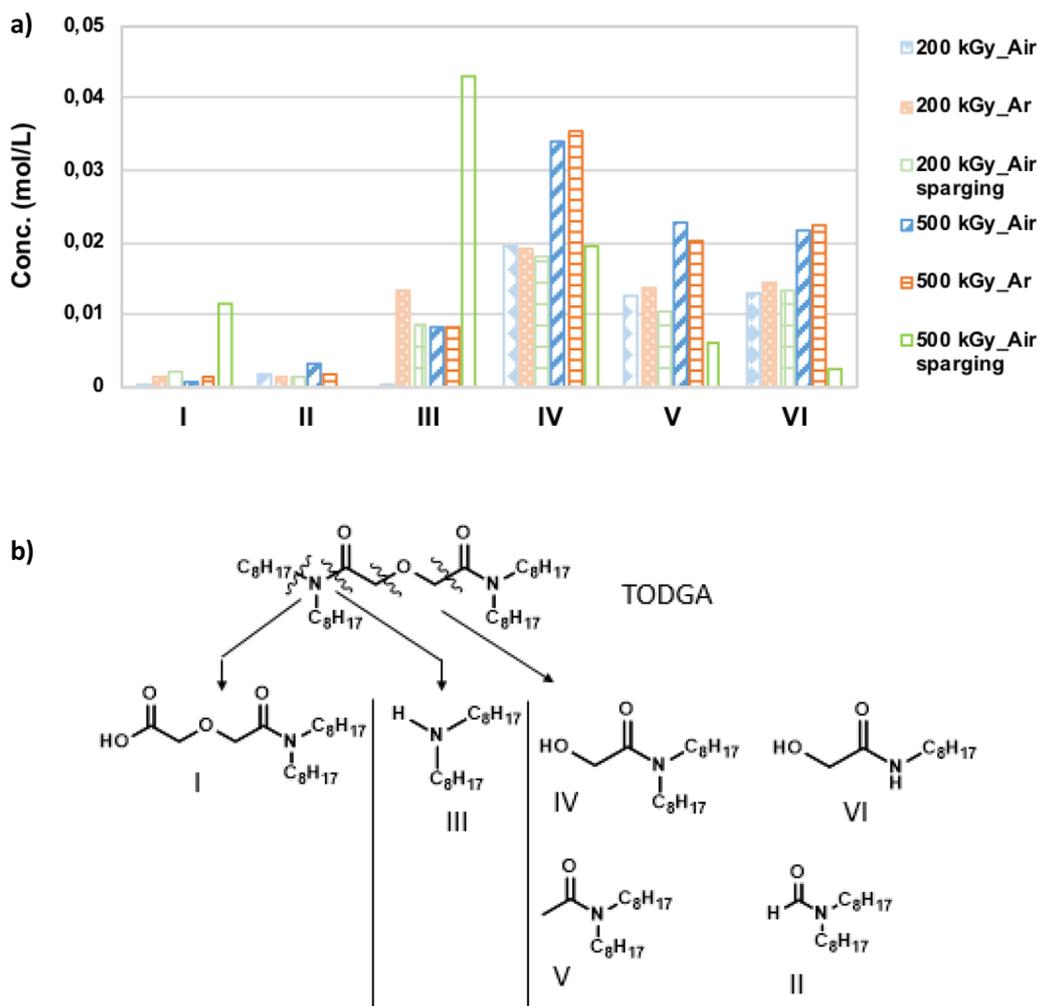


Fig. 6. (a) HPLC-MS quantitative studies of different TODGA degradation compounds at different experimental conditions: air, Argon, air sparging for 0.2 mol/L TODGA in OK irradiated in contact with 0.5 mol/L HNO_3 . (b) Structure of TODGA and its radiolytic pathway to produce DCs I, III, IV, V and VI.

sparging, TODGA concentration decreased to 70% of the initial concentration, as result of a higher degradation than experiments performed under air and Argon atmosphere where phases were not mixed, just contacted (50%).

Moreover, from qualitative studies performed by LC-MS, the expected 9 TODGA DCs were observed in all irradiation studied of this work. Besides, it has been observed the presence of new possible TODGA DCs when air sparging was used, pointing out to a change in the degradation pathway. The quantification of the TODGA known DCs confirmed this hypothesis. When air was bubbled, compounds form due to N-CO bond rupture increased their concentration, DCs I and III; meanwhile a reduction in the concentration of DCs V and VI was observed.

These results illustrate that an Argon atmosphere has the same effect on TODGA-solvent in static irradiation conditions as air atmosphere. Changes observed by using an air sparging flow could be due to a higher content of oxygen, since oxygen is reacting into the radiolysis process, but also due to the presence of radicals produced from water radiolysis. Hence, from the point of view of TODGA-solvent,

Euro-GANEX stability studies should be performed by simulating both phases by increasing contact between them. In this work we have learned that extended studies are necessary to going on to the identification of the relevant process conditions for a realistic simulation of long-term behaviour of advanced nuclear fuel extraction systems.

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Author contribution statement

Iván Sánchez-García has done mainly the work in this article. Hitos Galán has contributed to this work by providing technical support and expert viewpoints on the different topics discussed in the article. Jose Manuel Perlado and Joaquín Cobos have contributed to this work by supplying help in the writing the article providing a viewpoint on the different topics discussed in the article.

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