



Effect of Europium Complexation on *N,N,N',N'*-Tetraoctyldiglycolamide Degradation Against Gamma Radiation

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Received: 30 July 2023 / Accepted: 24 October 2023
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Abstract

Diglycolamide extractants (DGAs) are playing an important role for many of aqueous separation processes under development for the advanced nuclear fuel cycle. This family of ligands exhibits excellent extracting and resistant properties, with TODGA (*N,N,N',N'*-tetraoctyldiglycolamide) being a particularly successful extractant studied intensively in recent decades. Nowadays, the main issues for TODGA-based solvents are related to the understanding and simulation of the radiolytic degradation under realistic conditions, which is limiting aspect for the development of an advanced aqueous nuclear separation process. In that sense, in this work, TODGA ligand stability, solvent composition and performance were evaluated considering the effect of metal complexation under gamma radiation. For that, the irradiation of a TODGA solvent in the presence of Eu metal was carried out, varying the ligand/metal ratio. The goal was to not only study TODGA degradation using HPLC–MS technique but also to identify and quantify its degradation compound under these experimental conditions. The results revealed a protection of TODGA molecules due to metal ion complexation, with no observed changes in the degradation pathway, as confirmed by the quantification of formed degradation compounds.

Keywords TODGA gamma stability · Degradation compounds · Composition analysis · HPLC–MS

1 Introduction

One of the main issues currently facing the future of nuclear power is the proper and efficient management of nuclear waste. As one of the most sustainable solutions, the scientific community is working on advanced nuclear fuel cycles and particularly on the demonstration of closed fuel cycles. The recovery of valuable fissile and fertile materials is not the only main goals of this strategy but also the reduction of the volume and radiotoxicity of the waste to be emplaced in the geological disposal facility. This approach implies the reprocessing of spent nuclear fuel to recycle minor actinides (MAs: Am, Cm, Np, which are together with Pu, the main contributors of long-term radiotoxicity) with the aim of producing new fuels or transmutation blankets for advanced reactors [1–7].

Currently, aqueous processes (based on liquid–liquid extraction) are the most mature technology able to address the actinide recycling. However, its development implies some important challenges, such as dealing with the degradation and regeneration of the solvents due to the effect of the highly radioactive field and nitric acid concentration where spent nuclear fuel must be dissolved. In fact, the organic extractants typically used for selective separation are susceptible to radiolysis-induced breakdown, increasing both the cost and the amount of secondary wastes produced. Consequently, radiolytic and hydrolytic degradation can give rise to the formation of degradation compounds, which can modify the extraction performance by extracting undesirable elements, and/or causing the formation of insolubilities or third phases, which is considered one of the main causes for criticality accidents during the handling of radioactive fuel solutions [8]. Therefore, the resistance of solvents must be carefully studied and optimized for the development and industrialization of these kinds of processes.

Among the organic extractants proposed for MA partitioning applications, diglycolamides (DGAs) are renowned for their good extracting and resistant properties, which is why

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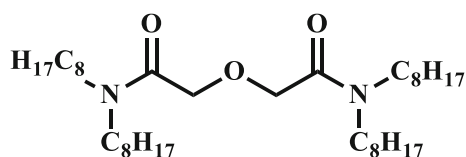


Fig. 1 Structure of *N,N,N',N'*-tetraoctyldiglycolamide (TODGA)

several compounds of this family of ligands have been studied in recent decades [9–11]. In particular, TODGA (*N,N,N',N'*-tetraoctyldiglycolamide, which structure is shown in Fig. 1), [12, 13] is a well-known efficient coextractant of trivalent actinides (An(III)) and lanthanides (Ln(III)), and consequently, several solvent extraction processes are currently under development based on it, such as the European *i*-SANEX [14–17], EURO-EXAM [18] and EURO-GANEX [19–25] processes.

In general, for sustainability consideration, it is desirable that organic phases be recycled as much as possible as part of the continuous operation. For this reason, in the latest years TODGA-based solvents have been the focus of many stability studies, not only radiolytic but also hydrolytic studies [26–34]. In general, it can be said that TODGA solvents show sufficient resistance to the harsh operational conditions expected; however, the formation of at least nine degradation compounds (DCs) has been reported in that studies. Typically, the major DCs formed involve the rupture of the C–O_{ether} bond, producing species such as 1-hydroxy-*N,N*-dicetylacetamide and *N,N*-dioctylacetamide. Nevertheless, from these studies, it is essential to note that variations in experimental conditions during the irradiation process, such as the presence of oxygen, solvent compositions, phases contact and initial concentration of the ligand, have demonstrated to give rise to different results [32, 35–37] in TODGA resistance and the formation of its DCs. For example, nitric acid plays an important role during irradiation, leading to less TODGA degradation and influencing changes in the degradation pathway. Specifically, it favors the rupture of the C_{carbonyl}-N bond, resulting in the production *N,N*-dioctyl-2-(2-(octylamino)-2-oxoethoxy)acetamide.

These DCs are of significant relevance because as they form and accumulate, and they can modify the original physicochemical properties of the solvent. This modification occurs due to the individual properties of the new species, potentially leading to a significant loss of separation efficiency, the formation of a third phase, or solubility problems. Few studies in the literature have found that DCs keeping the DGA structure exhibit similar extraction properties to TODGA. However, some other DCs formed can extract

undesirable elements for the aim of the extraction process or complicate the subsequent recovery An(III) and Ln(III). Therefore, the development of a successful industrial process demands an ability to understand and quantify stability issues, from the initial design of the extractant to a hot test in a pilot plant.

Stability studies of the solvent against radiolysis could be performed using different strategies. The initial studies irradiating individually molecules in the corresponding diluent, in batch and static conditions, allow the fundamental comprehension of the degradation pathways and are an easy way to compare the robustness of different extractants. Two approaches can be considered—internal or external irradiation—with internal alpha irradiation being the most representative option to simulate the real process. However, the use of external gamma radiation, typically ⁶⁰Co or ¹³⁷Cs sources, to simulate ligand stability is considered conservative and well established. Consequently, to predict and anticipate the long-term behavior during operations, a more realistic assessment of the process conditions must be considered. The current trend is going toward more realistic studies, taking into account relevant process conditions during irradiation, such as the effect of metal complexation on ligand stability. This effect is one of the aspects to be considered since it is one of the major factors affecting to the ligand environment. Recently, different studies on the implications of metal complexation on ligand stability have been published, concluding that, in general, the presence of the complexed ligand during irradiation results in less degradation by radiolysis [38–41]. In particular, for the TODGA ligand, only in a recent study performed by Kimberlin et al. [39], the radiolytic stability of TODGA-M complexes (neodymium and americium) has been reported. From this study, it can be concluded that there is a higher resistance of the ligand when the complex between ligand and metal is formed; nevertheless, there is no information reported about the quantification of the degradation compounds. Another study carried out by Horne et al. demonstrated that complexation of Ln(III) ions by TODGA afforded complexes that had increased chemical reactivity toward the radical RH⁺, but these enhanced reaction rates do not necessarily translate to more extensive TODGA radiolysis [42].

To enhance understanding of this issue, this study explores the evaluation of gamma radiolytic resistance of the TODGA ligand, considering its complexation with Eu metal. This effect was investigated by varying the ratio of the ligand/metal, aiming not only to study TODGA degradation after irradiation but also to identify and, for the first time, quantify its degradation compounds using the HPLC–MS technique under these experimental conditions.

2 Experimental

2.1 Materials

The extractant used in the organic phase was TODGA, purchased from Technocomm Ltd, and diluted in odorless kerosene (OK) supplied by Alfa Aesar (Germany). $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with a purity of 99.9% was obtained from Aldrich (Germany). Nitric acid, used as the aqueous diluent, was sourced from VWR Chemical as nitric acid (HNO_3) 65%, with the grade AnalaR NORMAPUR for analysis. The reagents were used without further purification, except for HNO_3 , which was additionally purified twice by a Quartz sub-boiling distillation system (MLS-Milestone) and was used within a short period. The diluents employed for the HPLC–MS measurements were MeOH, CH_3CN and HCOOH. MeOH and CH_3CN with grade LC–MS were supplied by J.T Baker, and HCOOH HiPerSolv CHROMANORM® with $\geq 99\%$ purity was purchased from VWR Chemicals. The TODGA degradation compounds employed in this work were individually synthesized, according to the procedure described in a previous work [43] to enable their quantification by HPLC–MS.

2.2 Irradiation Procedure

Irradiation experiments were conducted at the Náyade irradiation facility (CIEMAT) [44]. This facility comprises a 1.2-m² pool, 4.5 m deep, utilizing water as a biological shield. Sixty sources of ^{60}Co (each 15 mm in diameter and 135 mm long) can be distributed in six lots at the bottom of the pool. The use of a cylindrical irradiation container ensures a homogeneous irradiation flux."

Different samples of TODGA (0.1 mol/L in OK) pre-equilibrated with 3 mol/L HNO_3 were irradiated in steps of 50 kGy up to 500 kGy at a dose rate of 9.23 kGy/h, as determined by Fricke dosimetry [45]. To assess the effect of a metal on the degradation of this compound, TODGA samples were submitted to gamma radiation at the same absorbed doses, using an identical dose rate, after extraction with two different concentrations of europium (17 mmol/L and 33 mmol/L $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in 3 mol/L HNO_3). Europium, a lanthanide element present in the composition of the spent fuel solution, was chosen for a better simulation of the process conditions because it is well known that TODGA form complexes with this metal. The pre-equilibration and extraction experiments involved mixing both aqueous and organic phases for 30 min at room temperature (22 ± 2 °C). Then, the phases were separated by centrifugation (5 min at 5000 rpm), and aliquots of only the organic phase were taken for the irradiation experiment.

2.3 HPLC–MS Analysis

The chemical composition of the irradiated organic samples was characterized by HPLC–MS. These measurements were performed using an HPLC–MS Bruker EVOQ™ (Triple Quadrupole detector) with an ACE 3 C18-PFP column (50 mm \times 2.1 mm) at 40 °C, employing a gradient of mobile phase [(A: 0.1% HCOOH in H_2O), (B: 0.1% HCOOH in CH_3CN)]. APCI⁺ ionization mode was used for the quantification of TODGA, and ESI⁺ ionization mode was used for DCs. Samples for HPLC–MS studies were analyzed without pre-evaporation and diluted 1:30,000 in HPLC-grade MeOH. Calibration curves were generated for TODGA and each TODGA DC from 10 to 1000 ppb, with correlation coefficients in the range of 0.992–0.999 in all cases. All measurements were performed in duplicate to allow for uncertainty analysis, with results showing a maximum error of $\pm 4\%$.

3 Results and Discussion

In the present study, gamma irradiation was conducted up to 500 kGy on 0.1 mol/L TODGA in OK under three different conditions: pre-equilibrated with 3 mol/L HNO_3 (named TODGA w/o metal) and after extraction with 17 mmol/L and 33 mmol/L $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in 3 mol/L HNO_3 (referred to as TODGA + 17 mmol/L Eu and TODGA + 33 mmol/L Eu, respectively). The pre-equilibration aimed to saturate the organic phase with HNO_3 , since it is known that HNO_3 plays a role in the TODGA degradation results and to compare with the conditions where the metal is included. During the irradiation process, a small color change from slightly yellow to dark yellow was observed in all samples. However, no third phase formation, precipitate, or other physical changes were noted.

After irradiation, all samples were characterized by HPLC–MS to assess the TODGA resistance to gamma radiation under these conditions. Initially, the qualitative HPLC–MS analysis was performed on the reference, irradiated sample at 200 kGy and the most irradiated (500 kGy) samples of TODGA in the three studied conditions. The chromatograms are illustrated in Fig. 2. In the non-irradiated samples, only the signal corresponding to TODGA was observed. As expected, irradiation results in a decrease in TODGA signal intensity due to degradation, accompanied by the presence of several DCs (DC I–VIII), consistent with literature findings [26–28, 39]. The structure, name and m/z of these DCs are depicted in Fig. 3. While all irradiated samples analyzed exhibit practically the same chromatogram profile, it's noteworthy that the relative intensities of DCs and TODGA vary with the Eu concentration in the irradiated samples, resulting in lower intensities in the samples containing



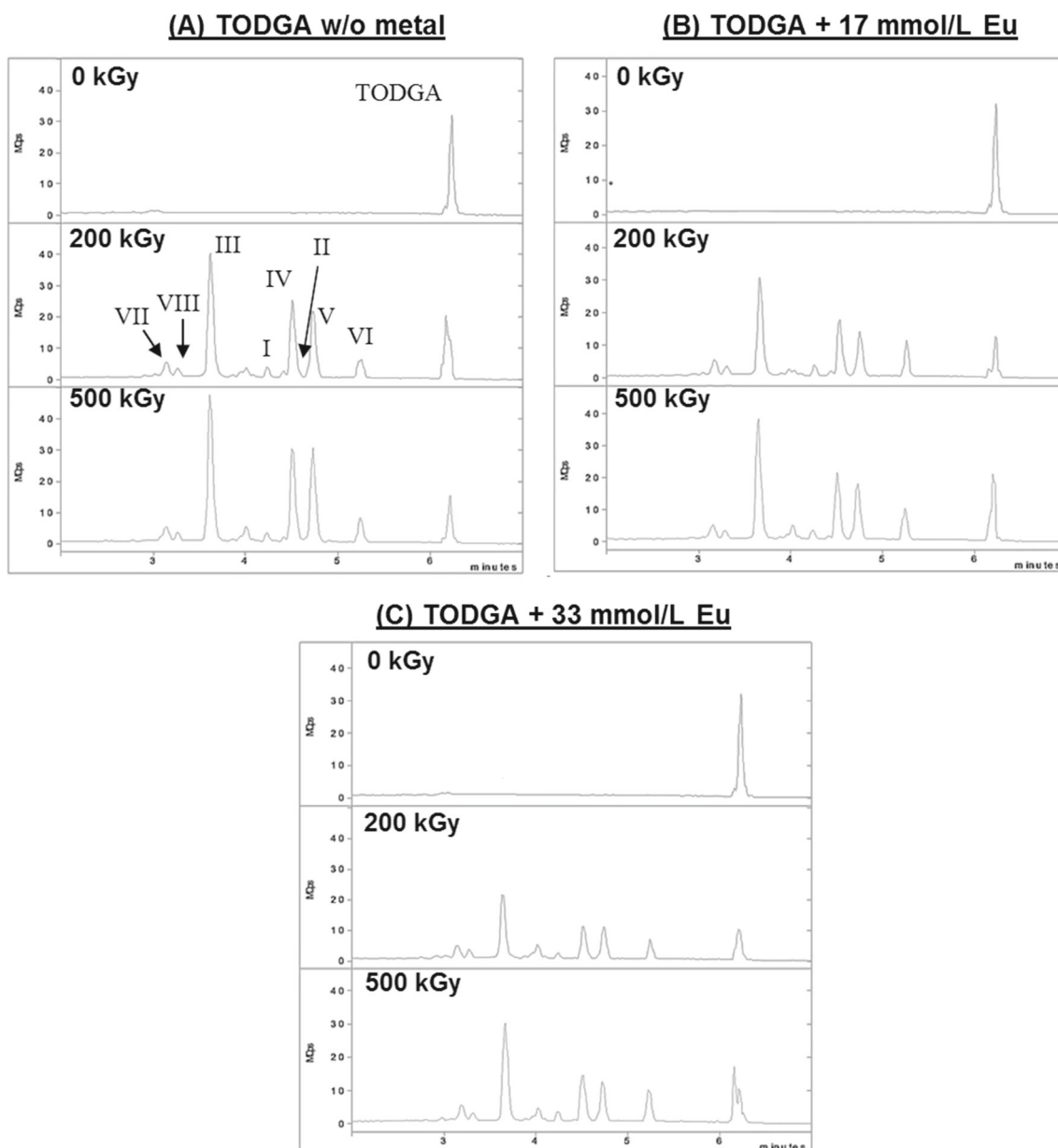


Fig. 2 Qualitative HPLC–MS chromatograms of 0.1 mol/L TODGA in OK at 0 kGy (fresh as reference material), 200 kGy and 500 kGy under the three conditions studied: (A) pre-equilibrated with 3 mol/L HNO₃

(named TODGA w/o metal) and after extraction with (B) 17 mmol/L and (C) 33 mmol/L Eu(NO₃)₃·6H₂O in 3 mol/L HNO₃ (referred to as TODGA + 17 mmol/L Eu and TODGA + 33 mmol/L Eu, respectively)

Europium. These observations suggest a lower degradation of TODGA during irradiation when Eu forms a complex with TODGA.

To clarify this hypothesis, quantitative HPLC–MS measurements were carried out, not only for TODGA but also for each DC, in all irradiated samples. Figure 4 shows the concentration of TODGA as a function of the absorbed dose for the three experimental conditions. The quantitative results confirm a decrease in TODGA concentration with the

absorbed dose in all cases, but notably, there is also a lower TODGA degradation with an increase in Eu concentration.

Considering the exponential decrease in TODGA concentration with absorbed dose, a pseudo-first-order kinetics can be suggested. Hence, the dose constant (k') was calculated following the equation: $C = C_0 e^{-k' \text{dos}}$, where C_0 and C are the initial and final concentrations of TODGA in mol/L, k' is the dose constant and dos is the absorbed dose by solvent in kGy. The results are given in Table 1. The obtained k' value for TODGA without metal aligns with that reported in

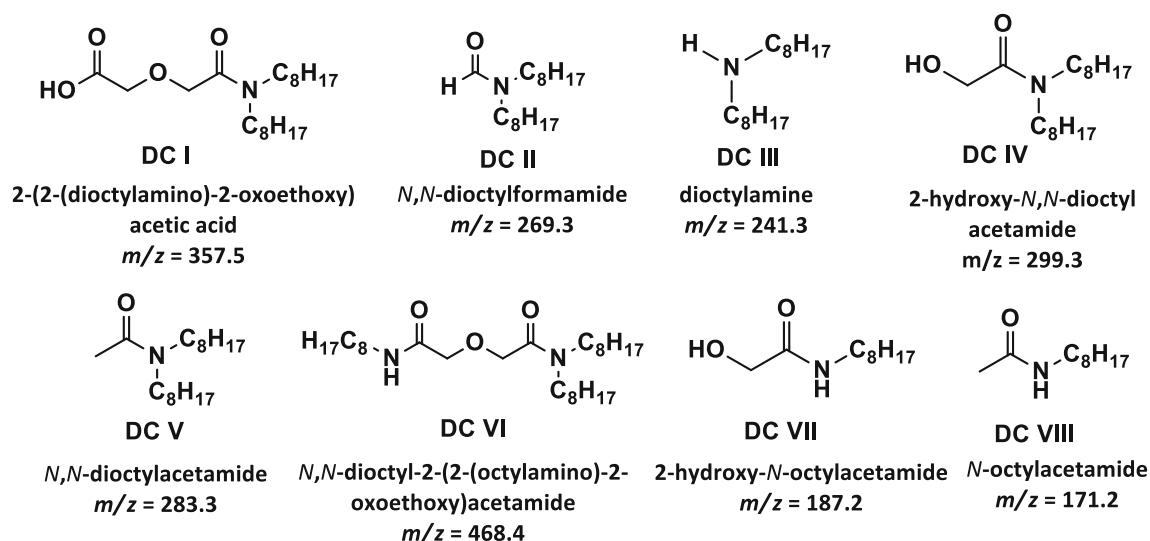


Fig. 3 TODGA degradation compounds (DCs) identified in the qualitative analysis by HPLC–MS

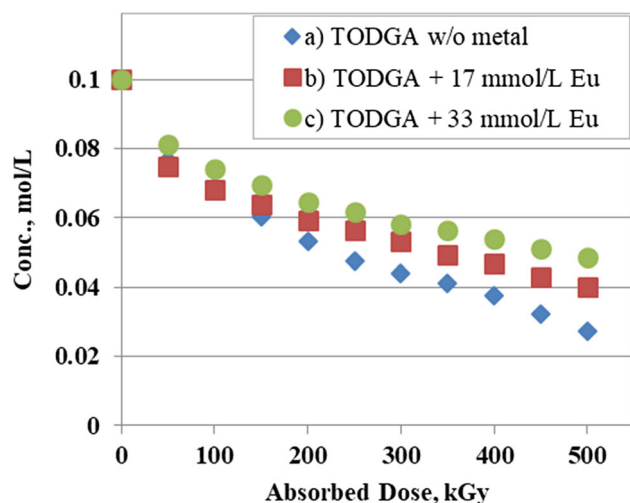


Fig. 4 Concentration of TODGA as a function of the dose for 0.1 mol/L TODGA irradiated under different conditions

Table 1 Dose constants for TODGA degradation under different conditions

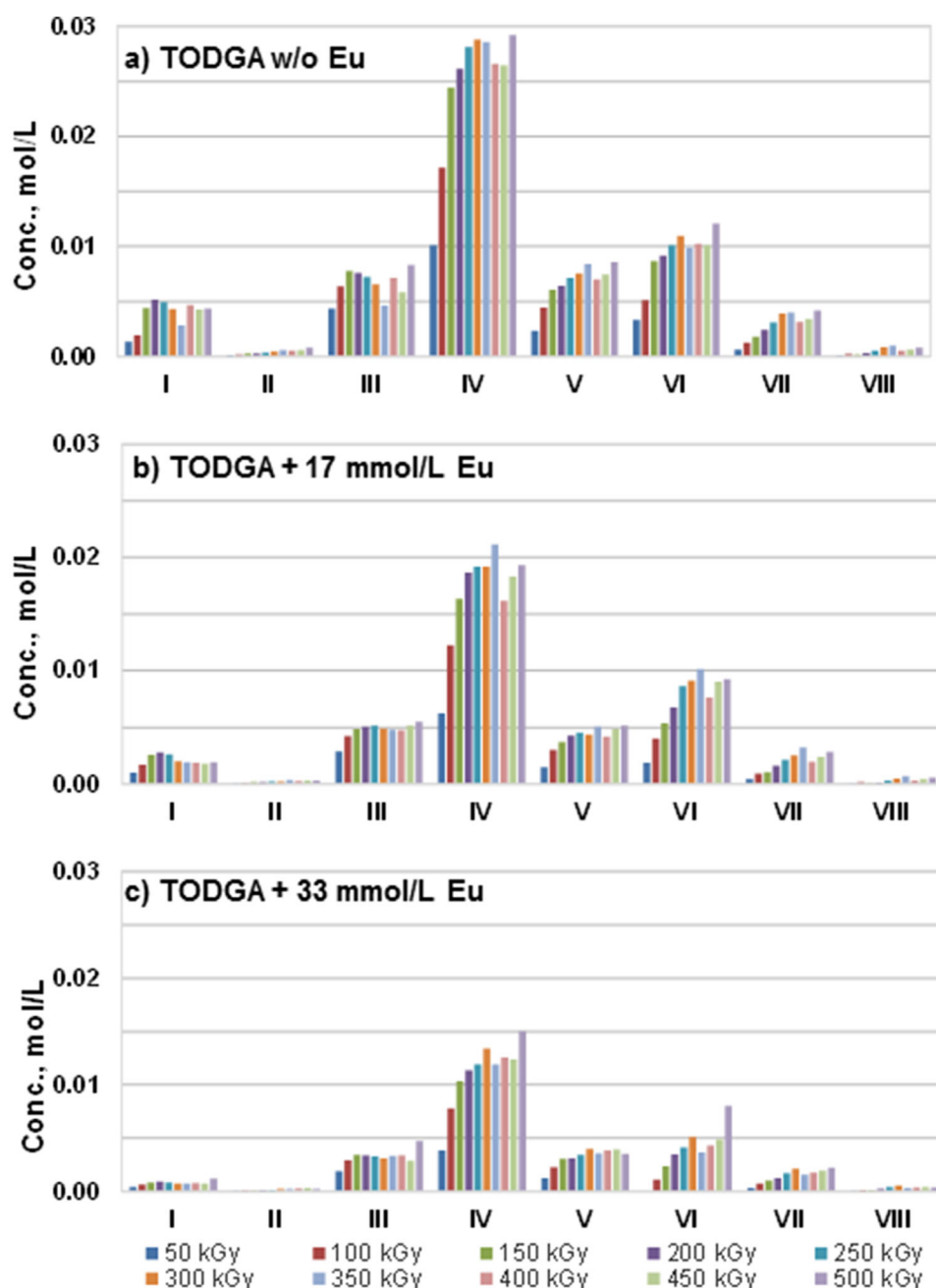
Sample type	k' (kGy ⁻¹)
TODGA w/o Eu	0.00232
TODGA + 17 mmol/L Eu	0.00156
TODGA + 33 mmol/L Eu	0.00126

the literature for TODGA degradation under irradiation after pre-equilibration with HNO₃ [27, 46]. In samples with metal, the trend is similar to that observed by Kimberlin et al. [39] using Nd, although the values are higher in their study, possibly due to a lower concentration of nitric acid (2.5 mol/L) employed.

The presence of a high Eu concentration (33 mmol/L) in the organic phase seems to have a higher protective effect than a low metal concentration (17 mmol/L). It can be found in the literature a stoichiometry 1:3 for Eu:TODGA complexes, which show a high constant association [47–49]. Thus, with an approximate Eu concentration of 30 mmol/L in the organic phase, every TODGA molecule should be involved in the Eu complex. However, with half the Eu concentration, a substantial proportion of free TODGA still exists in the medium. These results suggest that when TODGA is involved in a complex, it is less affected by gamma radiation. This behavior could be attributed to different effects or a combination of them. One possibility is the steric protective effect of the weakest point of the molecule due to complexation phenomena. Another reason could be the presence of more nitrate ions in the solution, providing a higher scavenger effect, as observed with hydrophilic diglycolamides by Horne et al. in the aqueous phase [33]. In that study, they reported that an increase in the nitrate ion concentration inhibits DGA decomposition. This effect might extend to the organic phase, where nitrate ions could react with the radical cation of diluent, which are the main species in organic solutions, avoiding the reaction of the extractant molecule with the radical cation. To confirm this possibility, extraction experiments using a counter ion different from nitrate ions would be necessary.

In addition to TODGA quantification, TODGA DCs identified previously were also quantified under the same conditions. Plotting the concentrations of DCs I to DC VIII as a function of absorbed dose for all irradiated samples (Fig. 5), an increase in the concentrations of all DCs is observed as a function of absorbed dose for all studied samples. The most abundant DCs are mainly IV and III, V and VI, in agreement with the literature [26, 27, 29, 30] resulting from the rupture

Fig. 5 HPLC–MS quantitative studies of different TODGA degradation compounds under different experimental conditions



of the weakest bonds of TODGA ($C-O_{\text{ether}}$ and $N-C$). As DCs are formed, they are also susceptible to radiolysis, producing more DCs and reaching an equilibrium between their formation and degradation. Initially, there is a sharp increase in their concentration (up to 250–350 kGy, depending on the nature of the DC), followed by a slight decrease and continued growth, indicating equilibrium between their formation and degradation. Furthermore, in the case of TODGA complexed with Eu (b) and (c) in Fig. 5, there is no change in the degradation pathway, as the most abundant TODGA DCs remain the same as in the previous case (IV and III, V and

VI). However, with the increasing concentration of europium during irradiation (and this the formation of the TODGA-Eu complex), the concentration obtained for all DCs is lower, further supporting the higher stability of TODGA when Eu is present. The absence of changes in the degradation pathway is a crucial issue to consider under process conditions, as this molecule will form Eu complexes and neither the resulting DCs nor their proportion will change for this reason. Therefore, future studies should explore the behavior and stability of the majority of TODGA fragments identified in this work

under similar conditions, aiming for a better prediction of the long-term performance of these solvent types.

4 Conclusions

In this work, the radiolytic stability of TODGA in odorless kerosene was analyzed, considering the impact of metal complexation during the irradiation process and assessing its degradation and the formation of DCs. From the results obtained in this study, it can be concluded that metal complexation protects TODGA molecules from degradation, being particularly more stable when all TODGA molecules are involved in Eu complex formation. This outcome highlights the importance of performing stability studies using more realistic experimental conditions, since TODGA resistance is higher than expected when it is complexed.

As a consequence of TODGA degradation, the TODGA degradation compounds are also analyzed and quantified, concluding that the most abundant are DCs IV, V and VI, consistent with findings in the literature. These compounds result from the breakdown of the weakest bonds of TODGA. Furthermore, this behavior is always observed, regardless of whether there is europium in the organic phase or not, so it can be concluded that there is no change in the degradation pathway because of metal complexation. The absence of changes in the degradation pathway is crucial to consider, as under realistic process conditions, TODGA will form complexes, and the resulting DCs and their proportion will align with expectations. Furthermore, all DCs undergo their own degradation, giving rise to new secondary DCs that could potentially interfere with the extraction of undesirable radionuclides during the extraction process. Therefore, studying the radiolysis of each isolated DC and its implication in the extraction process is of great interest, especially considering that DCs are more prone to accumulate in the organic phase.

Acknowledgements This work has been developed and funded under the framework of the CIEMAT-ENRESA collaboration agreement (ESASERC project, Contract n: 10907).

Author contributions I.S.-G. contributed to investigation, methodology, formal analysis, writing—original draft, writing—review and editing. H.G. contributed to supervision, methodology, conceptualization, validation, writing—review and editing.

Funding Open Access funding provided thanks to the CRUE-CSIC agreement with Springer Nature.

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