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Radiolytic degradation of sulphonated BTP and acetohydroxamic acid under EURO-GANEX process conditions

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ABSTRACT

In this work, we present a study which tackles the stability of molecules involved in EURO-GANEX aqueous phase, the acetohydroxamic acid (AHA) and the sulphonated BTP (SO_3-Ph-BTP), taking into account factors such as the known AHA hydrolysis, acidity of the media, and the radiolysis of AHA and SO_3-Ph-BTP. To better understand the system, the radiolysis of AHA and SO_3-Ph-BTP in HNO_3 has been studied first separately, at low doses (up to 50 kGy) compared with those expected for the recycled organic phase. The concentration after exposure to gamma radiation of AHA and its hydrolysis products, as well as of SO_3-Ph-BTP, was measured for the first time by using Quantitative Raman Spectroscopy (QRS), showing that this technique can be used as a reliable tool for assessing the stability of these systems. In addition, the proton concentration and extraction efficiency of each assay were monitored and assessed. Our study extends the knowledge about the resistance to radiation of extractants involved in the EURO-GANEX aqueous phase, showing greater robustness when both molecules are irradiated together, and contributes not only to design reliable simulation strategies of the long-term EURO-GANEX process performance, but also to develop analysing tools for further processes implementations.

1. Introduction

How to deal with nuclear radioactive waste and finding a more sustainable management is one of the current challenges of the scientific community. Plutonium (Pu) and the main minor actinides (MAs: neptunium (Np), americium (Am) and curium (Cm)) formed during the irradiation of the fuel in the reactor are the main responsibles for the long-term radiotoxicity of the spent nuclear fuel (SNF) (Taylor, 2015). Nowadays, a mature technology of uranium (U) and Pu recycling, along the lines of current PUREX process (Lanham and Runion, 1949), offers a reduction of the volume of waste disposal and the preservation of some natural resources. The demonstration of the new generation of reactors (4th-generation, GEN IV) would also allow minimizing the environmental impact by a multi-recycling of U and Pu, reducing the requirements of natural resources drastically, but would additionally allow the recycling of MAs (Baron et al., 2019). The favourable development of advanced nuclear fuel cycles relies on the demonstration of these new reactor concepts together with the consequent separation processes according to the MAs separation strategy chosen (Taylor, 2015; Baron et al., 2019).

Unfortunately, separation of trivalent actinides (An (III)) from trivalent lanthanides (Ln (III)), also present in the spent nuclear fuel in a much higher proportion, is still one of the challenges of separation technology. In general, to achieve this separation by liquid-liquid extraction, soft donor compounds (mainly with *N*-donor and *S*-donor functional groups) such as bistriazinylbipyridines (BTBPs) and bistriazinilypyridines (BTPs) (Hudson et al., 2006; Panak and Geist, 2013) are used to complex the An (III) selectively. Within the different strategies under study, the combination of a lipophilic extractant with an affinity towards Ln (III) and An (III) and hydrophilic stripping agents selective towards only one of those families has revealed successful results. For instance, the sulphonated bis-triazinylpyridine (SO_3-Ph-BTP), which is soluble in the aqueous phase, has been successfully tested for selective stripping of An (III) from the organic solvents developed for *i*-SANEX (*Innovative Selective Actinide Extraction*) (Geist et al., 2012; Panak and Geist, 2013; Wilden et al., 2012, 2015) and EURO-GANEX (EURO-*Grouped Actinide Extraction*) (Taylor et al., 2016; Carrott et al., 2014; Malmbeck et al., 2019) processes. EURO-GANEX process is part of

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the homogeneous strategy of An recycling, based on the Grouped Acti-Nide Extraction (GANEX) (Adnet et al., 2005) concept, where all transuranics elements (TRU) are co-separated from SNF. This concept includes a primary cycle (GANEX-1) (Miguirditchian et al., 2009b), where U(VI) is selectively extracted from the nuclear fuel solution in nitric acid before the grouped separation of transuranic elements (Np, Pu, Am, Cm), which occurs in the second cycle (GANEX-2). Different processes are available for GANEX-2: CEA-GANEX (Miguirditchian et al., 2009a), Chalmers-GANEX (Aneheim et al., 2011; Lyseid Authen et al., 2020) and EURO-GANEX (Taylor et al., 2016; Carrott et al., 2014, 2015; Malmbeck et al., 2019). The EURO-GANEX process has reached a notable level of demonstration even after hot tests (Carrott et al., 2014; Malmbeck et al., 2019). The EURO-GANEX solvent consists of a mixture of a diglycolamide and a malonamide ligand (0.2 mol/L N,*N*,*N*′,*N*′-tetraoctyl diglycolamide, TODGA (Ansari et al., 2005; Ansari et al., 2012) + 0.5 mol/L N,*N*′-dimethyl-*N*,*N*′-dioctylhexyloxyethyl malonamide, DMDOHEMA (Berthon et al., 2001)) in odourless kerosene (OK), which first co-extracts Ln and An from GANEX-1 raffinate. After that, all TRU elements are stripped into the aqueous phase using the SO_3-Ph-BTP combined with acetohydroxamic acid (AHA) (Malmbeck et al., 2019). The role of DMDOHEMA in EURO-GANEX solvent is to increase the Pu loading capacity of the organic phase (Brown et al., 2012) and that of AHA is to strip Pu(IV), Np(IV), and Np(VI) into the aqueous phase (Taylor et al., 2016; Malmbeck et al., 2019). The structure of all these molecules is represented in Fig. 1.

However, in order to scale up these kind of processes an in-depth knowledge of their resistance and long-term behaviour is still required, considering the high radioactivity present in those solutions and the high nitric acid concentration employed. Therefore, stability studies are the groundwork to understand, simulate and even predict what would happen along a real separation process, and in consequence, to be able to ensure a safe and stable operation.

The original properties and performance of solvents will be mainly affected by hydrolytic and radiolytic degradations, what leads to undesirable effects such as decrease of selectivity, third phase formation, insolubilities and gas generation, among others, minimizing the regeneration of solvents and increasing both the secondary waste and the process cost. Special attention must be paid to generated degradation compounds (DCs), which could have markedly differed extraction properties from those of the original system.

Concerning EURO-GANEX process, TODGA and DMDOHEMA based solvent has also been studied before by many authors and different points of view (Berthon et al., 2001; Galán et al., 2012; Sugo et al., 2002; Modolo et al., 2007; Zarzana et al., 2015; Mincher et al., 2009; Sánchez-García et al., 2019,Berthon et al., 2009), concluding that this solvent has a high resistance against high nitric acid concentration and gamma radiation. However, it is known that the results of stability studies depend on all actors present in solution, *i.e.*, on the chemical composition of all phases in contact during the irradiation. For example, several related studies demonstrate how the presence or absence of nitric acid, phase modifiers or even a higher oxygen content lead to different degradation results, since they can act as scavengers of radiation or modify the favoured degradation pathway (Galán et al., 2012; Peterman et al., 2016; Horne et al., 2019; Sánchez-García et al., 2019a, 2020b).

From the aqueous phases point of view, although they are not expected to be recycled, their degradation might lead to mass transference and accumulation into the recycled organic phases, and it might as well condition their resistance to radiation. According to our knowledge, there are no studies dealing with the resistance against radiation of the aqueous phase of EURO-GANEX containing both AHA and SO_3-Ph-BTP. In the literature, few studies dealing with the resistance of only AHA or only SO_3-Ph-BTP against gamma radiation can be found, but yet the results on their stability are not conclusive (Sánchez-García et al., 2019b, 2020a, 2020b; Peterman et al., 2016; Galán et al., 2014; Horne et al., 2019; Taylor et al., 1998; Alyapyshev et al., 2007; Andrieux et al., 2007; Carrott et al., 2008; Karraker, 2002; Wang et al., 2018).

Concerning SO_3-Ph-BTP, the excellent hydrolytic stability in 0.5–3 mol/L HNO_3 up to 120 days has been demonstrated (Galán et al., 2014). However, different stability results were obtained against radiation depending on gamma irradiation conditions during the experiment. In our first work, in which SO_3-Ph-BTP was dissolved in 0.5 mol/L HNO_3 and irradiated individually, effects of radiation were evident only after 50 kGy, with an estimated loss of SO_3-Ph-BTP concentration of ~90% after 250 kGy (Galán et al., 2014). Nevertheless, using a dynamic loop system where an organic phase containing TODGA and an aqueous phase containing SO_3-Ph-BTP were irradiated together, Peterman et al. demonstrated that the system keeps the performance almost unaltered up to 175 kGy (Peterman et al., 2016). Another study performed by Horne et al. (2019) reported that within 1 kGy, over 90% of the ligand is consumed if SO_3-Ph-BTP in water is irradiated in aerated condition and as a single-phase.

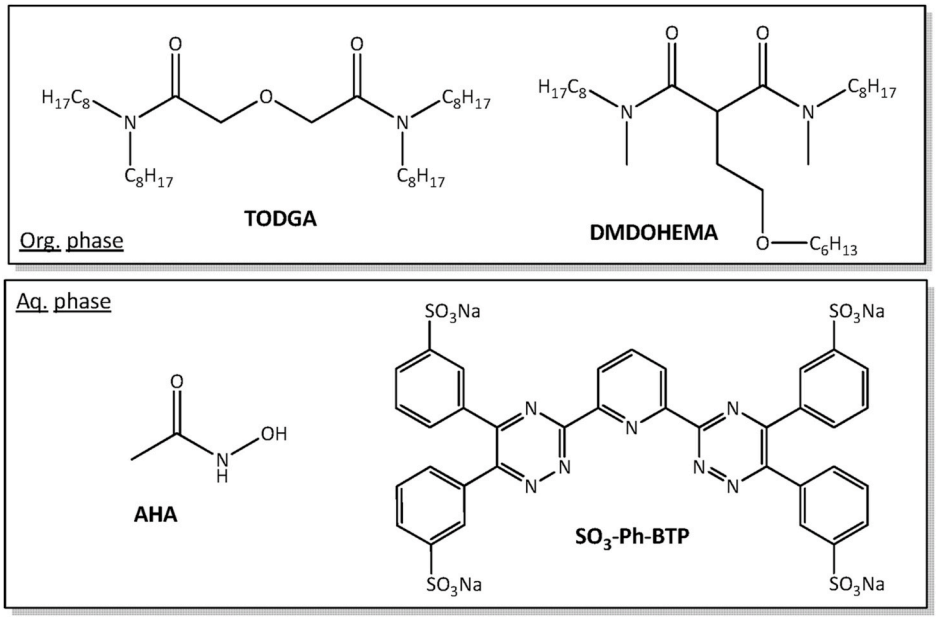


Fig. 1. Structures of the molecules involved in the TRU Stripping of EURO-GANEX process: TODGA, DMDOHEMA, $NaSO_3$-Ph-BTP and AHA.

The comparison of the mentioned studies highlights the controversial results of SO_3-Ph-BTP stability. Recently, we have explored the importance of identifying simple but realistic strategies to simulate the degradation of these systems (Sánchez-García et al., 2020a). The main conclusion of that work is that the suitability of theses extractants, as well as the general performance of the solvents submitted to radiation, should always be evaluated considering relevant factors of the full system (phase composition and irradiation of both phases together).

Referring to the other component of EURO-GANEX aqueous phase, AHA, several studies have been carried out with respect to its hydrolysis, identifying as its hydrolysis products acetic acid (AcOH) and hydroxylamine (HA) (Taylor et al., 1998;Taylor et al., 1999; Alyapyshev et al., 2007; Andrieux et al., 2007; Carrott et al., 2008). Talyor et al. concluded that this instability in acid would not affect the operation of planned flowsheets using centrifugal contactors in the separation processes, since the residence times are very low compared to the half-life of AHA in nitric acid solutions (Taylor et al., 1999). However, since an unusual storage or maloperation with longer periods could take place, and the global stability studies also imply long times, deeper AHA degradation studies are necessary and an important factor to consider for process demonstration. In all mentioned studies, AHA concentration as a function of time is obtained by an indirect method of measurement, the UV–visible spectrophotometric measurements of AHA-Fe(III) complex. Unlike those studies, in our previous works, a spectroscopic study using the Raman technique was carried out with the aim of analyzing its hydrolysis and quantifying its hydrolysis products (Sánchez-García et al., 2019b, 2020b). Furthermore, the effect of its hydrolysis on the behaviour of the global system was evaluated, concluding that the AHA hydrolysis time needs to be taken into account for experiments because one of its hydrolysis products, hydroxylamine (HA), reacts with HNO_3 producing an increase of pH, causing a loss of efficiency in the separation of An and Ln (Sánchez-García et al., 2019b).

Only two studies about the gamma radiolysis of AHA were found. In both studies, authors analyse the AHA concentration decrease by following the same indirect procedure mentioned above for the hydrolysis analysis. Karraker et al. (Karraker, 2002) studied the gamma radiolysis of AHA in HNO_3 at doses up to 11 kGy measuring the AHA concentration decrease. However, only AHA was measured in that work, *i.e.* none of its degradation (radiolysis and hydrolysis) compounds was analysed nor quantified. They concluded that radiation decomposed a minor fraction of AHA compared to the loss by hydrolysis and they explained that this effect could be due to scavenging of the primary radiolysis products ($OH^{\bullet}$, $H^{\bullet}$, e^{-}, etc.) by the acetic acid and hydroxylammonium nitrate (HAN) produced by hydrolysis. Wang et al. (2018) studied the gamma radiolysis of AHA in HNO_3 up to 25 kGy. In this work, besides the calculation of AHA concentration decrease by the absorption of the Fe(III)-AHA complex using the UV–Vis technique, they also analysed the degradation products produced by gamma radiolysis (gaseous products: H_2, N_2O, CH_4, C_2H_6 by gas chromatography; and liquids products: CH_3COOH, and HNO_2 by ion chromatography). As Karraker et al., Wang et al. also determined that radiation stability of AHA in HNO_3 depends on the absorbed dose and HNO_3 concentration, but the effect of the latter is greater than that of the former (Wang et al., 2018). Besides, it is worth noting that none of these studies reported the variation of the proton concentration produced by the AHA hydrolysis.

Notwithstanding, studies where only an aqueous phase with an as simple as possible solution is irradiated remain necessary for a more fundamental understanding of their radiation chemistry and resistance. In that sense and according to our knowledge, there are no studies on the stability against gamma radiation including both molecules, SO_3-Ph-BTP and AHA. Therefore, the goal of this work is to elucidate the stability to gamma radiation of these molecules together as part of EURO-GANEX system, as well as to evaluate its effects over the global performance of the extraction system. Even more important, this study contributes to a better understanding and to the creation of strategies to simulate degradation and behaviour of those systems involved in EURO-GANEX process. For that purpose, the study tackles the stability of AHA and SO_3-Ph-BTP when both of them are irradiated together up to 50 kGy under EURO-GANEX process conditions, taking into account factors such as AHA hydrolysis, the acidity of the media and AHA and SO_3-Ph-BTP radiolysis. For a better understanding of the system, first, the separated radiolysis of AHA and SO_3-Ph-BTP in HNO_3 under the same conditions has been studied.

The quantification of the mentioned molecules has been carried out by quantitative Raman spectroscopy (QRS). It should be noted that Raman technique has been chosen as a main tool due to two main reasons: (1) we had already demonstrated that Raman technique is a handy tool for the *in situ* analysis of the AHA hydrolysis (Sánchez-García et al., 2019b, 2020b); and (2) Raman spectroscopy can be used for quantifying not only AHA and its hydrolysis products but also the remaining concentration of SO_3-Ph-BTP after irradiation, as has been demonstrated for the first time in this work. Therefore, this technique constitutes a direct, easy and fast method for quantifying the mentioned molecules simultaneously.

Thereby, the work is structured as follows: In Section 2, the materials and methods used in this study are described. Then, in Section 3, the results obtained are presented, being organised in 3 experiments: Exp. 1 where 1 mol/L AHA in 0.5 mol/L HNO_3 is irradiated; Exp. 2 where 0.018 mol/L SO_3-Ph-BTP in 0.5 mol/L HNO_3 is irradiated, and Exp. 3 where both molecules are irradiated together in the same experimental conditions. For each experiment, the quantification of AHA, SO_3-Ph-BTP and proton concentrations, as well as the behaviour after those irradiations of the full EURO-GANEX extraction system, are shown. The conclusions of this work are presented in Section 4.

2. Experimental

2.1. Materials

Acetohydroxamic acid (AHA) with a purity of 98% and its hydrolysis products, acetic acid (AcOH) with a 99.7% and hydroxylamine (HA) with a 99.99% of purity were purchased from Acros (Belgium), Probus (Spain) and Merck (Germany), respectively. SO_3-Ph-BTP (2,6-bis(5,6-di-(sulfophenyl)-1,2,4-triazin-3-yl)-pyridine) tetrasodium salt ($NaSO_3$-Ph-BTP) with a purity of 98% by HPLC-MS was purchased from Technocomm Ltd (United Kingdom). Nitric acid as the aqueous diluent was purchased from VWR Chemical as nitric acid (HNO_3) 65% with the grade AnalaR NORMAPUR for analysis. Moreover, it was purified twice by a Quartz sub-boiling distillation system (MLS-Milestone) and used in a short time. The solutions of HNO_3 used as the aqueous diluent were prepared by diluting concentrated nitric acid with ultrapure water (18 MΩ/cm). All other reagents mentioned were used from commercially available sources without further purification.

The reagents used in the extraction experiments were: in the organic phase, a mixture of *N*,*N*,*N*′,*N*′-tetraoctyl diglycolamide (TODGA) and *N*,*N*′-dimethyl-*N*,*N*′-dioctylhexylethoxymalonamide (DMDOHEMA) dissolved in odourless kerosene (OK), which was purchased from Alfa Aesar (Germany); and in the aqueous phase a mixture of water-soluble BTP and AHA in HNO_3. TODGA was synthesized at CIEMAT modifying an existing literature procedure under air atmosphere and without drying solvent (de Mendoza et al., 2009). The raw product was then purified by column chromatography (silica gel, 98:2 Ch_2Cl_2/MeOH) to give TODGA as oil and the purity was determined by HPLC-MS and found to be 98%. DMDOHEMA with a purity of 99% by HPLC-MS was purchased from Technocomm Ltd (United Kingdom). The radioactive tracer solutions of ^{241}Am(III) and ^{152}Eu(III), which were used to simulate An and Ln, were obtained as MCl_3, in HCl 1 mol/L from Isotope Products Laboratories (California, USA).

2.2. Irradiation procedure

Irradiation experiments of the different samples were performed in

the Náyade irradiation facility (CIEMAT) (Náyade Facility, 2020). This facility consists of a pool of 1.2 m^2 and 4.5 m deep that uses water as 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 3.22 10^{14} Bq can be distributed in six lots. A cylindrical irradiation container has been employed to provide an homogeneous irradiation flux within a 60 mm diam. x 100 mm high volume.

Samples of AHA (1 mol/L in 0.5 mol/L HNO_3) and SO_3-Ph BTP (18 mmol/L in 0.5 mol/L HNO_3) or both together (a mixture of 1 mol/L AHA and 18 mmol/L SO_3-Ph-BTP in 0.5 mol/L HNO_3) were irradiated to doses of 10, 20, 30 and 50 kGy at a dose rate of 40.4 kGy/h, determined by Fricke dosimetry (Fricke and Hart, 1935). This dose rate has been used to reach relevant absorbed doses in the shortest possible time with the aim of minimizing the AHA hydrolysis effect. Samples were irradiated in sealed glass vessels. Spectroscopic measurements and extraction experiments (see below) using the reference sample, which was kept in the laboratory during the irradiation process for control, and the irradiated samples, were always performed 2 h after preparation of the sample to keep constant the effect of the AHA hydrolysis on the global results.

2.3. Spectroscopic measurements

For samples with irradiated AHA, Raman spectra were acquired by using a laser excitation source of 532 nm (operation power 50 mW) with a Horiba LabRam HR evolution spectrometer (Jobin Yvon Technology). The laser beam was focused onto the sample through the 50× objective of an Olympus B×41 microscope. The scattered radiation was then collected in backscattering geometry, dispersed using a 600 grooves/mm holographic grating and recorded by a CCD detector (256 × 1024 pixels), obtaining a resolution of ~1 cm^{-1}/pixel. Raman spectra were acquired from 200 to 4000 cm^{-1} with a typical exposition time of 200 s, and all acquired spectra were recalibrated daily using the Neon emission light.

For irradiated samples containing SO_3-Ph-BTP or SO_3-Ph-BTP and AHA, Raman spectra were acquired by using a laser excitation source of 785 nm (nominal power of 300 mW) with a B&W Tek i-Raman™ spectrometer, model BWS415–785 S, coupled to a video microscope (BAC151A). The spectral range available to this spectrometer is from 175 to 3200 cm^{-1}, with a spectral resolution of ~5 cm^{-1}/pixel.

In all samples, the proton concentration in the medium was also determined by using the potentiometrically acid-base titration with KOH using an automatic titrator Metrohm 798 MPT titrino with an Unitrode as electrode purchased from Metrohm. The dynamic method of titration previously verified in another work (Sánchez-Garcia et al., 2020a) was employed for the H^+ determination, adding KOH in variable volume steps. The electrode was calibrated employing buffer solutions of pH 4.00 and 7.00 supplied by Metrohm. The measurements were carried out in triplicate, and the calculated error was 0.01 mol/L.

2.4. Extraction procedure

The extraction system employed in EURO-GANEX process involves an organic phase containing 0.2 mol/L TODGA and 0.5 mol/L DMDOHEMA in kerosene, and 0.018 mol/L BTP and 1 mol/L AHA in 0.5 mol/L HNO_3 in the aqueous phase. In the first experiment, where AHA was irradiated alone, fresh SO_3-Ph-BTP was dissolved in the irradiated AHA solution before the extraction test, to evaluate the extraction capacity of the full system. In the second case, where SO_3-Ph-BTP is irradiated alone, fresh AHA was dissolved in the irradiated SO_3-Ph-BTP solution before the extraction test. In the last trial, where AHA and SO_3-Ph-BTP are irradiated together, the extraction test was carried out without any additional treatment. All extraction tests were carried out after 2 h after preparation of the sample to keep constant the AHA hydrolysis effect.

The extraction experiments were performed by mixing 500 μL of both phases, the aqueous and organic solutions, and spiked using 10 μL of a solution of ^{241}Am (100 kBq/mL) and ^{152}Eu (100 kBq/mL) for 30 min at room temperature (22 ± 2 °C). After that, centrifugation (at 5000 rpm) was carried out, and then, the phases were separated and aliquots of each phase (300 mL) were taken for analysis.

For high energy gamma spectrometry measurements, a Canberra High Purity–Germanium detector with a 20% of intrinsic efficiency was used, using Genie-2000 as gamma analysis software from Canberra. The gamma characteristic photopeaks at 59.5 keV and 121.8 keV were analysed for ^{241}Am and ^{152}Eu, respectively. The aqueous and organic phases were measured directly. The results are reported as distribution ratios D ($D_M = [M^{3+}]_{org.}/[M^{3+}]_{aq.}$). These experimental conditions show a limit of detection (LOD) of 2 and 6 Bq for Am and Eu, respectively. Distribution ratios between 0.01 and 100 exhibit a maximum error of ±5%.

3. Results and discussion

In order to investigate the effect of gamma radiation on the aqueous phase involved in the stripping step of EURO-GANEX, which contains SO_3-Ph-BTP and AHA molecules, three different irradiation experiments have been designed and carried out. These experiments (detailed in Table 1) lie in irradiating only the aqueous phase, first for each isolated molecule, 1 mol/L AHA in 0.5 mol/L HNO_3 in Exp.1 and 0.018 mol/L SO_3-Ph-BTP in 0.5 mol/L HNO_3 in Exp.2, and both of them together in Exp. 3.

After the irradiation, An (III) and Ln (III) extraction was measured and compared for all solvent compositions explored, in order to evaluate the performance of the system. For a real comparison of the D_M values obtained and the individual effects of AHA or BTP or AHA and BTP, extraction experiments were always performed using a fresh EURO-GANEX solvent, 0.2 mol/L TODGA +0.5 mol/L DMDOHEMA in OK. The aqueous phase employed during the extraction experiment contains 0.018 mol/L SO_3-Ph-BTP + 1 mol/L AHA in 0.5 mol/L HNO_3 (EURO-GANEX stripping composition). For those first experiments in which AHA was irradiated alone, fresh SO_3-Ph-BTP was dissolved in the irradiated AHA solution before the extraction test. In the second case, where SO_3-Ph-BTP was irradiated alone, fresh AHA was dissolved in the irradiated SO_3-Ph-BTP solution before the extraction test. In the last trial, AHA and SO_3-Ph-BTP were irradiated together. Therefore the extraction test was carried out without any additional treatment. Table 1 also shows the composition of the organic and aqueous phases used for the extraction experiments.

All experiments containing AHA were carried out using the same methodology that control samples, *i.e.* the quantification and extraction experiments were carried out always after 2 h after preparation of the

Table 1
Composition of the aq. Phases that have been irradiated (up to 50 kGy) and the org. and aq. Phases used for the extraction experiments.

Experiment		Sample Composition	
		Organic phase	Aqueous phase
Exp. 1	1.1) Irradiation	–	1 mol/L AHA in 0.5 mol/L HNO_3
	1.2) Extraction	0.2 mol/L TODGA +0.5 mol/L DMDOHEMA in OK	1 mol/L AHA **IRR** + 0.018 mol/L SO_3-Ph-BTP **FRESH** in 0.5 mol/L HNO_3
Exp. 2	2.1) Irradiation	–	0.018 mol/L SO_3-Ph-BTP in 0.5 mol/L HNO_3
	2.1) Extraction	0.2 mol/L TODGA +0.5 mol/L DMDOHEMA in OK	1 mol/L AHA **FRESH** + 0.018 mol/L SO_3-Ph-BTP **IRR** in 0.5 mol/L HNO_3
Exp. 3	3.1) Irradiation	–	1 mol/L AHA + 0.018 mol/L SO_3-Ph-BTP in 0.5 mol/L HNO_3
	3.2) Extraction	0.2 mol/L TODGA +0.5 mol/L DMDOHEMA in OK	1 mol/L AHA **IRR** + 0.018 mol/L SO_3-Ph-BTP **IRR** in 0.5 mol/L HNO_3

sample, to keep constant the hydrolysis effect of AHA in all studied samples.

3.1. Experiment 1: irradiation of AHA

In this experiment, 1 mol/L AHA in 0.5 mol/L HNO_3 was irradiated up to an integrated dose of 50 kGy and the QRS methodology was employed to calculate the concentration decrease. Raman spectra are shown in Fig. 2 and based on our last works (Sánchez-García et al., 2019b, 2020b), the bands at ~950 cm^{-1}, ~881 cm^{-1} and ~997 cm^{-1} were used to calculate AHA, AcOH, and HA concentrations, respectively.

Apart from the mentioned Raman features corresponding to the hydrolysis of the samples, spectra of AHA irradiated samples do not present any new Raman bands at our measure conditions, observed in our most recent studies (Sánchez-García et al., 2019a, 2020b). In addition, the relative intensity of all bands corresponding to AHA is equal. For this reason, using Raman spectroscopy at the studied conditions, different products to AHA, AcOH and HA are not observed.

Following the methodology used in the aforementioned works, both the decrease in the concentration of AHA and the increase in the concentration of AcOH and HA have been obtained using QRS, *i.e.* the Raman analysis of the relative integrated intensities of the mentioned bands gives us a measure of the concentration. The fitted and calibration curves are shown in Appendix A of the ESI.

First of all, control sample for the hydrolysis of AHA has been studied at 2 h and, as expected from known kinetics studies in the literature (Sánchez-García et al., 2020a), at 2 h the AHA concentration decreases from 1 mol/L to 0.87 ± 0.05 mol/L; AcOH and HA are formed by hydrolysis reaction from 0 mol/L to 0.11 ± 0.05 mol/L and 0.05 ± 0.07 mol/L, respectively; and proton concentration decreases from 0.50 mol/L to 0.41 ± 0.01 mol/L. This result was taken as our control sample to obtain the variation in the AHA, AcOH and HA concentrations (ΔConc) produced only by radiolysis as shown in Fig. 3, where our results are also compared with those obtained by Wang et al. (2018). The variation in the concentration (ΔConc) is defined as follows: $\Delta Conc = C_i - C_c$, where C_i is the concentration in the irradiated sample, and C_c is the concentration in the hydrolysed sample (0 kGy at 2 h of hydrolysis time).

The variation of AHA concentration is negative (−0.124 mol/L at 50 kGy) because the radiolysis produces the degradation of AHA. Moreover, the behaviour showed for AHA is in agreement with the one obtained by Wang et al. (2018), where the variation of the AHA concentration reported was −0.05 mol/L at 25 kGy, as can be observed in Fig. 3. However, as a consequence of AHA degradation, AcOH and HA are formed and so, the variation of AcOH and HA concentrations are positive. On the one hand, the variation in AcOH concentration increases slightly with the dose reaching ~0.07 mol/L at 50 kGy, in agreement with Wang et al. (2018), who showed a variation in the concentration of ~0.0375 mol/L at 25 kGy. Furthermore, it can be observed that the AcOH concentration is always higher than that of HA, and this could be explained because AcOH is also a radiolysis product while HA is only a hydrolysis product and, in consequence, its concentration increase less significantly, as also detailed in Wang et al. (2018).

Due to the known effect of nitric acid concentration over the Am and Eu extraction efficiency of EURO-GANEX solvent (Carrott et al., 2015),

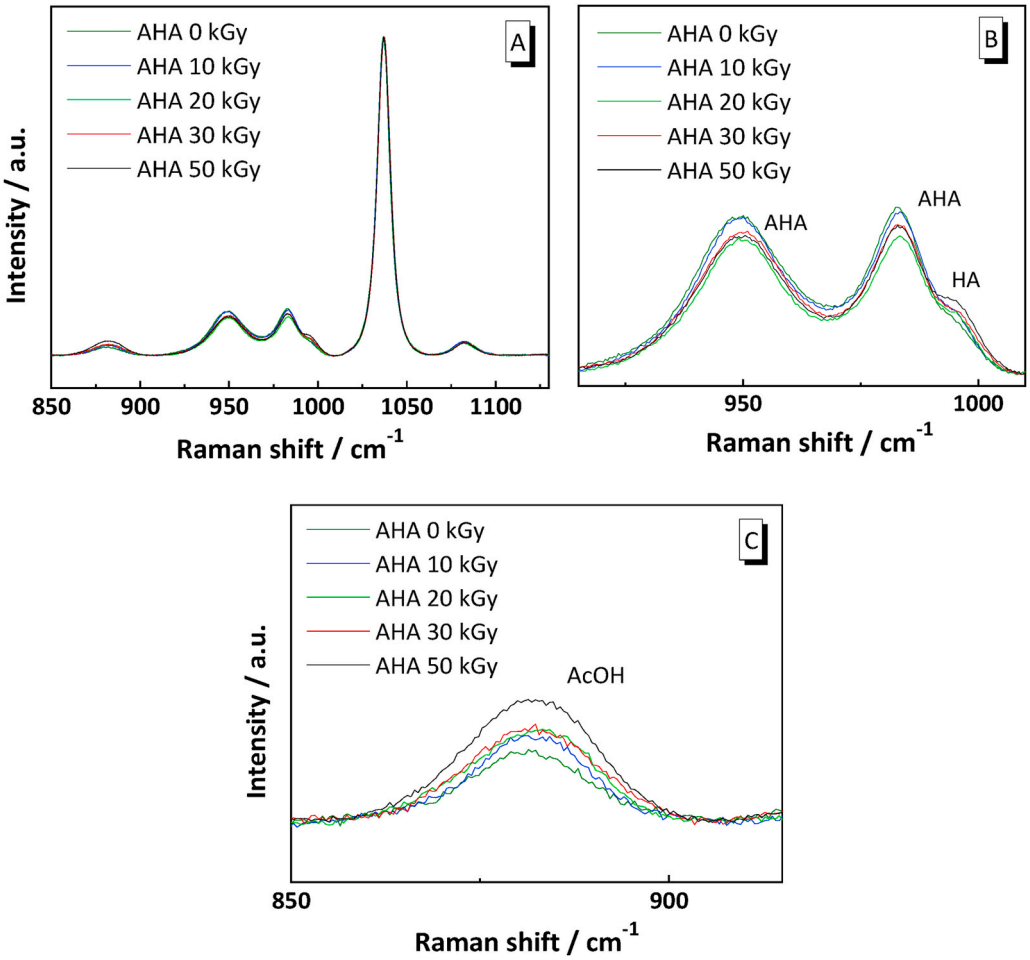


Fig. 2. Experimental Raman spectra corresponding to irradiated samples up to 50 kGy of 1 mol/L AHA in 0.5 mol/L HNO_3. A) from 850 to 1150 cm^{-1}, B) from 910 to 1010 cm^{-1}, and C) from 850 to 910 cm^{-1}. These spectra were acquired by using a laser excitation source of 532 nm with a Horiba LabRam HR evolution spectrometer.

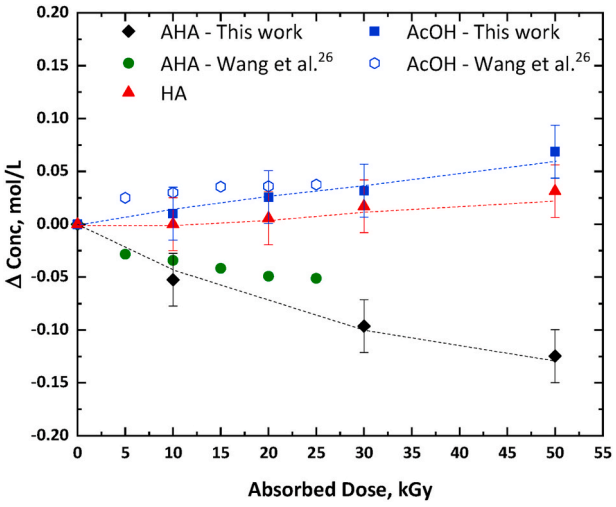


Fig. 3. Variation in the concentrations obtained for AHA, acetic acid (AcOH), and hydroxylamine (HA) in this work, and for AHA and AcOH obtained by Wang et al. (Wang et al., 2018), as a function of absorbed dose up to 50 kGy.

the proton concentration variation was evaluated, and the results are shown in Table 2. Proton concentration, as expected from our previous works (Sánchez-García et al., 2019a), shows a decrease in 2 h from 0.50 ± 0.01 mol/L to 0.41 ± 0.01 mol/L due to the increase in HA concentration because of the hydrolysis process. Nevertheless, a further slight decrease of proton concentration as a result of the absorbed dose is only observed for an absorbed dose of 50 kGy.

The evaluation of D_{Am} and D_{Eu} for Exp. 1 is shown in Fig. 4. As can be expected, since a fresh EURO-GANEX organic solvent is used, Eu is mainly kept in the organic phase although a slight decrease in its extraction can be observed. The slight decrease in D_{Eu} values as a function of absorbed dose could be attributed to a variation of free nitrate due to radiation. The reference value for the studied system without any hydrolysis or radiolysis effect presents a $D_{Am(III)}$ and $D_{Eu(III)}$ values of 0.08 and 18, respectively. Taking into account the hydrolysis effect, as expected, the $D_{M(III)}$ at 0 kGy but 2 h of hydrolysis present slightly lower values. As SO_3-Ph-BTP is also added fresh into the aqueous phase, Am is maintained in the aqueous phase ($D_{Am} < 1$). A slight decrease of D_{Am} is also observed as a function of absorbed dose, in agreement with the effects observed for D_{Eu}. Therefore, the individual irradiation of AHA has only a small effect on the extraction performance of the system, producing a slight decrease in both $D_{M(III)}$. Anyhow, at these absorbed doses, the separation factor of Ln and An is good enough ($SF_{Eu(III)/Am(III)} > 290$ at 50 kGy) to achieve the mentioned separation effectively.

The same extraction experiments were carried out at 192 h of hydrolysis, and the results corroborate our last works (Sánchez-García et al., 2019). Due to the AHA hydrolysis and the consequent decrease of the proton concentration ($[H^+]$ ~0.04 mol/L for 192 h), the $D_{Eu(III)}$ becomes much lower than 1 ($D_{Eu(III)}$ ~0.1, see Fig. S4 in Appendix B of ESI), producing an ineffective separation between Eu(III) and Am(III). Under these conditions, it becomes clear that hydrolysis is more significant than radiolysis at long times, and this is fundamental when designing simulation strategies to assess the system (composition and extraction properties) involved in EURO-GANEX process.

Table 2
Proton concentrations obtained in the AHA aqueous phase at 2 h as a function of dose taking into account the hydrolysis and radiolysis.

Sample	Absorbed Dose, kGy	$[H^+]$, mol/L
1 mol/L AHA in 0.5 mol HNO_3	0	0.41 ± 0.01
	10	0.41 ± 0.01
	20	0.43 ± 0.01
	30	0.40 ± 0.01
	50	0.36 ± 0.01

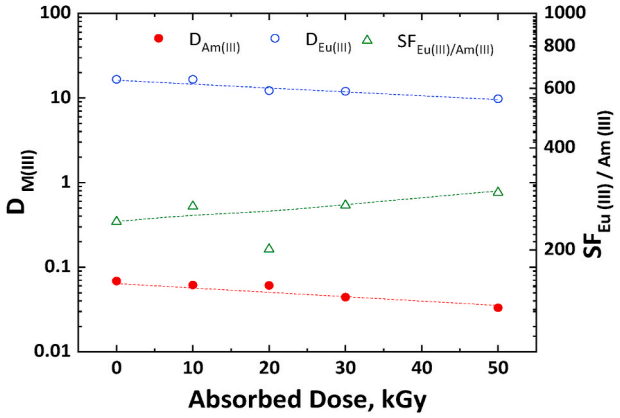


Fig. 4. Distribution ratios of Am(III) and Eu(III) as a function of dose for the Exp. 1, containing a fresh organic phase of 0.2 mol/L TODGA and 0.5 mol/L DMDOHEMA in OK and an aqueous phase of fresh 18 mmol SO_3-Ph-BTP and irradiated 1 mol/L AHA in 0.5 mol/L HNO_3, at 2 h.

3.2. Experiment 2: irradiation of SO_3-Ph-BTP

In the Exp. 2, SO_3-Ph-BTP in nitric acid medium was irradiated individually at the same absorbed doses as in the previous case. The irradiated solutions showed colour changes, as can be observed in Fig. 5, and as expected from other previous works (Sánchez-García et al., 2020b; Peterman et al., 2016; Galán et al., 2014). Samples turned from green in the unirradiated sample to brown at 50 kGy, but no precipitates were observed. The significant darkening of solutions was attributed to the radiolytic degradation of SO_3-Ph-BTP, in agreement with other studies performed in similar experimental conditions (Galán et al., 2014).

In this test, the degradation of SO_3-Ph-BTP was calculated by quantitative Raman spectroscopy after being irradiated. Fig. 6 shows the Raman spectra of SO_3-Ph-BTP irradiated samples. The spectra do not present any new Raman bands additional to the SO_3-Ph-BTP bands at our measure conditions, and the relative intensity of these bands does not suffer significant variations. Therefore, we assume that the band analysed for the QRS corresponds to the SO_3-Ph-BTP and possible degradation compounds are not detected. The fitted curves and calibration curves are shown in Appendix A of the ESI.

In order to verify the quantification done by Raman spectroscopy, the estimation of SO_3-Ph-BTP concentration after irradiation was carried out by using the indirect method by means of the dependence of D_{Am} on the SO_3-Ph-BTP concentration by gamma spectrometry, since the possible degradation compounds do not interfere negatively in the extraction behaviour of the system (Galán et al., 2014). The correlation of D_{Am} with the SO_3-Ph-BTP concentration, which is used to estimate the SO_3-Ph-BTP concentration, is shown in appendix C of the ESI.

The comparison between the SO_3-Ph-BTP concentrations obtained

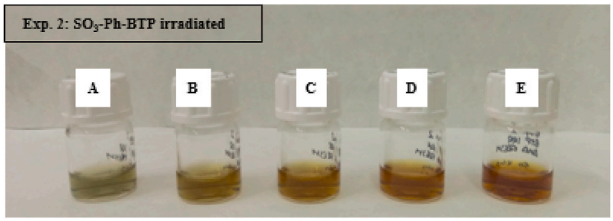


Fig. 5. Photographs of samples of 18 mmol/L SO_3-Ph-BTP in HNO_3 0.5 mol/L irradiated at different doses: (A) 0 kGy, (B) 10 kGy, (C) 20 kGy, (D) 30 kGy and (E) 50 kGy.

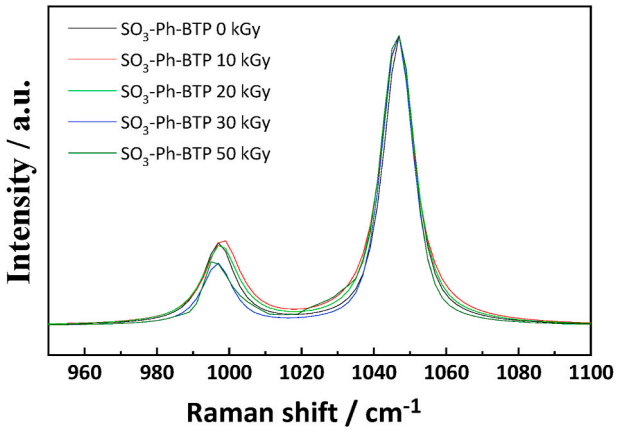


Fig. 6. Experimental Raman spectra corresponding to irradiated samples up to 50 kGy of 18 mmol/L SO_3-Ph-BTP in 0.5 mol/L HNO_3. Raman spectra were acquired by using a laser excitation source of 785 nm with a B&W Tek i-Raman™ spectrometer.

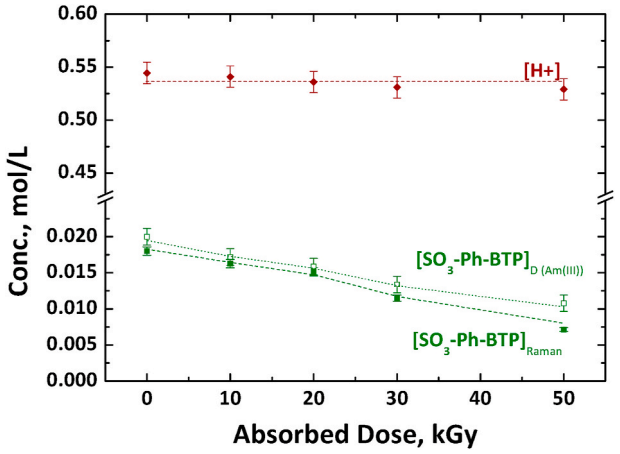


Fig. 8. Concentrations obtained of SO_3-Ph-BTP obtained by Raman spectroscopy ($[SO_3\text{-Ph-BTP}]_{Raman}$) and using the relation with the $D_{Am(III)}$ ($[SO_3\text{-Ph-BTP}]_{D(Am(III))}$) and protons ($H^+$) as a function of absorbed dose for Exp. 2.

by Raman spectroscopy and the estimation done using the $D_{Am(III)}$ relation is shown in Fig. 7. The results adjust to a linear function as $[SO_3\text{-Ph-BTP}]_{Raman} = (1.04 \pm 0.09)\ [SO_3\text{-Ph-BTP}]_{estimated} + (0.001 \pm 0.001)$ and with a coefficient of determination (R^2) equal to 0.972. This result verifies the SO_3-Ph-BTP concentration obtained by QRS.

Fig. 8 shows the SO_3-Ph-BTP quantification by Raman spectroscopy and the estimation of SO_3-Ph-BTP using the $D_{Am(III)}$ dependency, as well as the proton concentration as a function of absorbed dose.

The SO_3-Ph-BTP concentration decreases with the dose, *i.e.,* approx. 50% is lost at a dose of 50 kGy in both cases. These reductions in the SO_3-Ph-BTP concentrations highlighted that this compound is very susceptible to degradation under the studied radiation conditions, in agreement with our first SO_3-Ph-BTP stability studies (Galán et al., 2014), where we estimated a loss of 50% of the concentration of SO_3-Ph-BTP at 60 kGy, despite the fact that a higher dose rate has been used compared with that first study, ~40 kGy/h and ~4 kGy/h, respectively. However, in those works where SO_3-Ph-BTP aqueous phase has been irradiated in contact with an organic phase (Sánchez-García et al., 2020b; Peterman et al., 2016), a higher stability was reported. Peterman et al. (2016) observed no significant SO_3-Ph-BTP degradation in a dynamic irradiation experiment, based on distribution data, up to 175 kGy (at 3.3 kGy/h); and in our last work (Sánchez-García et al., 2020b), we reported ~50% of concentration decrease at 200 kGy depending on the organic phase contacted with. Therefore, these results highlight two issues: the importance of the way of irradiating to simulate and check the viability of these extractants; and the importance of verifying quantitative tools not only to measure the effects over the extraction of radionuclides but also to analyse the remaining concentration. The correlation between the behaviour observed after irradiation and the knowledge of the composition of the solvent is the key point to understand and predict the long-term performance of extraction systems.

Regarding proton concentration measurements, unlike the results observed in Experiment 1, in this case, the concentration is maintained approximately constant during the irradiation of SO_3-Ph-BTP up to 50 kGy (from 0.54 ± 0.01 mol/L to 0.53 ± 0.01 mol/L in 50 kGy), what indicates that at these conditions the aqueous phase acidity is not considerably affected by the degradation of SO_3-Ph-BTP.

The extraction experiment with ^{241}Am and ^{152}Eu was carried out using the same composition used before, *i.e.* 0.2 mol/L TODGA and 0.5 mol/L DMDOHEMA in OK in the organic phase, and the corresponding SO_3-Ph-BTP irradiated sample where 1 mol/L AHA (fresh) was dissolved. In order to compare these results with the ones obtained before, the extraction was carried out always after 2 h, keeping constant the effects of AHA hydrolysis. The reference value for the studied system without any hydrolysis or radiolysis effect is the same as in Experiment 1, and the values are therefore detailed in that experiment. The values obtained for $D_{Am(III)}$ and $D_{Eu(III)}$ are shown in Fig. 9. As happened in

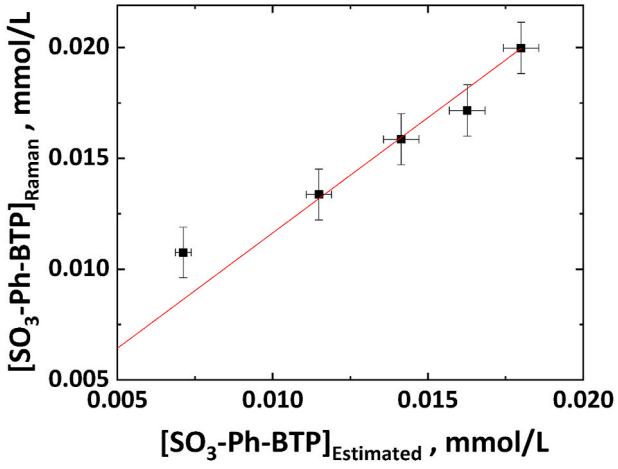


Fig. 7. Comparison between SO_3-Ph-BTP concentrations obtained by Raman spectroscopy ($[SO_3\text{-Ph-BTP}]_{Raman}$) and using the relation with the $D_{Am(III)}$ ($[SO_3\text{-Ph-BTP}]_{D(Am(III))}$).

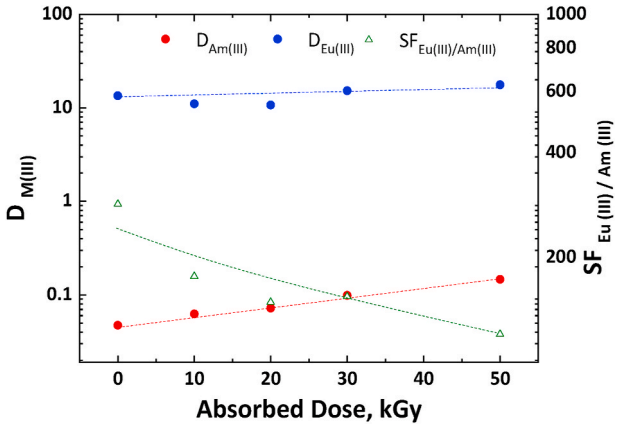


Fig. 9. Distribution ratios of Am(III) and Eu(III) as a function of dose for Exp. 2, containing a fresh organic phase of 0.2 mol/L TODGA and 0.5 mol/L DMDOHEMA in OK and an aqueous phase of irradiated 18 mmol SO_3-Ph-BTP and fresh 1 mol/L AHA in 0.5 mol/L HNO_3.

Experiment 1, the organic solvent shows an effective Eu extraction along the irradiation experiment, since the organic phase is not degraded; in fact, a slight increase with the absorbed dose is observed, which might be attributed to the degradation of SO_3-Ph-BTP. Regarding $D_{Am(III)}$, a progressive increase was measured, reducing the separation factor between Am(III) and Eu(III), what could be explained by the progressive destruction of SO_3-Ph-BTP as a function of the dose. Anyhow, even at 50 kGy $D_{Am(III)}$ is kept lower than 1, *i.e.,* the americium is retained mainly in the aqueous phase, maintaining a still good $SF_{Eu(III)/Am(III)}$, in agreement with our first work (Galán et al., 2014).

3.3. Experiment 3: simultaneous irradiation of AHA and SO_3-Ph-BTP

In Experiment 3, solutions containing both molecules, AHA and SO_3-Ph-BTP, were irradiated at the same absorbed dose as in the previous cases. As can be observed in Fig. 10, the irradiated solutions showed neither visual colour changes, in contrast with Exp. 2. (Fig. 5), nor precipitates after irradiation.

Following the same methodology as in the previous experiments, the concentration of AHA and SO_3-Ph-BTP as a function of absorbed dose was evaluated by using QRS. As this system contains AHA, the measurements were also carried out after 2 h as we had done for Exp.1. The experimental Raman spectra of all irradiated samples are shown in Fig. 11. The areas obtained for the irradiated samples were practically invariant with respect to unirradiated samples. The fitted curves and calibration curves are shown in Appendix A of the ESI.

Fig. 12 shows the results of the AHA and SO_3-Ph-BTP quantification by QRS, as well as the proton concentration by automatic titrator as a function of absorbed dose. Results obtained show that concentrations for both molecules (AHA and SO_3-Ph-BTP) are practically invariable with increasing absorbed dose, unlike it was observed for Exp.1 and Exp. 2. These results could be explained by the presence of additional solutes in the phase, which often enhances the radiolytic stability of extractants, as occurs in different studies found in the literature with other extractants (Berthon, L. & Charbonnel, M.C., 2009).

In this experiment, it was not possible to calculate the concentration of products of AHA hydrolysis (HA and AcOH) because the spectra obtained by using a 785 nm laser with the B&W Tek i-Raman™ spectrometer have a lower detection limit than those obtained with the laser excitation source of 532 nm of the Horiba LabRam HR evolution spectrometer, which provides a higher resolution (see spectra in Fig. 2).

As a consequence of the lack of reduction in AHA concentration, an increase in proton concentration along the irradiation process is not observed, what points out that the aqueous phase acidity is not affected by gamma radiation in this experiment.

The D_{Am} and D_{Eu} values obtained for Exp. 3 are showed in Fig. 13. The reference value for the studied system without any hydrolysis or radiolysis effect is the same as in Experiments 1 and 2, and the values are detailed in Experiment 1. In this case, $D_{Eu(III)}$ is practically invariable as a function of absorbed dose, maintaining the Eu mainly in the organic phase. However, the $D_{Am(III)}$ behaviour differs considerably from the previous experiments, causing the separation factor between Eu and Am

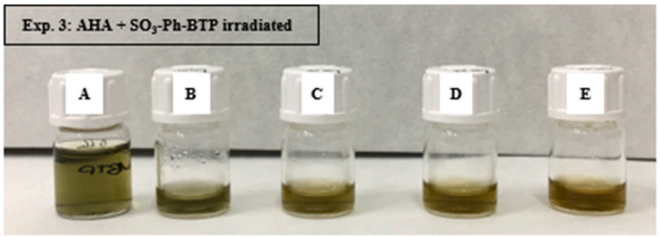


Fig. 10. Photographs of samples of 1 mol/L AHA and 18 mmol/L SO_3-Ph-BTP in HNO_3 0.5 mol/L irradiated at different doses: (A) 0 kGy, (B) 10 kGy, (C) 20 kGy, (D) 30 kGy and (E) 50 kGy.

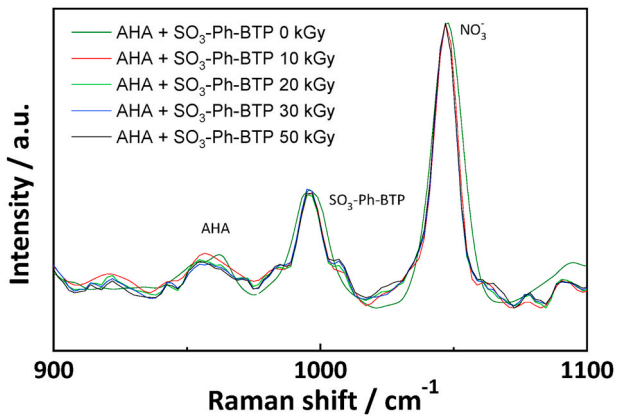


Fig. 11. Experimental Raman spectra corresponding to irradiated samples up to 50 kGy of 1 mol/L AHA +18 mmol/L SO_3-Ph-BTP in 0.5 mol/L HNO_3. Raman spectra were acquired at 2 h by using a laser excitation source of 785 nm with a B&W Tek i-Raman™ spectrometer.

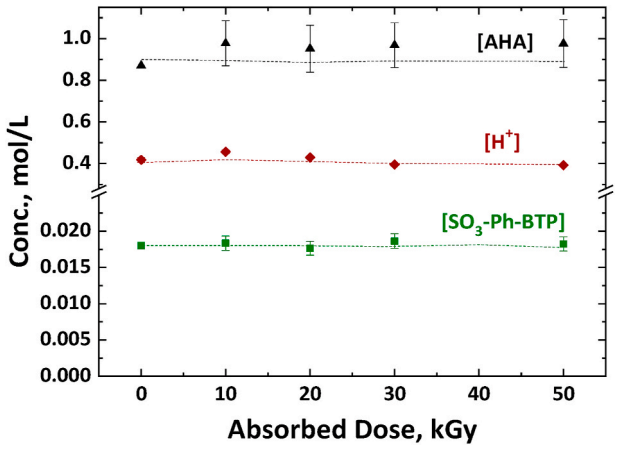


Fig. 12. Concentrations obtained for AHA, SO_3-Ph-BTP and protons (H^+) as a function of absorbed dose, always at 2 h of AHA hydrolysis.

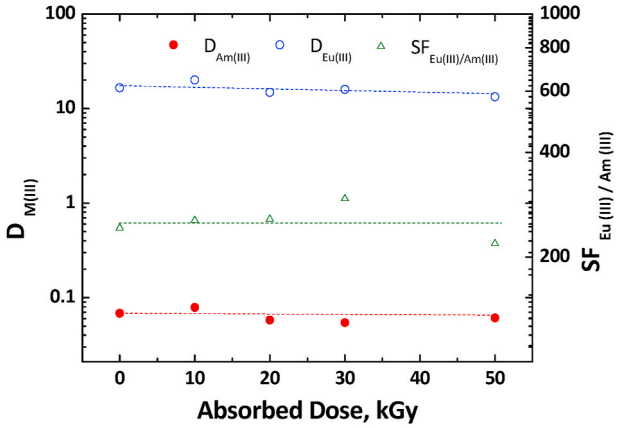


Fig. 13. Distribution ratios of Am(III) and Eu(III) as a function of dose for Exp. 3, containing a fresh organic phase of 0.2 mol/L TODGA and 0.5 mol/L DMDOHEMA in OK and an irradiated aqueous phase of 18 mmol SO_3-Ph-BTP and 1 mol/L AHA in 0.5 mol/L HNO_3 at 2 h.

to remain essentially unchanged. Therefore, in this case the extraction system has kept a better performance, suggesting that when both molecules (AHA and SO_3-Ph-BTP) are irradiated together, the resistance

against radiolysis is higher than that expected for individual experiments, also according to the insignificant colour changes observed.

As in Experiment 1, the extraction efficiency was also measured at 192 h and the results are in good agreement with those obtained in Exp. 1 and our last works (Sánchez-García et al., 2019a), reporting $D_{Eu(III)}$ lower than 1 ($D_{Eu(III)} \sim 0.1$, see Fig. S5 in Appendix B of ESI). This produces an ineffective separation of An (III) and Ln (III), as a consequence of the proton concentration decrease ($[H^+] \sim 0.05$ mol/L) due to AHA hydrolysis and the following reaction between HA and HNO_3. This result highlights the importance of the AHA hydrolysis at long times, being more significant than the radiolysis effect. Therefore, simulation strategies of the resistance without AHA will allow a better estimation of the SO_3-Ph-BTP system resistance; but if AHA is involved, the stability studies must be carefully designed and monitored along the time.

4. Conclusions

The resistance to γ-radiation of the molecules involved in the aqueous phase of EURO-GANEX stripping step, AHA and SO_3-Ph-BTP, has been explored simultaneously for the first time.

With the aim of completing the different stability studies already published and in order to obtain a right comparison of the effects of each compound on the media, they were first individually studied. These initial results indicated that SO_3-Ph-BTP is more susceptible to radiolysis effects than AHA. Additionally, it allowed exploring the effects on the pH of the media of each molecule during the irradiation experiment, being AHA degradation the main one contributing to pH variation. Furthermore, the same methodology of quantification by Raman spectroscopy that had been previously reported for AHA, has been likewise established for SO_3-Ph-BTP, showing that this technique can be used as a reliable tool for monitoring the stability of these systems.

AHA and SO_3-Ph-BTP were irradiated together using the experimental conditions of the EURO-GANEX process and simulating the low expected doses for aqueous phases that will not be recycled (at a maximum of 50 kGy). This experimental configuration allowed us to investigate at the same time factors such as AHA hydrolysis, the acidity of the media and AHA and SO_3-Ph-BTP degradation due to radiation effect. The results obtained did not only show the higher resistance of SO_3-Ph-BTP against radiation when irradiated in presence of AHA, but also indicated a lower AHA degradation and an invariable acidity of the media during the first 2 h studied. This scarce degradation is reflected in the excellent Ln and An separation factor maintained during the irradiation experiment. Taking into account that SO_3-Ph-BTP stability is underestimated when the aqueous phase is irradiated individually, these studies point out to a better behaviour against radiation than initially expected for the full EURO-GANEX system (Org.+Aq.: TODGA-DMDOHEMA/AHA–SO_3–Ph-BTP).

These outcomes also manifest clearly that the effects of irradiation observed on solvent extraction systems depend upon experimental design and conditions employed. Therefore, although basic stability studies remain relevant for the fundamental understanding of degradation pathways, it is essential to design reliable simulating strategies to predict the long-term performance of extraction systems submitted to nuclear fuel radiation. In that sense, these results provide important key factors to take into account during the design of EURO-GANEX stability experiments and an easy monitoring tool.

Credit author statement

I. Sánchez-García: Investigation, conceptualization, methodology, formal analysis, writing –original draft and writing – Review & Editing.

L.J. Bonales: Investigation, methodology, formal analysis, validation, writing – Review & Editing.

Hitos Galán: Methodology, validation, writing – Review & Editing.

J.M Perlado: Validation and funding acquisition.

J. Cobos: Supervision, validation and funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.radphyschem.2021.109402.

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