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# New insight on the simultaneous H<sub>2</sub> and HNO<sub>2</sub> production in concentrated HNO<sub>3</sub> aqueous solutions under alpha radiation†

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Knowledge of hydrogen and nitrous acid yields ( $G(\text{H}_2)$  and  $G(\text{HNO}_2)$ ) from  $\alpha$  radiolysis of nitric acid solutions is of critical importance for the technological aspects of reprocessing of spent nuclear fuel (SNF). This study provides critical information on the  $G$  values for external alpha irradiation of concentrated HNO<sub>3</sub> solutions. An investigation-specifically developed experimental setup allows performing this investigation without encountering issues related to extreme high local doses. *In situ* monitoring of the UV-visible induced absorption in irradiated HNO<sub>3</sub> solutions permitted quantification of HNO<sub>2</sub> production, and mass spectrometry was used to quantify H<sub>2</sub>. The influence of the dose rate and HNO<sub>3</sub> concentration was investigated, and the primary yields of these two species were determined. It was found that dose rate increase leads to diminished production of HNO<sub>2</sub> and H<sub>2</sub>, while HNO<sub>3</sub> concentration increase leads to increased HNO<sub>2</sub> formation and reduced H<sub>2</sub> production. The values of the primary yields of these two species were determined and compared to the literature reported values. While the determined values show similar trends as those reported, this study provides accurate radiolytic yields for H<sub>2</sub> and HNO<sub>2</sub> that are radioelement-independent compared to the  $\alpha$  radiolysis using radioisotope/HNO<sub>3</sub> mixtures and provides the basis for perfecting numerical codes used for simulating the radiolytic processes associated with SNF reprocessing.

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## Introduction

The share of nuclear energy in the context of climate change and of the 2015 Paris agreement<sup>1</sup> is dependent on many factors, the most important one being closing the nuclear fuel cycle, aiming at turning nuclear energy into a virtually zero waste energy source.

The technology surrounding recycling of nuclear fuel has been developed and implemented on a reasonably large scale in several countries. Historically, the main process used for nuclear fuel recycling is the PUREX (Plutonium and Uranium Extraction) process that relies on separation of Pu and U from spent fuel dissolved in HNO<sub>3</sub>. The challenge however remains the recovery of all-long lived actinides and recycling them so as to produce short lived fission products, improving the proliferation resistance, reducing waste volume, and making this process cost-effective. For any large-scale separation process to be adopted and fulfil the above requirements, it must be robust under high dose-rate radiation. The effect of radiation on

solvent (HNO<sub>3</sub>) extractions may result in decreased ligand concentrations, and accumulation of possibly dangerous degradation products. Among these, the most hazardous product is H<sub>2</sub> that can be formed during the radiolytic degradation of HNO<sub>3</sub>,<sup>2–4</sup> due to its flammability range, low ignition energy and high deflagration index<sup>5,6</sup> inside a canister. Due to the multi-component aspect of spent nuclear fuel, a multidirectional approach is needed, taking into account the alpha, beta and gamma radiation induced degradation. Many studies were dedicated to the radiolytic degradation of HNO<sub>3</sub> soon after the development of the PUREX process in the '50s, providing a wealth of information on the radiolytic mechanism and yields of H<sub>2</sub>, NO<sub>3</sub><sup>•</sup> and NO<sub>2</sub><sup>–</sup>/HNO<sub>2</sub> in the  $\gamma$ <sup>3,7–25</sup> or  $\beta$  radiolysis<sup>8,16,17,22,26–37</sup> of aqueous nitrate and nitric acid solutions. However, fewer studies have been dedicated to the  $\alpha$  radiolysis of these solutions, and the majority of these investigations were performed in the radiolysis of HNO<sub>3</sub> in the presence of radionuclides (<sup>243</sup>Am, <sup>241</sup>Am, <sup>244</sup>Cm, <sup>210</sup>Po, <sup>240</sup>Pu, <sup>238</sup>Pu).<sup>3,4,38–51</sup> The formation of radiolytic products (H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, NO<sub>3</sub><sup>•</sup> and NO<sub>2</sub><sup>–</sup>/HNO<sub>2</sub>) is generally evaluated using direct methods such as spectrophotometry, gas chromatography, ion chromatography or mass spectrometry<sup>40</sup> or indirect methods such as the classical or modified Shinn<sup>52,53</sup> or Ghormley method.<sup>54</sup> For the gas detection, all measurements are performed by sampling the headspace at the end of irradiations or at different residence

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times and replacing the sampled gas by laboratory air. These studies unanimously point to a decrease in the production of  $\text{H}_2$ , and increased  $\text{NO}_2^-/\text{HNO}_2$  production with increasing  $\text{HNO}_3$  concentration. Elevated linear energy transfer (LET) associated with  $\alpha$  irradiation implies generally higher primary yields ( $G$  values) than those corresponding to  $\beta$  and  $\gamma$  rays, due to increased second order processes as a result of closely spaced spurs and intra-track recombination favouring molecular products yields.<sup>55,56</sup> The measured  $G$ -values of  $\text{H}_2$  range between  $9.1 \times 10^{-9} - 4.6 \times 10^{-8} \text{ mol J}^{-1}$  and  $1.93 \times 10^{-7} \text{ mol J}^{-1}$  for pure water under  $\gamma$ <sup>55,57,58</sup> and  $\alpha$ <sup>57</sup> irradiation respectively, decreasing to  $2.1 \times 10^{-9} \text{ mol J}^{-1}$  for  $6 \text{ mol dm}^{-3} \text{ HNO}_3$ , under  $\gamma$  radiation. The vast majority of these studies has been performed using radionuclides as  $\alpha$  sources, raising the problem of nuclides-specific yields and chemical interactions.

In this article we investigate, using energetic external helions, the  $\alpha$ -radiation processes occurring in nitric acid solutions with concentrations ranging from 2 to  $5 \text{ mol dm}^{-3}$ . For gaseous products analysis, we perform sampling of the headspace using volumes that do not disturb the system and/or do not require replacing them with laboratory air that may affect the investigated process. A specially designed quartz cell allowing fast sample circulation and dose evaluation, enables us to perform the *in situ* dosimetry and follow-up experiments. Comparison with the dose evaluated from the  $\alpha$  particle flux and from *in situ* Fricke dosimetry shows agreement, ensuring that the extremely high doses generally associated with the use of particle accelerators are eliminated. At the same time, this study does not involve the use of radioelements as  $\alpha$ -source, avoiding their chemical implication in the system and supplies independent radiolytic yields. The information provided by these measurements offers a comprehensive understanding of the radiolytic processes occurring in  $\text{HNO}_3$ , creating a baseline for evaluations of future nuclear solvent extraction systems.

## Experimental

$\text{HNO}_3$  70% was purchased from Sigma-Aldrich and used without further purification. The investigated solutions are prepared from its dilution to reach 2, 3, 4 and  $5 \text{ mol dm}^{-3} \text{ HNO}_3$  using ultrapure Milli-Q water with less than 5 ppb organic carbon and a resistivity of  $18.2 \text{ M}\Omega \text{ cm}$ . 100 ml of fresh solutions are prepared prior to irradiations. The physicochemical properties of the investigated solutions are presented in Table 1.

**Table 1** Physicochemical properties of the investigated solutions.  $f_s$ ,  $f_w$  are the electron fractions of the solute and water respectively.  $\rho$  is the density of the solutions, and  $F$  is the dose factor calculated according to eqn (2)

| $[\text{HNO}_3]$<br>( $\text{mol dm}^{-3}$ ) | $\rho$<br>( $\text{kg cm}^{-3}$ ) | $f_s$ | $f_w$ | $F$<br>( $\text{kg cm}^{-3}$ ) |
|--|-----------------------------------|-------|-------|--------------------------------|
| 0  | 1.00                              | 0     | 1     | 1                              |
| 2  | 1.06                              | 0.11  | 0.89  | 1.053                          |
| 3  | 1.09                              | 0.16  | 0.84  | 1.08                           |
| 4  | 1.1                               | 0.21  | 0.79  | 1.1                            |
| 5  | 1.13                              | 0.26  | 0.74  | 1.13                           |

For the irradiations, a special monoblock quartz cell was developed that allows continuous circulation of the solution, avoiding accumulation of degradation products and exalted local doses. The total volume of the irradiation cell is 200 ml, and the volume of the irradiated solution is 100 ml, keeping a liquid : gas ratio of 1 : 1. Alpha particles delivered by the cyclotron enter the cell through a quartz window with a thickness of  $500 \mu\text{m}$ , and a surface diameter of 6 mm. The beam diameter is fixed at the same size as the entrance window, so no gas phase irradiation occurs. Using a BVP-Z standard Ismatec pump (IDEX Corp., Cole-Palmer, DE) pump, the solution is continuously flown, at a rate of  $3.6 \text{ dm}^3 \text{ min}^{-1}$ , so that the solution passes in a thin jet in front of the quartz window and is then sprayed onto the cell walls, favouring the liquid–gas exchange, and allowing the two phases to reach an equilibrium very efficiently. The irradiated solution is then injected into a 1 cm optical pathlength quartz cell (Hellma Analytics, DE), before returning to the irradiation loop. An optical fiber-connected spectrometer (AvaSpec, Avantes, NL) allows *in situ* monitoring of the UV-vis absorption inside the cells. The spectra are recorded for the entirety of the irradiation (5400 s for each sample), with spectra collected every 60 s as an average of 50 scans, in the wavelength range from 300 to 400 nm. To this irradiation cell, a loop is attached with a gas micro-pump (KNF, DE) that continuously circulates the gaseous phase. Periodically, the gas phase is sampled using a home-built remotely controlled electro-valves system. Each gas sample consists of a 2 ml volume. The gas samples are analysed post-irradiation using a Prisma Pro QMG 220 gas phase quadrupole mass spectrometer (Pfeiffer Vacuum, DE) to quantify the production of  $\text{H}_2$ . The Prisma Pro QMG 220 has a quadrupole analyser QMA 200 and yttriated iridium filaments, allowing detection in the mass range 1–100 u, with a resolution of 0.5 u, and a minimum detection limit of  $3 \times 10^{-15} \text{ mbar}$ . The sampled volume does not induce any disturbance in the measurement, as verified by irradiating  $2 \text{ mol dm}^{-3}$  solutions of  $\text{HNO}_3$ , at a dose rate of  $0.11 \text{ Gy s}^{-1}$ . These solutions were irradiated for 7200 s, and for 14 400 s. In the first solution irradiation case the gaseous atmosphere is sampled every 1200 s, whereas for the second irradiated solution, the sampling started 7200 s after the beginning of the irradiation, every 1200 s. The coherence of data and correspondence of hydrogen concentration at 7200 s (832 Gy) – last point of the first solution and first point of the second solution – evidence that no perturbation was induced by sampling the gas atmosphere. Fig. 1S in ESI† presents these data.

All irradiations are performed at the CEMHTI cyclotron (Orleans, France) that delivers  $\alpha$  particles with an energy of 45 MeV. The delivered helions pass through titanium screen sheets and the quartz window before entering the solution, losing part of their energy. The energy loss was calculated using SRIM (The Stopping Power and Range of Ions in Matter), based on the TRIM code,<sup>59,60</sup> with an evaluated energy inside the irradiation cell at 12.98 MeV, and the LET of the helions at  $102 \times 10^{-3} \text{ MeV } \mu\text{m}^{-1}$ .

The flux of particles within the irradiation cell is measured using a Faraday cup, and is set at 1, 2.5, 4, 5 and 10 nA before



experiments. The irradiation time for each sample is of 5400 s. The dose rate is calculated considering the  $\alpha$  particle flux and energy according to eqn (1):

$$D = \frac{IE}{2qVF} \quad (1)$$

where  $I$  is the current (A),  $E$  is the alpha particles energy (J),  $q$  is the electron charge ( $1.6 \times 10^{-19}$  C),  $V$  the irradiated volume ( $\text{m}^3$ ), and  $F$  the dose factor ( $\text{kg m}^{-3}$ ) given by:

$$F = \rho \times \frac{p \times \frac{Z_{\text{HNO}_3}}{M_{\text{HNO}_3}} + (100 - p) \times \frac{Z_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}}}{100 \times \frac{Z_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}}} \quad (2)$$

Because of the continuous circulation (flow rate =  $60 \text{ cm}^3 \text{ s}^{-1}$ ) of the target solutions inside the irradiation cell, the locally irradiated volume,  $V_i$  ( $V_i = S \times l$ ,  $S$  – beam facing cell surface,  $l$  – penetration depth of the  $\alpha$  particles  $l = 163.4 \mu\text{m}$  from SRIM calculations) is constantly refreshed, so that in one second the irradiated volume is  $V = 60 \text{ cm}^3$ . The evaluated dose rates for the set currents are presented in Table 2.

The maximum dose rate deposited was evaluated by looking at the Bragg curve (presented in Fig. 2S†) in our solution, determined using the SRIM software,<sup>59</sup> according to:

$$D_{\text{max}} = \frac{I \left( \frac{dE}{dx} \right)_{\text{max}} \times l}{2qVF} \quad (3)$$

where  $I$  is the current (A),  $\left( \frac{dE}{dx} \right)_{\text{max}}$  is the LET at Bragg peak ( $\text{keV } \mu\text{m}^{-1}$ ),  $l$  the penetration depth of the  $\alpha$  particles ( $163.4 \mu\text{m}$ ),  $q$  is the electron charge ( $1.6 \times 10^{-19}$  C),  $V$  the irradiated volume ( $\text{m}^3$ ), and  $F$  the dose factor ( $\text{kg m}^{-3}$ ). The evaluated maximum dose rates are presented in Table 2.

Prior to all irradiation, an *in situ* dosimetry is also performed using the super Fricke dosimeter, with the UV absorption of the irradiated solutions monitored in real-time using two 10 m optical fibers-coupled AvaSpec – dual channel spectrophotometer (Avantes. NL), attached to the quartz optical cell. The super Fricke dosimeter resides on the classical chemical dosimeter principles: oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  by the radiolytically produced oxidizing species, but its limited dose range is extended by increasing the  $\text{O}_2$  and ferrous sulfate concentrations.<sup>61</sup> Solutions of  $10^{-2} \text{ mol dm}^{-3}$   $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$  (>99%, AnalaR Normapur, UK) are prepared in  $0.4 \text{ mol dm}^{-3}$   $\text{H}_2\text{SO}_4$

(>98%, Carlo Erba, IT), with  $10^{-3} \text{ mol dm}^{-3}$  NaCl (Sigma-Aldrich, DE) added to suppress the effect of any impurities and bubbled with  $\text{O}_2$  prior to irradiations. The ferric ions' concentration is monitored following the absorption of target solutions at 304 nm ( $\epsilon = 2197 \text{ M}^{-1} \text{ cm}^{-1}$ ). According to the literature, the radiolytic yield of ferric ions for  $\alpha$  particles of 12.98 MeV was extrapolated at  $6.22 \times 10^{-7} \text{ mol J}^{-1}$ .<sup>62–65</sup> From the evolution of the absorbed dose in time, calculated according to eqn (4) and presented in Fig. 3S† in ESI,† we can evaluate the dose rate. The obtained values are presented in Table 2.

$$D_{\text{Fricke}} = \frac{[\text{Fe}^{3+}]}{G(\text{Fe}^{3+})F} \quad (4)$$

For the discussion herein, the dose rate we consider in all yield evaluations is the one measured using the super Fricke system, as it is determined under the same experimental conditions as the measurements in  $\text{HNO}_3$  solutions.

## Results and discussion

Nitrous acid ( $\text{HNO}_2$ ) and  $\text{H}_2$  are the most important stable radiolytic products issued from exposure of  $\text{HNO}_3$  solutions to high ionizing radiation fields, and that can have deleterious effects on the reprocessing technology.  $\text{HNO}_2$  can react with actinides, changing their oxidation state, impacting their separation and extraction efficiency, while production and accumulation of  $\text{H}_2$  is associated with flammability hazards.

The principal reactions occurring when ionizing radiation passes  $\text{HNO}_3$  aqueous solutions are listed in Table 3. Nitrite ions are produced indirectly *via* attack on nitrate ions by the water radiolysis primary species (reactions (13)–(31)) or directly by ionizing radiation (reaction (9)). Kazanjian *et al.*<sup>2</sup> showed that the formation of  $\text{HNO}_2$  in  $\text{HNO}_3$  in solutions of concentrations higher than  $1 \text{ mol dm}^{-3}$  is a result of both direct and indirect action of ionizing radiation; Balcerzyk *et al.*<sup>35</sup> showed that even in  $\text{HNO}_3$  solutions of concentrations of  $1 \text{ mol dm}^{-3}$ , the direct effects of ionizing radiation have a non-negligible contribution to the formation of nitrate radicals or ions, which in turn can lead to formation of nitrite. Considering the acidity of the investigated solution and following its  $\text{pK}_a$  value:  $\text{pK}_a(\text{HNO}_2/\text{NO}_2^-) = 3.24$  at  $25 \text{ }^\circ\text{C}$ ,<sup>66</sup> nitrite ions exist as nitrous acid.

The time evolution of the transient absorbance spectra recorded up to 5400 s with the AvaSpec fiber-coupled spectrometer is presented in Fig. 1. The 3D plot and time slices of the recorded data show the well-known spectrum of  $\text{HNO}_2$  with three absorbance maxima at 348, 358 and 372 nm.<sup>33,67</sup> From Fig. 1, we extracted the time evolution of the absorbance at 358 nm, and converted it into  $\text{HNO}_2$  formation ( $\epsilon_{358\text{nm}} = 57.05 \text{ M}^{-1} \text{ cm}^{-1}$ ,<sup>68</sup>).

While for low concentrations of  $\text{HNO}_3$  ( $< 1 \text{ mol dm}^{-3}$ ), the indirect effects represent the exclusive nitrite formation mechanism, this is not the case for the investigated solutions in this study: even for the lowest concentration investigated,  $2 \text{ mol dm}^{-3}$   $\text{HNO}_3$  solution, as we can see from the electron fraction of  $\text{NO}_3^-$  relative to water (Table 1), 11% of the deposited dose is

**Table 2** Dose rates evaluated from the alpha particle flux and from *in situ* Fricke dosimetry for the chosen current intensities

| Current (nA) | $D$ ( $\text{Gy s}^{-1}$ ) | $D_{\text{max}}$ ( $\text{Gy s}^{-1}$ ) | $D_{\text{Fricke}}$ ( $\text{Gy s}^{-1}$ ) |
|--------------|----------------------------|---|--|
| 1            | 0.105                      | 0.31                                    | 0.11                                       |
| 2.5          | 0.26                       | 0.78                                    | 0.32                                       |
| 4            | 0.42                       | 1.25                                    | 0.52                                       |
| 5            | 0.525                      | 1.57                                    | 0.65                                       |
| 10           | 1.05                       | 3.14                                    | 1.15                                       |



Table 3 Main reactions occurring in the radiolysis of concentrated nitric acid

|   |  |
|---|--|
| $\text{H}_2\text{O} \xrightarrow{\text{e}_{\text{pre}}^-, \text{e}_{\text{sol}}^-} \text{H}_2\text{O}^+, \text{H}_3\text{O}^+, \text{OH}^-, \text{H}^+$ | (5)  |
| $\text{H}_2\text{O} \xrightarrow{\text{e}_{\text{pre}}^-} \text{H}_2\text{O}^*$   | (6)  |
| $\text{H}_2\text{O}^* \rightarrow \text{H}^+ + \text{OH}^*$   | (7)  |
| $\text{H}_2\text{O}^* \rightarrow \text{H}_2 + \text{O}^*$  | (8)  |
| $\text{NO}_3^- \xrightarrow{\text{e}_{\text{pre}}^-} \text{NO}_3^{*-} \rightarrow \text{NO}_2^- + \text{O}^*$   | (9)  |
| $\text{NO}_3^- \xrightarrow{\text{e}_{\text{pre}}^-} \text{NO}_3^{\cdot-} + \text{e}^-$   | (10)   |
| $\text{HNO}_3 \xrightarrow{\text{e}_{\text{pre}}^-} \text{NO}_3^{\cdot-} + \text{H}^+$  | (11)   |
| $\text{HNO}_3 \xrightarrow{\text{e}_{\text{pre}}^-} \text{HNO}_3^* \rightarrow \text{HNO}_2 + \text{O}^*$   | (12)   |
| $\text{O}^*(^1\text{D}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2$  | (13)   |
| $\text{O}^*(^3\text{P}) + \text{NO}_3^- \rightarrow \text{NO}_2^- + \text{O}_2$   | $2.2 \times 10^{8,69}$ (14)  |
| $\text{NO}_3^- + \text{H}^+ \leftrightarrow \text{HNO}_3$   | $\text{p}K_{\text{a}15} = 1.4^{66}; k_{15} = 6 \times 10^{8,32} k_{-15} = 2 \times 10^{10} \text{ s}^{-1,32}$ (15) |
| $\text{NO}_2^- + \text{H}^+ \leftrightarrow \text{HNO}_2$   | $\text{p}K_{\text{a}16} = 3.24; k_{16} = 5 \times 10^{10,70} k_{-16} = 3 \times 10^7 \text{ s}^{-1,70}$ (16)       |
| $\text{NO}_3^- + \text{e}_{\text{pre}}^- \rightarrow \text{NO}_3^{2-}$  | $4.5 \times 10^{12,71}$ (17)   |
| $\text{NO}_3^- + \text{e}_{\text{sol}}^- \rightarrow \text{NO}_3^{2-}$  | $9.7 \times 10^{9,72}$ (18)  |
| $\text{NO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{NO}_2^- + 2\text{OH}^-$  | $1 \times 10^{3,73}$ (19)  |
| $\text{NO}_3^{2-} \xrightleftharpoons{\text{H}^+} \text{HNO}_3^-$   | $\text{p}K_{\text{a}20} = 4.8^{74} 5 \times 10^{8,74}$ (20)  |
| $\text{NO}_3^{2-} + \text{OH}^- \rightarrow \text{NO}_3^- + \text{OH}^-$  | $2.5 \times 10^{9,73}$ (21)  |
| $\text{HNO}_3^- \xrightleftharpoons{\text{H}^+} \text{H}_2\text{NO}_3$  | $\text{p}K_{\text{a}22} = 7.5^{74}$ (22)   |
| $\text{H}_2\text{NO}_3 \rightarrow \text{NO}_2^- + \text{H}_2\text{O}$  | $7 \times 10^{5,73}$ (23)  |
| $\text{NO}_3^- + \text{H}^+ \rightarrow \text{HNO}_3^-$   | $1 \times 10^{7,73}$ (24)  |
| $\text{HNO}_3^- \rightarrow \text{NO}_2^- + \text{OH}^-$  | $2.31 \times 10^5 \text{ s}^{-1,74}$ (25)  |
| $\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{OH}^+ + \text{H}_3\text{O}^+$  | $\sim 10^{13,75,76}$ (26)  |
| $\text{H}_2\text{O}^+ + \text{NO}_3^- \rightarrow \text{NO}_3^{\cdot-} + \text{H}_2\text{O}$  | $1 \times 10^{12,35}$ (27)   |
| $\text{OH}^+ + \text{HNO}_3 \rightarrow \text{NO}_3^{\cdot-} + \text{H}_2\text{O}$  | $5.3 \times 10^{7,37}$ (28)  |
| $\text{OH}^+ + \text{NO}_3^- \rightarrow \text{NO}_2^- + \text{HO}_2^{\cdot}$   | $1.1 \times 10^{10,36}$ (29)   |
| $2\text{NO}_2^{\cdot} \rightleftharpoons \text{N}_2\text{O}_4$  | $k_{30} = 4.5 \times 10^{8,73,77} k_{-30} = 6.9 \times 10^3 \text{ s}^{-1,77,78}$ (30)                             |
| $\text{N}_2\text{O}_4 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HNO}_2$   | $18^{77} 1 \times 10^3 \text{ s}^{-1,77}$ (31)   |
| $\text{NO}_2^{\cdot} + \text{H}^+ \rightarrow \text{HNO}_2$   | $1 \times 10^{10} \text{ s}^{-1,73}$ (32)  |
| $\text{H}^+ + \text{e}_{\text{pre}}^- \rightarrow \text{H}^*$   | (33)   |
| $\text{H}^+ + \text{e}_{\text{sol}}^- \rightarrow \text{H}^*$   | $2.3 \times 10^{10,79}$ (34)   |
| $\text{e}_{\text{sol}}^- + \text{e}_{\text{sol}}^- \rightarrow \text{H}_2 + \text{OH}^- + \text{OH}^-$  | $7.3 \times 10^{9,80}$ (35)  |
| $\text{e}_{\text{sol}}^- + \text{H}^+ \rightarrow \text{H}_2 + \text{OH}^-$   | $2.7 \times 10^{10,80}$ (36)   |
| $\text{e}_{\text{sol}}^- + \text{OH}^+ \rightarrow \text{OH}^-$   | $3.5 \times 10^{10,80}$ (37)   |
| $\text{OH}^+ + \text{HNO}_3 \rightarrow \text{NO}_3^{\cdot-} + \text{H}_2\text{O}$  | $5.3 \times 10^{7,37,81}$ (38)   |
| $\text{OH}^+ + \text{NO}_3^- \rightarrow \text{NO}_2^- + \text{HO}_2^{\cdot}$   | $1.1 \times 10^{10,36}$ (39)   |
| $\text{H}^+ + \text{H}^+ \rightarrow \text{H}_2$  | $5.1 \times 10^{9,80}$ (40)  |
| $\text{H}^+ + \text{OH}^+ \rightarrow \text{H}_2\text{O}$   | $1.1 \times 10^{10,80}$ (41)   |
| $\text{OH}^+ + \text{OH}^+ \rightarrow \text{H}_2\text{O}_2$  | $4.8 \times 10^{9,80}$ (42)  |
| $\text{H}^+ + \text{HO}_2^{\cdot} \rightarrow \text{H}_2\text{O}_2$   | $1.3 \times 10^{10,80}$ (43)   |

absorbed by nitrate, leading to the formation of nitrite ions and nitrate radicals (reactions (9) and (10)). The direct action of ionizing radiation can result in the formation of excited O<sup>\*</sup> atom, in the singlet (<sup>1</sup>D) or triplet state (<sup>3</sup>P), *via* reaction (9),<sup>69</sup> leading to H<sub>2</sub>O<sub>2</sub> (ref. 82–84) or HNO<sub>2</sub> (ref. 69) formation, respectively *via* reactions (13) and (14). When considering the radiolytic yield of HNO<sub>2</sub>, we need to also take into account its depletion *via* reactions with species resulting from the radiolysis of water 44–47, or from NO<sub>3</sub><sup>\*</sup> radicals' consumption of nitrites (reactions (48) and (49)):

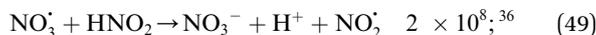
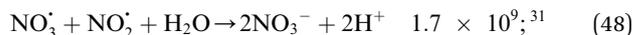
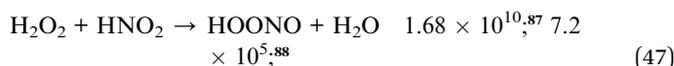
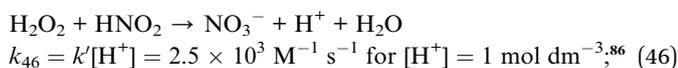


Fig. 2 presents the production of HNO<sub>2</sub> in solutions of 2 mol dm<sup>-3</sup> HNO<sub>3</sub>, irradiated at dose rates from 0.11 to 1.14 Gy s<sup>-1</sup> in the upper panel, and in solutions of several HNO<sub>3</sub> concentrations in the middle panel. As previously observed in  $\alpha$  self-radiolysis, the formation of nitrite in HNO<sub>3</sub> is proportional to the absorbed dose. Kazanjian *et al.*<sup>89</sup> observed an increase of nitrite, that reaches a maximum concentration in  $\gamma$  radiolysis for HNO<sub>3</sub> solutions with concentrations lower than 1 mol dm<sup>-3</sup> while at concentrations higher than 1 mol dm<sup>-3</sup>, the nitrite increase is linear. The authors suggest that a similar maximum concentration of nitrites for higher doses and  $\beta$  and  $\alpha$  radiation,



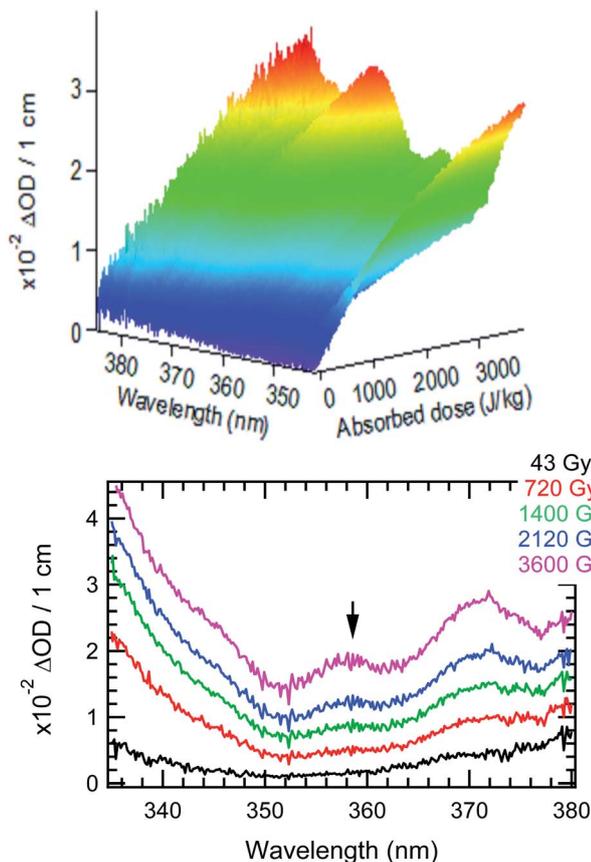


Fig. 1 (Top) Recorded image of the induced absorbance in a solution of  $3 \text{ mol dm}^{-3}$   $\text{HNO}_3$  by  $\alpha$  radiation at a dose rate of  $0.64 \text{ Gy/s}$ . (Bottom) Same data visualized as transient spectra at different absorbed doses.

is not excluded. Our measurements show that a new regime (break in the slope), or possibly a maximum of the  $\text{HNO}_2$  production is reached at the lowest dose rate and lowest concentration. As Fig. 2 shows, such slope-breaking could be expected for the other solutions at higher doses, and for more concentrated  $\text{HNO}_3$  solutions at increased dose rates. This new regime of  $\text{HNO}_2$  production could correspond to a steady state regime where accumulation of  $\text{HNO}_2$  is equilibrated by its degradation and consumption by products resulting from the radiochemical transformations of water (reactions (46)–(49)).

The observed nonlinear dose dependency of  $\text{HNO}_2$  concentration is a result of the complex processes involved in its production: both inhomogeneous (intra-track) and homogeneous chemistry are impacting  $\text{HNO}_2$  formation.<sup>23</sup> As listed in Table 3, the capture of presolvated and solvated electron by  $\text{NO}_3^-$  leads to formation of  $\text{NO}_3^{2-}$ , that can in turn lead to the  $\text{HNO}_2$  precursor,  $\text{NO}_2^\cdot$  (reaction (18)), or can be back oxidized by  $\text{O}_2$  or  $\text{H}_2\text{O}_2$  to  $\text{NO}_3^-$ :

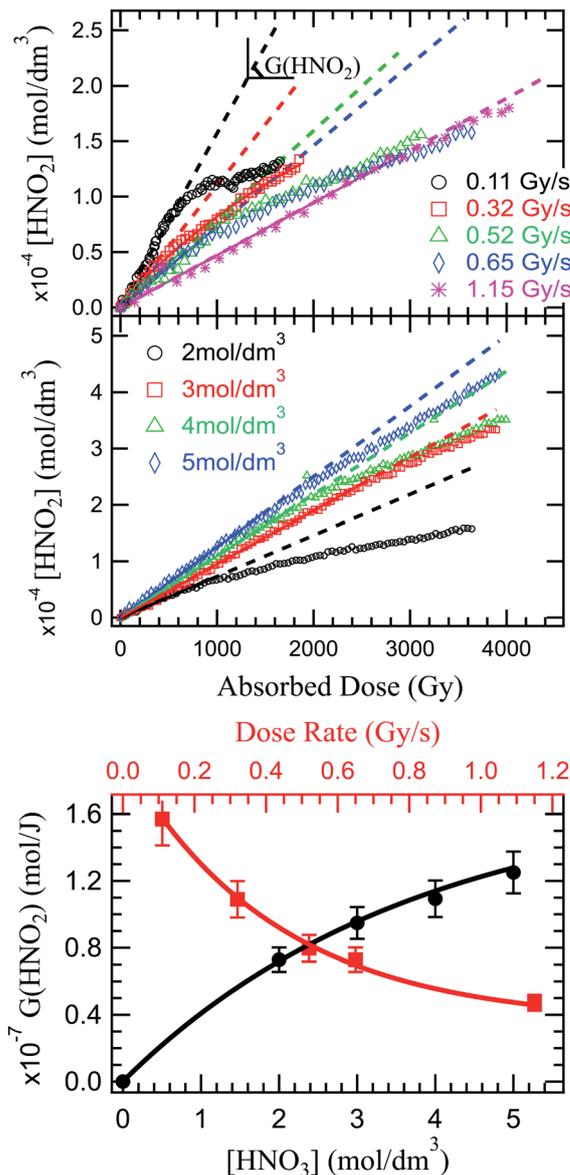
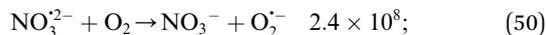


Fig. 2 Top image: dose dependence of the  $\text{HNO}_2$  concentration in solutions of  $2 \text{ mol dm}^{-3}$   $\text{HNO}_3$  under  $\alpha$  irradiation at various dose rates. Middle image:  $\text{HNO}_2$  concentration as a function of the absorbed dose in solutions of 2, 3, 4 and  $5 \text{ mol dm}^{-3}$  at  $0.64 \text{ Gy s}^{-1}$ . Lower image:  $\text{HNO}_2$  radiolytic yield dependence on  $\text{HNO}_3$  concentration (black) and  $G(\text{HNO}_2)$  dependence on the dose rate in a  $2 \text{ mol dm}^{-3}$   $\text{HNO}_3$  solution (red).

$\text{H}_2\text{O}_2$  can progressively accumulate in the system, and in time, reactions ((46) and (47)) and (51) start playing a more important role, which may lead to the levelling observed at high doses. Further investigations are required to see if such a stationary regime is also observed for other dose rates and concentrations.

Unlike previous observations that reported no dose rate effect for  $\text{HNO}_2$  production in  $1 \text{ mol dm}^{-3}$  and higher concentrations of  $\text{HNO}_3$  at dose rates ranging from  $0.93$  to  $1.5 \text{ Gy s}^{-1}$ , but rather assigned observed yield differences as a result of LET effects,<sup>3</sup> a distinct dose rate effect can be observed in the present



investigation: an increase of the dose rate leads to a decrease in  $G(\text{HNO}_2)$  (Fig. 2 lower panel). An increase in the dose rate will lead to an overlap of the heterogeneous zones, and to an increase of biradical reactions, favouring formation of molecular products ( $\text{H}_2\text{O}_2$  *via* reactions (42) and (43),  $\text{H}_2$  *via* (35)–(37)).<sup>90</sup> If the concentrations of  $\text{HNO}_3$  solutions is high enough,  $\text{HNO}_3$  can interfere in this mechanism. Otherwise,  $\text{HNO}_3$  will only react with the molecular products resulting from  $\text{H}_2\text{O}$  radiolysis. Considering the concentration of the studied solutions, the molecular products formed in the radiolysis of  $\text{HNO}_3$ , can react with the molecular products issued from radiolysis of  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O}_2$  ( $\text{H}_2$  having a low reactivity) is therefore responsible for the decrease in the  $\text{HNO}_2$  production, either by consumption of its precursor (reaction (51)) or its decomposition (reaction (46)/(47)). Dose rate also affects the solvated electron yield<sup>91</sup> which in turn is critical in the formation of  $\text{HNO}_2$  precursors.

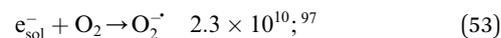
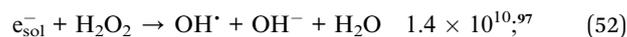
$\text{NO}_3^-$  is effectively converted into precursors of  $\text{NO}_2^{\cdot}$  ( $\text{NO}_3^{2-}$ ) through capture of presolvated and solvated electrons. Therefore we expect an increase of  $\text{HNO}_3$  concentration to lead to an increase of  $\text{HNO}_2$  production. Another contribution to this increase could be due to less important destruction of  $\text{HNO}_2$  by  $\text{H}_2\text{O}_2$ . Moisy *et al.*<sup>92</sup> showed that in concentrated solutions of  $\text{HNO}_3$ , the  $G(\text{H}_2\text{O}_2)$  decreases linearly with increasing  $\text{HNO}_3$  concentrations.  $\text{H}_2\text{O}_2$  is mainly formed *via* recombination of  $\cdot\text{OH}$  radicals, and increased concentrations of  $\text{HNO}_3$  will lead to  $\cdot\text{OH}$  scavenging *via* reaction (21) and (28). As the concentration of  $\text{HNO}_3$  increases, the dissociation degree decreases, as shown in Fig. 4S (see ESI†). Therefore, the  $\cdot\text{OH}$  reaction with the undissociated  $\text{HNO}_3$  molecules becomes more important with the increase in  $\text{HNO}_3$  concentration, leading to a decrease in  $\text{H}_2\text{O}_2$ , and ultimately to an increase of  $\text{HNO}_2$ . This is confirmed experimentally in measurement of  $\text{HNO}_2$  production in solutions of 2, 3, 4 and 5 mol dm<sup>3</sup>  $\text{HNO}_3$  irradiated at the same dose rate (0.64 Gy s<sup>-1</sup>). The results are presented in Fig. 2 (middle panel).

The radiolytic yields were determined from the slope at origin of these curves, and are presented in Fig. 2 (lower panel). Moisy *et al.*<sup>92</sup> reported that the radiolytic yield rises with the acidity until it reaches a plateau for concentrations of  $\text{H}^+$  higher than 1 mol dm<sup>-3</sup>. However, these measurements were performed in  $\text{NaNO}_3$ – $\text{HNO}_3$  mixtures, and both the  $\text{NO}_3^-$  concentration and  $\text{H}^+$  concentration impact the  $\text{HNO}_2$  production. Probably due to the lower  $\text{NO}_3^-$  concentration, our measurements show no plateau in the investigated  $\text{HNO}_3$  concentration range, but we do not exclude its existence at higher concentrations of  $\text{HNO}_3$ .

In the production of molecular hydrogen in the radiolysis of water, two main mechanisms have been suggested: intra-track chemistry, where the role of the  $\text{H}_2$  precursors (reactions (33)–(36)) has been identified and underlined by several authors,<sup>20,50,93</sup> and dissociative chemistry of excited water molecules (reactions (7) and (8)) formed by direct excitation or recombination reaction of the water radical cation with the presolvated electron. In  $\text{HNO}_3$  solutions, competition reactions leading to production of H atom through direct effects (reaction (11), and consumption of  $\text{H}_2$  precursors (reactions (17) and (18)) occur; but the overall reported trend is a decrease of  $\text{H}_2$  in

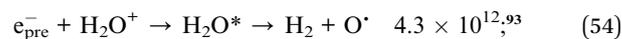
concentrated  $\text{HNO}_3$  solutions. As for  $\text{HNO}_2$ , we looked at what impact of the dose rate and the solution concentration has on  $\text{H}_2$  production in the external  $\alpha$  radiolysis of  $\text{HNO}_3$ .

The dose rate effect on the production of solvated electron has been already shown in the literature,<sup>90,91,94</sup> indicating an increased recombination of solvated electron with  $\text{H}^{\cdot}$  and  $\cdot\text{OH}$  radicals in the complicated process of spur overlap (reactions (36) and (37)). Higher quantities of  $\text{H}_2\text{O}_2$  produced favorably at higher dose rates and under aerated conditions as is the case of these investigations can also play a role in scavenging this  $\text{H}_2$  precursors.<sup>95,96</sup>



As the solvated electrons recombinations (reactions (34)–(36)) are a great contributor to  $\text{H}_2$  production in the radiolysis of water,<sup>20,98,99</sup> a dose rate increase implying a reduced solvated electron production, will ultimately lead to a decrease in hydrogen production. This behavior is observed experimentally and reported in Fig. 3 (upper panel). The production of  $\text{H}_2$  is proportional to the absorbed dose, and inversely proportional to the dose rate. No stationary regime is observed in the production of  $\text{H}_2$  under the investigated conditions, leaving room for debate whether this regime exists or not.

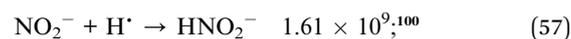
It has been shown that the excited water molecule decomposition is the greatest contributor to  $\text{H}_2$  formation (~70%) in the radiolysis of water, and the role of the presolvated electron has been underlined.<sup>93</sup> This latter species can undergo dissociative recombination with the parent water cation:



In  $\text{HNO}_3$  solutions, these precursors are scavenged by nitrate ions (reaction (17)). Horne *et al.*<sup>24</sup> showed that these reactions are not sufficient to account for the decrease of  $\text{H}_2$  yield in high  $\text{HNO}_3$  concentration, and identified the excited water molecule quenching by nitrate ion as responsible for the observed decrease:



$\text{H}^{\cdot}$  atoms, which are also produced can at their turn be scavenged by nitrate and nitrite ions and radicals as follows:



Previous reports indicated a decreased  $\text{H}_2$  production with increased nitrate concentration, due to the scavenging of  $\text{H}_2$  precursors ( $e_{\text{pre}}^-$  and  $e_{\text{sol}}^-$ ) by nitrate (reaction (17) and (18)).



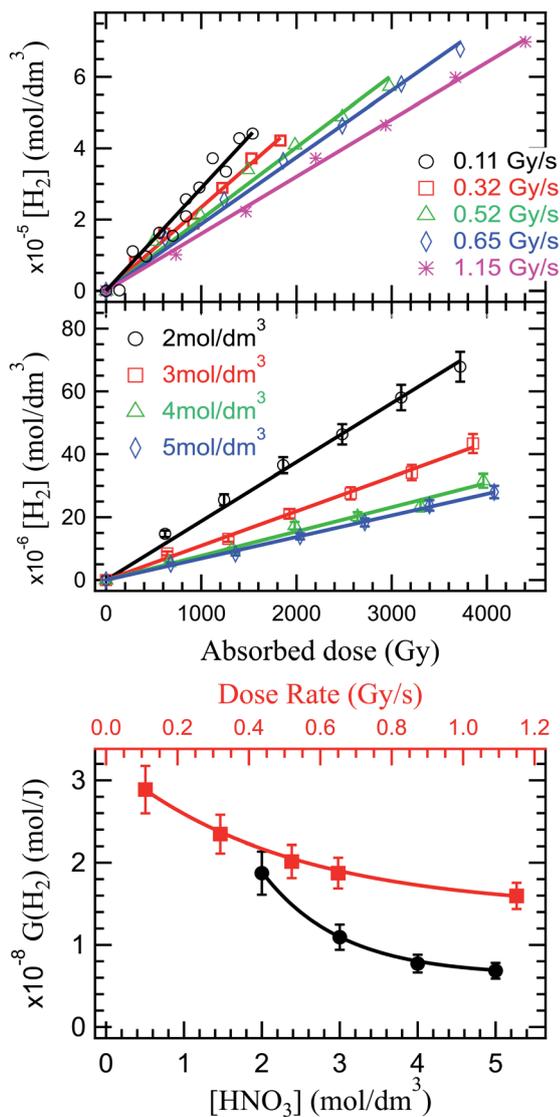


Fig. 3 Top image: dose dependence of the  $\text{H}_2$  concentration (top) in solutions of  $2 \text{ mol dm}^{-3}$   $\text{HNO}_3$  under  $\alpha$  irradiation at various dose rates. Middle image:  $\text{H}_2$  concentration as a function of the absorbed dose in solutions of  $\text{HNO}_3$  for several concentrations indicating a decrease in  $\text{H}_2$  with increasing concentrations. Lower image:  $\text{H}_2$  radiolytic yield dependence on the concentration of  $\text{HNO}_3$  (black) and  $G(\text{H}_2)$  dependence on the dose rate in a  $2 \text{ mol dm}^{-3}$   $\text{HNO}_3$  solution (red).

But, as shown above, a complex series of reactions occurs in  $\text{HNO}_3$  solutions that results in a diminished  $\text{H}_2$  production decrease. This trend is observed in our investigations in Fig. 3 (middle and lower panel).

Fig. 4 shows a compilation of literature reported values of radiolytic yields of  $\text{H}_2$  and  $\text{HNO}_2$  measured in the  $\alpha$  radiolysis of  $\text{HNO}_3$  solutions.

Looking at the previously reported  $G(\text{HNO}_2)$ , our results are closest to the ones obtained for  $\alpha$  radiolysis using plutonium nitrate in  $\text{HNO}_3$ ,<sup>47</sup> and rather inconsistent with measurements using helions.<sup>92</sup> However, as mentioned, the external  $\alpha$  irradiations were performed in  $\text{NaNO}_3$ - $\text{HNO}_3$  mixtures of constant  $\text{NO}_3^-$  concentration, by varying the  $\text{H}^+$  concentration. These

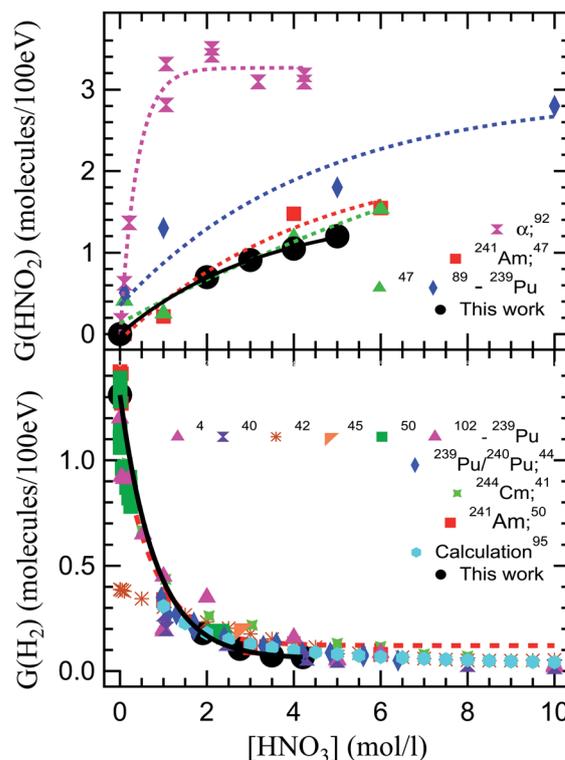


Fig. 4 Comparison of our radiolytic yields of  $\text{HNO}_2$  (top image) and  $\text{H}_2$  (lower image) with the values reported in the literature. The  $G(\text{HNO}_2)$  values are extracted from alpha radiolysis of  $\text{HNO}_3$  using helions,<sup>92</sup>  $^{241}\text{Am}$ ,<sup>47</sup> and  $^{239}\text{Pu}$ .<sup>47,89</sup>  $G(\text{H}_2)$  are the values reported in the alpha radiolysis of  $\text{HNO}_3$  solutions using  $^{239}\text{Pu}$ ,<sup>4,40,42,45,50,102</sup> mixtures of  $^{239}\text{Pu}/^{240}\text{Pu}$ ,<sup>44</sup>  $^{244}\text{Cm}$ ,<sup>41</sup>  $^{241}\text{Am}$ ,<sup>50</sup> and calculated values.<sup>51,103</sup>

results are obtained from measurements using hydrazinium as an  $\text{HNO}_2$  scavenger and following the decay of  $\text{N}_2\text{H}_5^+$  as well as the formation of  $\text{NH}_3$ . This reaction occurs in competition with  $\text{H}_2\text{O}_2$  consumption of  $\text{HNO}_2$ , explaining the observed differences. Pu and Cm self-radiolysis of  $\text{HNO}_3$  provide higher values for  $G(\text{H}_2)$ , while Am yielded closer values to these external  $\alpha$  investigations. No external  $\alpha$  irradiation measurements on the radiolytic yield of  $\text{H}_2$  have been reported before this work. Compared to previous reports, we observe that our measurement indicate a slightly lower production of  $\text{H}_2$  in the  $\alpha$  radiolysis of  $\text{HNO}_3$ , but careful consideration needs to be taken when such comparisons are made, as the experimental conditions are different. For the  $\alpha$  radiolysis investigations, there is a long standing debate over the use of external helions *versus* internal  $\alpha$  particle emitters. This concerns the homogenous dose that is usually measured by performing a dosimetry *versus* the very high local dose deposited in solution in the case of external helions, and the localized dose deposition *versus* the calculation of the average deposited doses from the activities of the different actinides used as internal alpha sources. The discrepancies between the local dose deposited by external helions, evaluated from the ion current densities, and the dosimetry evaluated deposited dose have lead authors to the use of radionuclides in the detriment of cyclotrons for  $\alpha$  sources. However, this is not applicable for these investigations.

Table 4 H<sub>2</sub> and HNO<sub>2</sub> radiolytic yields as a function of the HNO<sub>3</sub> concentration and as a function of the dose rate in 2 mol dm<sup>-3</sup> HNO<sub>3</sub>

| [HNO <sub>3</sub> ]<br>(mol dm <sup>-3</sup> ) | G(H <sub>2</sub> )<br>(mol J <sup>-1</sup> ) | G(HNO <sub>2</sub> )<br>(mol J <sup>-1</sup> ) | Dose rate<br>(Gy s <sup>-1</sup> ) | G(H <sub>2</sub> ), 2 mol dm <sup>-3</sup><br>HNO <sub>3</sub> (mol J <sup>-1</sup> ) | G(HNO <sub>2</sub> ), 2 mol dm <sup>-3</sup><br>HNO <sub>3</sub> (mol J <sup>-1</sup> ) |
|--|--|--|------------------------------------|---|---|
| 0  | 1.9 × 10 <sup>-7,57</sup>                    | 0  | 0.11                               | 2.4 × 10 <sup>-8</sup>  | 1.6 × 10 <sup>-7</sup>  |
| 2  | 1.8 × 10 <sup>-8</sup>                       | 7.2 × 10 <sup>-8</sup>                         | 0.32                               | 2.3 × 10 <sup>-8</sup>  | 1.1 × 10 <sup>-7</sup>  |
| 3  | 1.1 × 10 <sup>-8</sup>                       | 9.6 × 10 <sup>-8</sup>                         | 0.52                               | 2.1 × 10 <sup>-8</sup>  | 7.6 × 10 <sup>-8</sup>  |
| 4  | 7.6 × 10 <sup>-9</sup>                       | 1.1 × 10 <sup>-7</sup>                         | 0.65                               | 1.9 × 10 <sup>-8</sup>  | 7.2 × 10 <sup>-8</sup>  |
| 5  | 7.1 × 10 <sup>-9</sup>                       | 1.3 × 10 <sup>-7</sup>                         | 1.15                               | 1.7 × 10 <sup>-8</sup>  | 4.6 × 10 <sup>-8</sup>  |

Continuous intense flow of our solutions insures (see Experimental section – dosimetry) that the irradiated volume is constantly refreshed, avoiding accumulation of degradation products and the mentioned enormous local doses, while insuring the rapid liquid/gas exchange. Moreover, when using internal  $\alpha$  particle emitters, radionuclides-specific yields have been recorded due to the progressive disproportionation as a function of the nitric acid concentration induced by the complexing nature of HNO<sub>3</sub> and its chemical involvement in the investigated processes.<sup>46,49,104–113</sup> Simultaneously, investigations using radionuclides may pose exposure and contamination risks to the manipulators and require special equipment for safe handling that render them cumbersome. At the same time, questions are imposed about loss of products during handling. Working in a closed circuit allows us to avoid sampling of the headspace and replacing the sampled volume with laboratory air that can dilute the gaseous volume or induce leaks of H<sub>2</sub> produced, considering the fugacity of H<sub>2</sub> gas. Radioisotope/HNO<sub>3</sub> mixtures result in self-radiolysis and high locally deposited energy, issue partially alleviated by stirring the solutions. Our experimental set-up allowed us to perform experiments, sampling the gas phase without inducing perturbations of the system. To the best of our knowledge, this is the first time that this type of experiment has been performed using external  $\alpha$  irradiation.

## Conclusions

The two most important species resulting from the radiolysis of HNO<sub>3</sub> are HNO<sub>2</sub> and H<sub>2</sub>. When considering the use of HNO<sub>3</sub> in the retreatment of spent nuclear fuel, and therefore its radiolysis due to the high radiation fields it is exposed to, reliable information on the radiolytic yield of G(HNO<sub>2</sub>) and G(H<sub>2</sub>) is essential. If not scavenged, HNO<sub>2</sub> can be responsible for partitioning failure as it plays on the oxidation state of U, Pu and minor actinides. H<sub>2</sub> concentrations have to be closely monitored in order to avoid its accumulation in the retreatment units and the associated explosion risk. The main scope of these experiments was to gain insight into the  $\alpha$ -radiolytic production of these two species, and identify any dose rate and concentration effects. UV-visible spectroscopy and gas mass spectrometry are versatile and extremely sensitive tools for performing quantitative analysis of desired products. Continuously monitoring HNO<sub>2</sub> and H<sub>2</sub> allowed us to perform measurements and quantify their production. These

productions show dose rate effects that have been neglected up to now in the production of HNO<sub>2</sub>, as well as in the production of H<sub>2</sub>. Increasing concentrations of HNO<sub>3</sub> have opposite effects on these products, leading to HNO<sub>2</sub> increase and H<sub>2</sub> decrease.

Table 4 summarizes the determined radiolytic yields as a function of the HNO<sub>3</sub> concentration and dose rate. Our measurements provide accurate values for the radiolytic yields of these species that are chemically independent of any radioisotope that could be used as an  $\alpha$  radiation source. The information provided by this study is the first of this kind and starts shedding light on the complexity of the HNO<sub>3</sub> chemical system under irradiation.

From both fundamental and practical aspects, this study paves the way for further investigations on the radiolytic processes occurring in HNO<sub>3</sub> mixtures relevant to SNF retreatment.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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