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# Influence of plutonium oxidation state on the formation of molecular hydrogen, nitrous acid and nitrous oxide from alpha radiolysis of nitric acid solution

Brandon Perrin, Laurent Venault<sup>1</sup>, Emilie Broussard, Johan Vandendorre, Guillaume Blain, Massoud Fattahi, Sergey Nikitenko

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**Abstract.** The study of the formation of radiolytic products, such as molecular hydrogen and nitrous acid, is of primary importance in the reprocessing of spent nuclear fuel and the storage of aqueous solutions containing radioactive materials. The radiolytic yields of molecular hydrogen, nitrous acid and nitrous oxide from alpha radiolysis of nitric acid solutions containing plutonium have been experimentally investigated. The results have shown that the yields of radiolytic products depends on the nitric acid concentration as well as the oxidation state of plutonium. However, the influence of plutonium oxidation state on radiolytic yields is less notable as the nitric acid concentration increases. Molecular hydrogen production decreases with increasing nitric acid concentration while nitrous acid and nitrous oxide productions increase. While radiolytic yields from plutonium(IV) nitric acid solutions have been previously investigated, this study provide radiolytic yields from alpha radiolysis of plutonium(III) and plutonium(VI) nitric acid solutions for molecular hydrogen, nitrous acid and nitrous oxide. These information provide insight into the role played by plutonium redox behaviour on the formation of radiolytic products.

**Keywords.** plutonium, oxidation state, alpha radiolysis, nitric acid, radiolytic products

## 1 Introduction

Nitric acid is widely used in the nuclear industry. During the reprocessing of spent nuclear fuel, nitric acid is subject to an intense radiation field leading to the degradation of the aqueous phase and the formation of numerous radiolytic products. Some of these radiolytic products, mainly  $H_2O_2$  and  $HNO_2$ , have redox properties that can be detrimental to the reprocessing process. Moreover, the formation of gaseous radiolytic products ( $H_2$ ,  $NO_x$ , ...) can raise safety concerns [1]–[6].

Molecular hydrogen is a well-known product of radiolysis of aqueous solutions. Its production can lead to the formation of flammable gas mixture and induce the pressurization of sealed containers. The radiolytic formation of molecular hydrogen have been greatly studied with  $\gamma$  radiations whereas only a few studies used  $\alpha$  radiations. The available literature data for molecular hydrogen production are summarized in Figure 1, for better reading, only few data from  $\gamma$  radiolysis are showed here. In nitric acid solutions, nitrate ions are known to scavenge the precursors of molecular hydrogen, lowering its radiolytic yield with increasing nitric acid concentrations [7]. Under  $\alpha$  radiation, molecular hydrogen is produced with higher yields than under  $\gamma$  radiation due to the higher linear energy transfer of  $\alpha$  particles, leading to closer radiation spurs which enhance the recombination of primary radicals and hence molecular yields over

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radical yields [8]. Among  $\alpha$  radiation, results from plutonium solutions trend to present lower radiolytic yields than with other  $\alpha$  sources as a consequence of plutonium(IV) scavenging the precursors of molecular hydrogen.

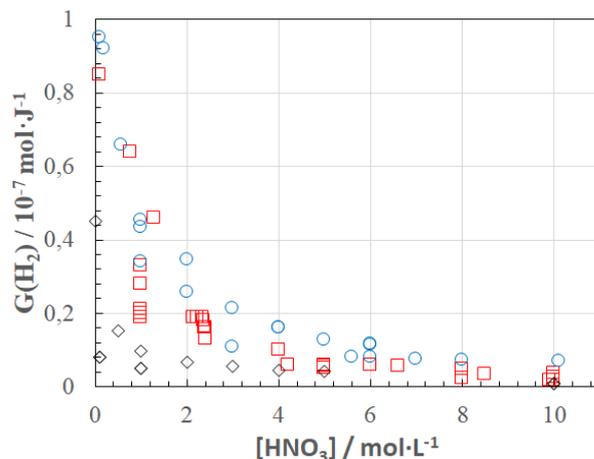
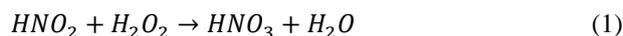


Figure 1: Available literature data for  $G(\text{H}_2)$  from radiolysis of aerated aqueous nitric acid solutions.  $\diamond$  :  $\gamma$ -radiolysis [8]–[10].  $\square$  :  $\alpha$ -radiolysis using plutonium(IV) [11]–[15].  $\circ$  :  $\alpha$ -radiolysis using americium [11], curium [16], polonium [17] and external irradiations [8].

Nitrous acid is the main aqueous product of nitric acid radiolysis, it can affect the performance of the reprocessing process as it presents a complex redox behaviour with multiple actinides. In PUREX process, nitrous acid is detrimental during the plutonium extraction step as it quickly reacts with plutonium(III) in an auto-catalytic reaction leading to a complete oxidation of plutonium(III) into plutonium(IV) and thus preventing the extraction of plutonium [18]. For this reason, hydrazinium nitrate is added in aqueous phase during the process as it consumes nitrous acid, avoiding the oxidation of plutonium(III). Alongside the formation of nitrous acid caused by nitric acid radiolysis, hydrogen peroxide is formed from water radiolysis. This two species react with each other according to reaction (1) [19], [20].



For that reason, both species cannot be observed at the same time. For nitric acid concentrations lower than  $0.5 \text{ mol}\cdot\text{L}^{-1}$ , hydrogen peroxide is the main product, while for higher concentrations nitrous acid is formed with a higher yield [1]. Only a few studies investigated the formation of nitrous acid from nitric acid solutions under  $\gamma$  or  $\alpha$  radiolysis. The radiolytic yield of nitrous acid is sometimes determined in presence of sulphanilamide [21], p-nitroaniline [9], [10] or cerium(IV) [22] as they react with nitrous acid, avoiding its consumption by hydrogen peroxide and therefore allowing to calculate the total amount of nitrous acid formed by radiolysis. The available literature data for nitrous acid production are summarized in Figure 2.

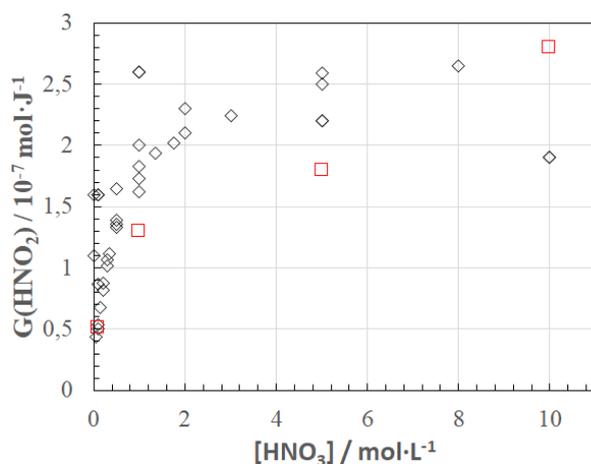


Figure 2: Available literature data for  $G(\text{HNO}_2)$  from radiolysis of aerated aqueous nitric acid solutions in presence of additives.  $\diamond$  :  $\gamma$ -radiolysis [9], [10], [21], [22].  $\square$  :  $\alpha$ -radiolysis [9], [10].

Nitrogen oxides such as  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{N}_2\text{O}$  are also formed from nitric acid radiolysis. However, only a few studies reported their formation from nitric acid solutions at high concentrations [12]. Among these radiolytic products, nitrous

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oxide is commonly observed and presents a very low radiolytic yield with G-values lower than  $10^{-9}$  mol·J<sup>-1</sup>. While the mechanism leading to the formation of nitrous oxide is still under question, its reactivity as an aqueous electron scavenger has been widely investigated [23], [24]. The available literature data for nitrous oxide production give radiolytic yields around  $6 \times 10^{-11}$  mol·J<sup>-1</sup> in 1 and 5 mol·L<sup>-1</sup> nitric acid solutions and around  $3.6 \times 10^{-10}$  mol·J<sup>-1</sup> in 10 mol·L<sup>-1</sup> nitric acid solutions [12].

Due to the complex redox behaviour of plutonium, different oxidation state can react with different radicals or molecular compounds produced by radiolysis. This behaviour can influence the formation of radiolytic products such as molecular hydrogen and nitrous acid. While data from literature were obtained using plutonium(IV) solutions, the present work investigates the radiolytic yields of H<sub>2</sub>, HNO<sub>2</sub> and N<sub>2</sub>O from  $\alpha$  radiolysis of nitric acid containing plutonium, as a function of HNO<sub>3</sub> concentrations using plutonium(III), plutonium(IV) and plutonium(VI) solutions. The information obtained by these experiments will provide better understanding on the influence of plutonium redox behaviour on the formation of radiolytic products.

## 2 Materials and methods

### 2.1 Caution

*Because of the radioactive nature of plutonium, special precautions as well as appropriate equipment and facilities for radiation protection are required for handling this material. For this reason, experiments were carried out by trained persons in handling of radioactive materials in depressurized glove boxes with very restrictive protocols.*

### 2.2 Chemicals

Concentrated nitric acid 65% and solid sodium acetate were purchased from VWR chemicals. Solid sulfamic acid and solid silver(II) oxide were purchased from Acros Organics. Griess reagent for nitrite and solid chloroacetic acid were purchased from Sigma-Aldrich. Concentrated hydrochloric acid 37% was purchased from Merck. All chemicals were used as received without further purification.

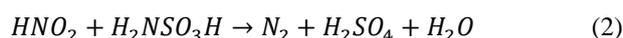
### 2.3 Preparation of plutonium solutions

A plutonium stock solution (14.53 g·L<sup>-1</sup> Pu in 1.22 mol·L<sup>-1</sup> HNO<sub>3</sub>) was prepared by anion exchange purification in order to remove <sup>241</sup>Am resulting from <sup>241</sup>Pu decay. The isotopic distribution was determined by Thermal Ionization Mass Spectrometry, percentage and properties of the isotopes are given in Table 1.

Table 1. Isotopic composition of plutonium stock solution and properties.

Isotope	mol%	Half-life (years)	Decay mode	Energy (keV)
<sup>238</sup> Pu	5.487 ± 0.039	87.7	$\alpha$	5480
<sup>239</sup> Pu	82.768 ± 0.228	24110	$\alpha$	5140
<sup>240</sup> Pu	11.345 ± 0.063	6561	$\alpha$	5151
<sup>241</sup> Pu	0.169 ± 0.005	14.3	$\beta^-$	5.2
<sup>242</sup> Pu	0.231 ± 0.005	375000	$\alpha$	4887

In nitric acid solutions with concentration higher than 0.5 mol·L<sup>-1</sup>, plutonium(III) is unstable due to its oxidation by nitrous acid formed by radiolysis [25]. For this reason, experiments with plutonium(III) were performed in presence of sulfamic acid as it quickly react with nitrous acid according to reaction (2) and only weakly influences the redox behaviour of plutonium [26], [27]. Similar experiments with plutonium(IV) and plutonium(VI) are also made and compared to the experiments without sulfamic acid.



$$k_2 = 33.5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$$

Experiments were prepared following the procedures provided hereinafter and the compositions of plutonium solutions obtained this way are detailed in Table 2.

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Plutonium(IV) experiments were carried out by dilution of 0.660 mL of plutonium stock solution, made up to 4 mL in order to obtain 10 mmol·L<sup>-1</sup> Pu solution, using the appropriate concentration of HNO<sub>3</sub> with or without sulfamic acid (experiments Pu1 - Pu6, Table 2).

Plutonium (III) experiments were prepared by dilution of 0.660 mL of plutonium stock solution, made up to 4 mL in order to obtain 10 mmol·L<sup>-1</sup> Pu solution, using the appropriate concentration of HNO<sub>3</sub> with sulfamic acid and reducing the plutonium by electrochemical reduction on platinum electrode afterward. Reaction compartment of working Pt-electrode was separated from auxiliary Pt-electrode by a ceramic diaphragm while redox potential in solution was referenced versus Hg/Hg<sub>2</sub>Cl<sub>2</sub>-electrode. Complete reduction of plutonium was achieved in 1 hour at 400 mV (vs Hg/Hg<sub>2</sub>Cl<sub>2</sub>) (experiments Pu7 - Pu8, Table 2).

Plutonium (VI) was prepared by oxidation of an aliquot of plutonium stock solution by Ag<sup>II</sup>O. Small weighted amount of AgO were added under agitation and the oxidation was monitored by spectrophotometry following the absorbance peaks of plutonium(IV) and plutonium(VI) at 476 nm and 830 nm respectively with their corresponding molar absorption coefficients being 68 and 470 L·mol<sup>-1</sup>·cm<sup>-1</sup> in 1 mol·L<sup>-1</sup> HNO<sub>3</sub> [28]. The reaction of oxidation is describe as reaction (3). Complete oxidation of plutonium was achieved with an average of 5 equivalents of AgO (vs Pu). Ag<sup>+</sup> were precipitated as AgCl by adding 1.05 equivalent of concentrated hydrochloric acid (vs Ag). The AgCl precipitate was separated from the supernatant by centrifugation. Pu(VI) experiments were prepared by dilution of the supernatant, made up to 4 mL in order to obtain 10 mmol·L<sup>-1</sup> Pu solution, using the appropriate concentration of HNO<sub>3</sub> with or without sulfamic acid (experiments Pu9 – Pu14, Table 2).



Table 2. Compositions of plutonium solutions.

Experiment	[Pu] (mmol·L <sup>-1</sup> )	Oxidation state	[H <sub>2</sub> NSO <sub>3</sub> H] (mol·L <sup>-1</sup> )	[HNO <sub>3</sub> ] (mol·L <sup>-1</sup> )
Pu1	10	+IV	/	1
Pu2	10	+IV	/	3
Pu3	10	+IV	/	6
Pu4	10	+IV	0.1	1
Pu5	10	+IV	0.1	3
Pu6	10	+IV	0.1	6
Pu7	10	+III	0.1	1
Pu8	10	+III	0.1	3
Pu9	10	+VI	/	1
Pu10	10	+VI	/	3
Pu11	10	+VI	/	6
Pu12	10	+VI	0.1	1
Pu13	10	+VI	0.1	3
Pu14	10	+VI	0.1	6

## 2.4 Irradiation procedure

Self-irradiation of the solutions occurs from the  $\alpha$ -decay of plutonium. Dose rates were calculated from the activities and were corrected for the decay of the isotopes and the ingrowth of additional radionuclides (<sup>241</sup>Am), leading to an average initial dose rate of 7.71×10<sup>-2</sup> J·s<sup>-1</sup>·L<sup>-1</sup>. Experimental sample were kept until the desired doses had been reached and analysed.

## 2.5 Analytical methods

Measurements of nitrous acid concentrations were performed by a modified Griess method. The procedure consists in the addition of an aliquot of the irradiated solutions to 0.3 mL of Griess Reagent made up to 1 mL using a buffer (CH<sub>3</sub>COONa 0.8 mol·L<sup>-1</sup> / ClCH<sub>2</sub>COOH 3.2 mol·L<sup>-1</sup>). The resulting azo-dye was analysed spectrophotometrically after 30 min using a Shimadzu UV-3150 spectrophotometer implemented in glove box. An extinction coefficient of  $\epsilon = 41630 \pm 850$  L·mol<sup>-1</sup>·cm<sup>-1</sup> was determined at  $\lambda_{max} = 530$  nm.

Molecular hydrogen and nitrous oxide concentrations were measured by gas chromatography using a SRA Instrument  $\mu$ GC3000 with two channels : a molecular sieve 5Å column with thermal conductivity detector and argon carrier gas for the quantification of molecular hydrogen and a PoraPlotQ column with thermal conductivity detector and helium carrier

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gas for the quantification of nitrous oxide. An aliquot of 2 mL of solution containing plutonium is introduced into a beaker and then placed in an airtight cell, specifically designed for gas analysis, with a headspace of 130 mL. The pressure inside the cell is monitored continuously during the experiment using a pressure sensor. The atmosphere is replaced with air containing 1 vol% of neon, used as internal standard, at an initial pressure of 1.2 bar. Molecular hydrogen and nitrous oxide concentrations were determined by sampling the headspace gas of the cell multiple times at different times.

### 3 Results and discussion

#### 3.1 Radiolytic yields

Radiolytic yields values were determined from the slope of the studied compound production (expressed in mol) versus the energy received by the media (expressed in J). Radiolytic yields are often expressed as G-values given in the conventional radiation chemical unit of ions or molecules·100 eV<sup>-1</sup>. However, throughout this work, G-values will be expressed in the SI unit (mol·J<sup>-1</sup>) with the relation 1 ion or molecule·100 eV<sup>-1</sup> = 1.036×10<sup>-7</sup> mol·J<sup>-1</sup>. Uncertainties in G-values were estimated from the error in the slope of the production versus energy. For example, H<sub>2</sub> produced versus energy are plotted in Figure 3 at different nitric acid concentrations and in Figure 4 at different plutonium oxidation states. All G-Values and uncertainties are reported in Table 3.

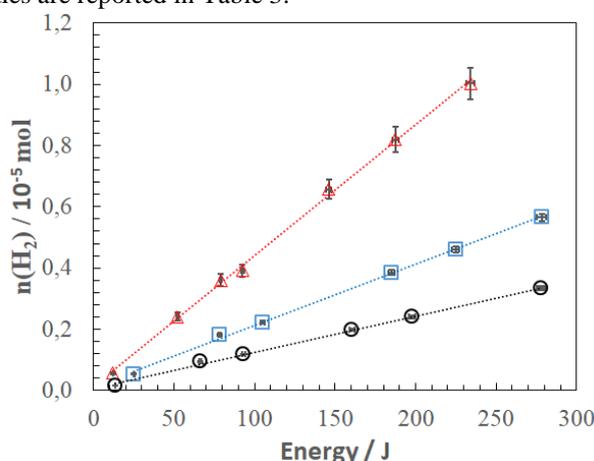


Figure 3. H<sub>2</sub> produced versus energy from plutonium(IV) solutions at different nitric acid concentration.  $\Delta$  : [HNO<sub>3</sub>] = 1 mol·L<sup>-1</sup> (Pu1).  $\square$  : [HNO<sub>3</sub>] = 3 mol·L<sup>-1</sup> (Pu2).  $\circ$  : [HNO<sub>3</sub>] = 6 mol·L<sup>-1</sup> (Pu3).

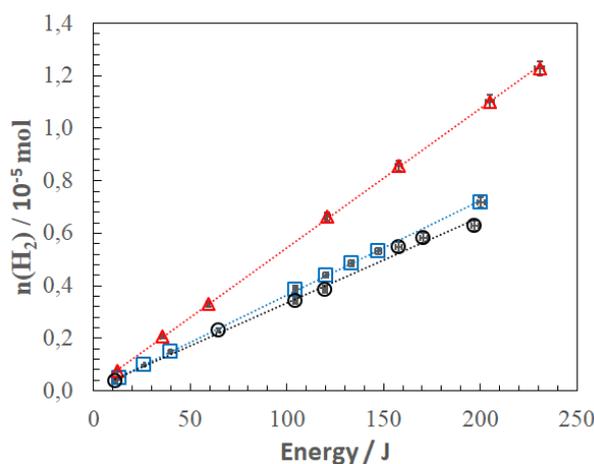


Figure 4. H<sub>2</sub> produced versus energy in [HNO<sub>3</sub>] = 1 mol·L<sup>-1</sup> solutions in presence of [H<sub>2</sub>NSO<sub>3</sub>H] = 0.1 mol·L<sup>-1</sup> at different plutonium oxidation states.  $\Delta$  : plutonium(III) (Pu7).  $\square$  : plutonium (IV) (Pu4).  $\circ$  : plutonium (VI) (Pu12).

Table 3. Radiolytic yields and uncertainties.

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Experiment	G(H <sub>2</sub> ) (10 <sup>-7</sup> mol·J <sup>-1</sup> )	G(HNO <sub>2</sub> ) (10 <sup>-7</sup> mol·J <sup>-1</sup> )	G(N <sub>2</sub> O) (10 <sup>-7</sup> mol·J <sup>-1</sup> )
Pu1	0.428 ± 0.015	0.35 ± 0.02	0.009 ± 0.002
Pu2	0.200 ± 0.007	1.27 ± 0.06	0.021 ± 0.004
Pu3	0.118 ± 0.005	1.83 ± 0.09	0.083 ± 0.018
Pu4	0.358 ± 0.006	/	0.042 ± 0.010
Pu5	0.194 ± 0.006	/	0.046 ± 0.009
Pu6	0.101 ± 0.005	/	0.075 ± 0.014
Pu7	0.522 ± 0.010	/	0.870 ± 0.170
Pu8	0.237 ± 0.006	/	1.451 ± 0.272
Pu9	0.372 ± 0.018	0.70 ± 0.04	0.008 ± 0.003
Pu10	0.178 ± 0.009	1.38 ± 0.07	0.020 ± 0.004
Pu11	0.105 ± 0.006	1.84 ± 0.10	0.064 ± 0.012
Pu12	0.327 ± 0.024	/	0.041 ± 0.009
Pu13	0.162 ± 0.013	/	0.043 ± 0.010
Pu14	0.078 ± 0.007	/	0.138 ± 0.026

### 3.2 Molecular hydrogen

Radiolytic yields of molecular hydrogen from plutonium +IV and +VI solutions without sulfamic acid (experiments Pu1–Pu3 and Pu9–Pu11) as well results from literature are shown as a function of nitric acid concentration in Figure 5. The results show that G(H<sub>2</sub>) decrease with increasing nitric acid concentration without sulfamic acid as reported in the literature. Radiolytic yields of molecular hydrogen from Pu(IV) solutions ranges from 0.43×10<sup>-7</sup> mol·J<sup>-1</sup> in 1 mol·L<sup>-1</sup> nitric acid solution to 0.12×10<sup>-7</sup> mol·J<sup>-1</sup> in 6 mol·L<sup>-1</sup> nitric acid solution, which corresponds to the high data values given in the literature but are still in good agreements with previously reported results [11], [14]. The higher G(H<sub>2</sub>) values obtained with these experiments can be the consequence of the uses of lower plutonium concentrations [29] and/or lower dose rate, as recently reported by Musat *et al.* [30].

Radiolytic yields of molecular hydrogen from plutonium +III, +IV and +VI solutions with sulfamic acid are shown in Figure 6. The G-values in presence of sulfamic acid are lower for both Pu(IV) and Pu(VI) series, indicating that either molecular hydrogen is formed with a lower yield or that molecular hydrogen is consumed. Molecular hydrogen production clearly depends on the oxidation state of plutonium following the order Pu(III) >> Pu(IV) > Pu(VI). Radiolytic yields of molecular hydrogen from Pu(III) solutions ranges from 0.52×10<sup>-7</sup> mol·J<sup>-1</sup> in 1 mol·L<sup>-1</sup> nitric acid solution to 0.24×10<sup>-7</sup> mol·J<sup>-1</sup> in 3 mol·L<sup>-1</sup> nitric acid solution. These latter are higher than previously reported values for Pu(IV) and external radiations, implying that Pu(III) enhance the production of molecular hydrogen. Presence of sulfamic acid and different oxidations states of plutonium have a strong impact on molecular hydrogen production in 1 mol·L<sup>-1</sup> nitric acid solution, however their impact decreases at higher nitric acid concentration.

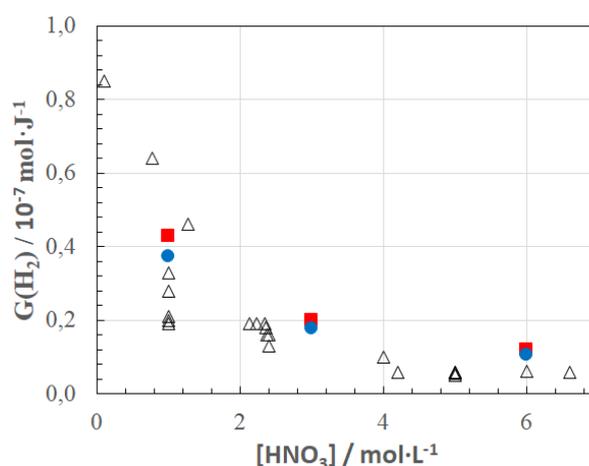


Figure 5. Radiolytic yields of molecular hydrogen G(H<sub>2</sub>) as a function of nitric acid concentration from ■ : plutonium(IV) (Pu1-Pu3). ● : plutonium(VI) (Pu9-Pu11). Δ : data from literature obtained from plutonium(IV) solutions [11]–[15].

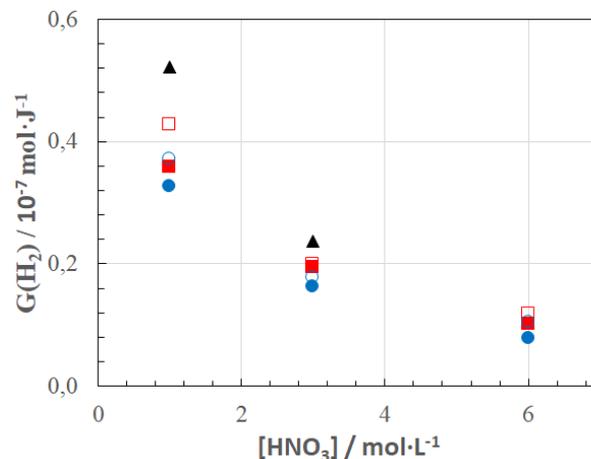
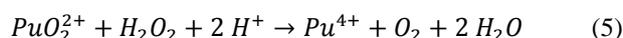
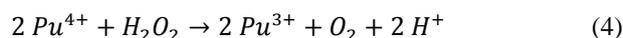


Figure 6. Radiolytic yields of molecular hydrogen  $G(\text{H}_2)$  as a function of nitric acid concentration from ▲ : plutonium (III) +  $\text{NH}_2\text{SO}_3\text{H}$  (Pu7-Pu8). □ : plutonium (IV) (Pu1-Pu3). ● : plutonium (VI) (Pu9-Pu11). ◻ : plutonium (IV) +  $\text{NH}_2\text{SO}_3\text{H}$  (Pu4-Pu6). ◐ : plutonium (VI) +  $\text{NH}_2\text{SO}_3\text{H}$  (Pu12-Pu14).

### 3.3 Nitrous acid

Radiolytic yields of nitrous acid from plutonium +IV and +VI without sulfamic acid (experiments Pu1 – Pu3 and Pu9 – Pu11) are shown as a function of nitric acid concentration in Figure 7. In presence of sulfamic acid, nitrous acid was not observed due to the fast reaction (2). The quantification of hydrogen peroxide formation in presence sulfamic acid has been attempted spectrophotometrically by Ti(IV) method [31] using an extinction coefficient of  $\epsilon = 849 \pm 9 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$  at  $\lambda_{\text{max}} = 408 \text{ nm}$ . For plutonium(IV) and plutonium(VI) experiments, no hydrogen peroxide has been detected due to the fast reduction reaction of plutonium by  $\text{H}_2\text{O}_2$  described by reaction (4) and (5) [32]. For plutonium(III) experiments, hydrogen peroxide was observed but concentration was below quantification limit which was determined at  $6 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ .



As observed from the available literature data,  $G(\text{HNO}_2)$  increases with increasing nitric acid concentrations. In the experiments conditions, hydrogen peroxide produced from water radiolysis reacts with nitrous acid, decreasing the observed nitrous acid radiolytic yield. Therefore the observed nitrous acid radiolytic yield must be compared to  $[G(\text{HNO}_2) - G(\text{H}_2\text{O}_2)]$  when these values have been determined separately. Radiolytic yields of nitrous acid from Pu(IV) solutions are in good agreement with the results previously reported by Horne *et al.* [33], with  $G$ -values ranging from  $0.35 \times 10^{-7} \text{ mol}\cdot\text{J}^{-1}$  in  $1 \text{ mol}\cdot\text{L}^{-1}$  nitric acid solution to  $1.83 \times 10^{-7} \text{ mol}\cdot\text{J}^{-1}$  in  $6 \text{ mol}\cdot\text{L}^{-1}$  nitric acid solution. Results from Pu(VI) solutions are found to be higher at 1 and 3  $\text{mol}\cdot\text{L}^{-1}$  nitric acid than the ones obtained from Pu(IV) solutions and identical at 6  $\text{mol}\cdot\text{L}^{-1}$  nitric acid. Oxidations states of plutonium have a strong impact on nitrous acid production in  $1 \text{ mol}\cdot\text{L}^{-1}$  nitric acid solution, however its impact decreases at higher nitric acid concentration.

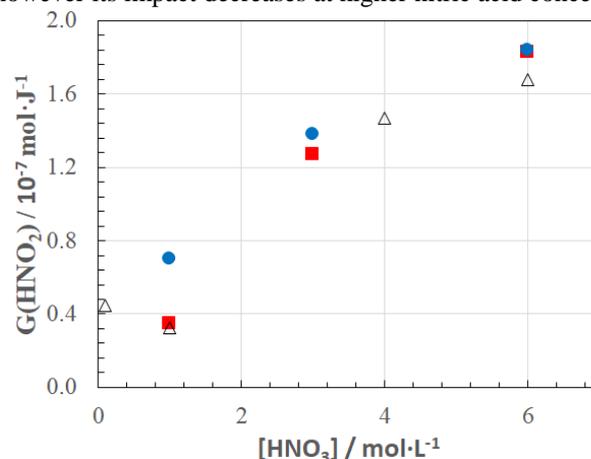


Figure 7. Radiolytic yields of nitrous acid  $G(\text{HNO}_2)$  as a function of nitric acid concentration from ■ : plutonium (IV) (Pu1-Pu3). ● : plutonium (VI) (Pu9-Pu11). △ : data from literature obtained from plutonium(IV) solutions [33].

### 3.4 Nitrous oxide

Radiolytic yields of nitrous oxide from plutonium +III, +IV and +VI solutions with and without sulfamic acid (experiments Pu1 – Pu14) are shown as a function of nitric acid concentration in Figure 8.

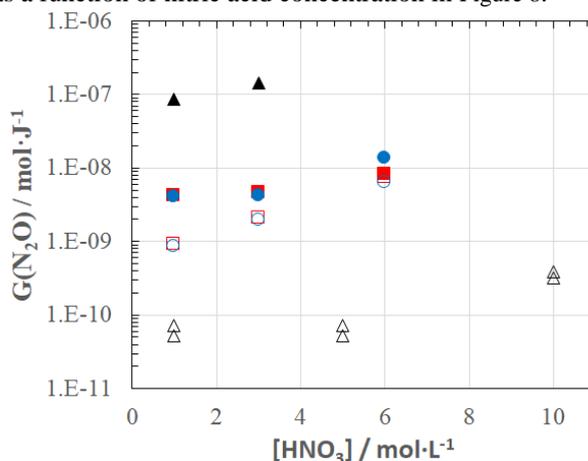


Figure 8. Radiolytic yields of nitrous oxide  $G(\text{N}_2\text{O})$  as a function of nitric acid concentration from ▲ : plutonium (III) +  $\text{NH}_2\text{SO}_3\text{H}$  (Pu7-Pu8), ■ : plutonium (IV) +  $\text{NH}_2\text{SO}_3\text{H}$  (Pu4-Pu6), ● : plutonium (VI) +  $\text{NH}_2\text{SO}_3\text{H}$  (Pu12-Pu14), □ : plutonium (IV) (Pu1-Pu3), ○ : plutonium (VI) (Pu9-Pu11), △ : data from literature obtained from plutonium(IV) solutions [12].

The results show that  $G(\text{N}_2\text{O})$  increase with increasing nitric acid concentration and both in presence and absence of sulfamic acid. However, the results are not in accordance with data from literature pointing out a difference of multiple order of magnitude. Experiments with Pu(IV) and Pu(VI) gives similar results with  $G(\text{N}_2\text{O})$  ranging from  $0.009 \times 10^{-7} \text{ mol} \cdot \text{J}^{-1}$  in  $1 \text{ mol} \cdot \text{L}^{-1}$  nitric acid solution to  $0.07 \times 10^{-7} \text{ mol} \cdot \text{J}^{-1}$  in  $6 \text{ mol} \cdot \text{L}^{-1}$  nitric acid solution. In presence of sulfamic acid, results from Pu(IV) and Pu(VI) experiments present similar G-values in 1 and 3  $\text{mol} \cdot \text{L}^{-1}$  nitric acid solutions, with  $G(\text{N}_2\text{O})$  around  $0.04 \times 10^{-7} \text{ mol} \cdot \text{J}^{-1}$  in these conditions. Results in  $6 \text{ mol} \cdot \text{L}^{-1}$  nitric acid solution with sulfamic acid presents a small difference between Pu(IV) and Pu(VI) experiments with  $G(\text{N}_2\text{O})$  equals to  $0.08 \times 10^{-7} \text{ mol} \cdot \text{J}^{-1}$  and  $0.13 \times 10^{-7} \text{ mol} \cdot \text{J}^{-1}$  respectively. The formation of nitrous oxide from Pu(III) solutions is significantly higher than the one from Pu(IV) and Pu(VI) solutions, with  $G(\text{N}_2\text{O})$  ranging from  $0.87 \times 10^{-7} \text{ mol} \cdot \text{J}^{-1}$  in  $1 \text{ mol} \cdot \text{L}^{-1}$  nitric acid solution to  $1.45 \times 10^{-7} \text{ mol} \cdot \text{J}^{-1}$  in  $3 \text{ mol} \cdot \text{L}^{-1}$  nitric acid solution, thus becoming the main gaseous product in these conditions.

### 3.5 Effect of nitric acid concentration

The radiolysis of water is a complex phenomenon that proceed via the main reaction (6)-(22) described in Table 4 [7], [34]. In nitric acid solutions of concentrations higher than  $1 \text{ mol} \cdot \text{L}^{-1}$ , direct and indirect radiolysis of nitrate ions and undissociated nitric acid have to be considered. The radiolysis of nitric acid occur via the main reaction (23)-(43) also described in Table 4 [1], [11], [33], [35], [36].

The impact of nitric acid on the radiolytic yields of molecular hydrogen and nitrous acid have been previously reported [7]. The increase of nitric acid concentration enhance the scavenging of precursors of molecular hydrogen  $\text{H}_2\text{O}^*$ ,  $e_{pre}^-$ ,  $e_{aq}^-$  and  $\text{H}^*$ , according to reactions (27), (32)-(34) and therefore decrease the  $G(\text{H}_2)$ . These scavenging reactions lead to the formation of  $\text{NO}_3^{*-}$ ,  $\text{NO}_3^{*2-}$  and  $\text{HNO}_3^{*-}$  which then reacts according to reactions (29),(35) and (36) increasing the  $G(\text{HNO}_2)$ . With increasing nitric acid, direct effect of ionizing radiation on nitrate ion and undissociated nitric acid increases and enhances the formation of nitrous acid.

Increase in nitric acid concentration also lead to higher  $G(\text{N}_2\text{O})$ . A proposed mechanism by Pikaev *et al.* [37] for the formation of nitrous oxide involve reactions (44)-(48). With increasing nitric acid concentration,  $G(\text{NO})$  and  $G(\text{NO}_2)$  increase thus favouring the formation of  $\text{N}_2\text{O}$  through these reactions. However, the mechanism also involve  $e_{aq}^-$  and  $\text{H}^*$  that are most likely scavenged by nitrate ion and therefore can explain the low yield of formation of  $\text{N}_2\text{O}$ .

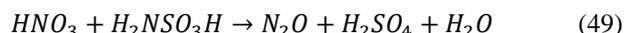
Table 4. Main reactions of water and nitric acid radiolysis.

	<b>k (L·mol<sup>-1</sup>·s<sup>-1</sup>)</b>	
<b>Water radiolysis</b>		
$H_2O \rightsquigarrow e^-, H_2O^{*+}, H_3O^+, H^\bullet, OH^\bullet$	-	(6)
$H_2O \rightsquigarrow H_2O^*$	-	(7)
$e^- \xrightarrow{110 fs} e_{pre}^- \xrightarrow{240 fs} e_{aq}^-$	-	(8)
$H_2O^{*+} + e^- \rightarrow H_2O^*$	$4.3 \times 10^{12}$	(9)
$H_2O^* \rightarrow H^\bullet + OH^\bullet$	-	(10)
$H_2O^* \rightarrow H_2 + O^\bullet$	-	(11)
$H_2O^{*+} + H_2O \rightarrow OH^\bullet + H_3O^+$	$1.8 \times 10^{11}$	(12)
$e_{aq}^- + H^+ \rightarrow H^\bullet$	$2.3 \times 10^{10}, pK_a = 9.8$	(13)
$e_{aq}^- + H^\bullet + H_2O \rightarrow H_2 + 2OH^-$	$2.5 \times 10^{10}$	(14)
$e_{aq}^- + OH^\bullet \rightarrow OH^-$	$3.0 \times 10^{10}$	(15)
$2e_{aq}^- + 2H_2O \rightarrow H_2 + 2OH^-$	$5.5 \times 10^9$	(16)
$e_{aq}^- + H_2O_2 \rightarrow OH^\bullet + OH^-$	$1.1 \times 10^{10}$	(17)
$H^\bullet + H^\bullet \rightarrow H_2$	$7.8 \times 10^9$	(18)
$H^\bullet + OH^\bullet \rightarrow H_2O$	$7.0 \times 10^9$	(19)
$H^\bullet + H_2O_2 \rightarrow OH^\bullet + H_2O$	$9.0 \times 10^7$	(20)
$OH^\bullet + OH^\bullet \rightarrow H_2O_2$	$5.5 \times 10^9$	(21)
$H^+ + OH^- \rightarrow H_2O$	$1.4 \times 10^{11}, pK_a = 14$	(22)
<b>Nitric acid radiolysis</b>		
$HNO_3 \rightsquigarrow NO_3^\bullet, H^\bullet$	-	(23)
$HNO_3 \rightsquigarrow HNO_3^*$	-	(24)
$NO_3^- \rightsquigarrow NO_3^\bullet, e^-$	-	(25)
$NO_3^- \rightsquigarrow NO_3^{*-}$	-	(26)
$H_2O^* + NO_3^- \rightarrow NO_3^{*-} + H_2O$	$1.0 \times 10^{13}$	(27)
$HNO_3^* \rightarrow HNO_2 + O^\bullet$	-	(28)
$NO_3^{*-} \rightarrow NO_2^- + O^\bullet$	-	(29)
$O^\bullet + NO_3^- \rightarrow NO_2^- + O_2$	-	(30)
$H_2O^{*+} + NO_3^- \rightarrow NO_3^* + H_2O$	-	(31)
$e_{pre}^- + NO_3^- \rightarrow NO_3^{*2-}$	$1.0 \times 10^{13}$	(32)
$e_{aq}^- + NO_3^- \rightarrow NO_3^{*2-}$	$9.7 \times 10^9$	(33)
$H^\bullet + NO_3^- \rightarrow HNO_3^{*-}$	$5.6 \times 10^6$	(34)
$HNO_3^{*-} \rightarrow NO_2^* + OH^-$	$2.0 \times 10^5 s^{-1}$	(35)
$H_2NO_3^* \rightarrow NO_2^* + H_2O$	$7.0 \times 10^5$	(36)
$H^\bullet + NO_2^* \rightarrow HNO_2$	$1.0 \times 10^{10}$	(37)
$NO_2^* + NO_2^* \rightarrow N_2O_4$	$4.5 \times 10^8$	(38)
$N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2$	$1.8 \times 10^1$	(39)
$H^+ + NO_3^- \rightarrow HNO_3$	$pK_a \approx 1.37$	(40)
$H^+ + NO_2^- \rightarrow HNO_2$	$pK_a = 3.2$	(41)
$H^+ + NO_3^{*2-} \rightarrow HNO_3^{*-}$	$pK_a = 4.8$	(42)
$H^+ + HNO_3^{*-} \rightarrow H_2NO_3^*$	$pK_a = 7.5$	(43)
$NO_2^* + H^\bullet \rightarrow NO^\bullet + OH^\bullet$	-	(44)
$NO^\bullet + NO^\bullet \rightarrow N_2O_2$	-	(45)
$N_2O_2 + H^\bullet \rightarrow N_2O + OH^\bullet$	-	(46)
$N_2O_4 + H^\bullet \rightarrow N_2O_3 + OH^\bullet$	-	(47)
$N_2O_3 + H^\bullet \rightarrow N_2O + HO_2^\bullet$	-	(48)

### 3.6 Effect of sulfamic acid

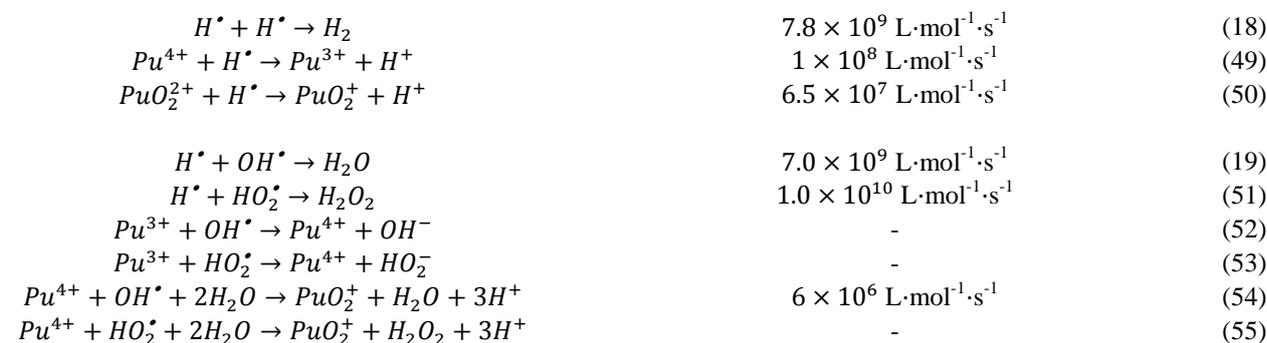
Sulfamic acid is used as an anti-nitrous reagent as it quickly react with nitrous acid according to reaction (2). In presence of sulfamic acid all nitrous acid is consumed avoiding its reaction with Pu(III) and letting the hydrogen peroxide to accumulate in the media. The  $G(H_2)$  values for Pu(IV) and Pu(VI) in presence of sulfamic acid are lower than the ones obtained without. This decrease in molecular hydrogen formation can be assigned to a possible reaction between sulfamic acid and molecular hydrogen precursors, however no such reaction have been found in the available literature. Another hypothesis is that the accumulation of hydrogen peroxide enhance the reactions (17) and (20) which would decrease the  $G(H_2)$ . With increasing nitric acid concentration, the mains scavenging reactions for the molecular hydrogen precursors become the ones involving nitrate ions, therefore the influence of sulfamic acid on molecular hydrogen production become less significant.

Moreover, sulfamic acid is unstable in nitric acid solution as it slowly react with nitric acid according to reaction (49) [38], [39]. The reaction leads to the formation of nitrous oxide and therefore the experiments with sulfamic acid show higher  $G(N_2O)$  than the similar experiments without. With increasing nitric acid concentration, the degradation of sulfamic acid by nitric acid should increase as well as the production of nitrous oxide by reaction (49). Therefore, the difference in  $G(N_2O)$  between experiments with and without sulfamic acid should increase, however such behaviour isn't observed.



### 3.7 Effect of plutonium oxidation state

Molecular hydrogen production depends on the oxidation state of plutonium following the order Pu(III) >> Pu(IV) > Pu(VI). Plutonium is known to have a complex redox behaviour and can be reduced or oxidized by radiolytic products. Pu(IV) and Pu(VI) can be reduced by  $H^\bullet$  according to reactions (46) and (50) [40], decreasing the production of molecular hydrogen through reaction (18) and thus decreasing  $G(H_2)$ . Pu(III) and Pu(IV) can be oxidized by  $HO^\bullet$  and  $HO_2^\bullet$  according to reactions (52)-(55) preventing these radicals to react with  $H^\bullet$  through reactions (19) and (51) and increasing  $G(H_2)$ . With increasing nitric acid concentration, these radicals are more likely to be scavenged by nitrate ions, reducing the impact of plutonium oxidation state.



Radiolytic yields of nitrous acid from Pu(VI) solutions are higher than the ones obtained from Pu(IV) solutions for concentration of nitric acid of 1 and 3 mol·L<sup>-1</sup> and identical at 6 mol·L<sup>-1</sup>. According to Liu *et al.* [41], the main reactions leading to the formation of nitrous acid are reactions (56) and (57). Therefore the increase in nitrous acid production from Pu(VI) solutions is attribute to an increase in  $NO_2$ .



Nitrous acid can react with Pu(IV) and Pu(VI) to produce  $NO_2$  according to reactions (58) and (59). The  $NO_2$  produced by these reactions can in turn react with Pu(V) and Pu(III) in the reverse reaction to produce nitrous acid through reactions (60) and (61) [40]. Reactions with Pu(VI) and Pu(V) are faster than the ones with Pu(IV) and Pu(III), leading to a higher  $NO_2$  concentration and thus increasing  $G(HNO_2)$ .



Radiolytic yields of nitrous oxide from Pu(IV) and Pu(VI) solutions are similar while radiolytic yields from Pu(III) solutions are significantly higher. The mechanism leading to the formation of nitrous oxide involve NO,  $\text{NO}_2$  and  $\text{H}^*$ . As previously described, Pu(IV) and Pu(VI) can react with  $\text{H}^*$ , preventing this latter to react with NO and  $\text{NO}_2$ , thus decreasing  $\text{G}(\text{N}_2\text{O})$  in comparison to Pu(III) solutions. However, this mechanism alone cannot fully explain the difference of  $\text{G}(\text{N}_2\text{O})$  between Pu(III) and Pu(IV) or Pu(VI) as the difference is around  $0.8 \times 10^{-7} \text{ mol}\cdot\text{J}^{-1}$  at  $1 \text{ mol}\cdot\text{L}^{-1}$   $\text{HNO}_3$  and around  $1.4 \times 10^{-7} \text{ mol}\cdot\text{J}^{-1}$  at  $3 \text{ mol}\cdot\text{L}^{-1}$   $\text{HNO}_3$ . Therefore the difference could be assigned to reactions between Pu(III) and NO or  $\text{NO}_2$ , leading to the formation of  $\text{N}_2\text{O}$ , but no experimental data allow us to prove that these reactions occur.

## 4 Conclusion

Molecular hydrogen, nitrous acid and nitrous oxide from  $\alpha$  radiolysis of nitric acid solution containing plutonium have been investigated using gas chromatography and spectrophotometry. The results showed that G-values greatly depends on nitric acid concentrations. As reported in the literature, radiolytic yields of molecular hydrogen decrease with increasing nitric acid concentration while radiolytic yields of nitrous acid increase. These effects are attributed to the scavenging of hydrogen precursors by nitrate ions, decreasing the formation of molecular hydrogen and leading to the formation of nitrous acid. New values of radiolytic yields of nitrous oxide were obtained for nitric acid concentration ranging from  $1 \text{ mol}\cdot\text{L}^{-1}$  to  $6 \text{ mol}\cdot\text{L}^{-1}$  and pointed out a difference of multiple order of magnitude with previously reported data. Radiolytic yields from plutonium(III) and plutonium(VI) solutions for molecular hydrogen, nitrous acid and nitrous oxide were also obtained. It has been shown that plutonium oxidation states have a significant influence on radiolytically generated products. Molecular hydrogen and nitrous oxide productions were found to be highly increased in presence of plutonium(III), while plutonium(VI) only lightly decrease molecular hydrogen production and have no effect on nitrous oxide production in comparison to plutonium(IV) experiments. Nitrous acid production have been found to be increased in presence of plutonium(VI). Impact of plutonium oxidation state decrease with increasing nitric acid concentration. Moreover, the presence of sulfamic acid induces lower molecular hydrogen production and higher nitrous oxide production whatever the plutonium oxidation state. The presented research highlights the complexity of  $\alpha$ -radiolysis of nitric acid solutions containing plutonium and provide insight into the role played by plutonium redox behaviour on the formation of molecular hydrogen, nitrous acid and nitrous oxide.

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