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# Airborne release fraction of dissolved materials during the combustion of liquids representatives of nuclear waste treatment process.

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## Abstract

Experimental results are reported on the airborne release, under fire conditions, of hazardous materials dissolved in mixture of organic solvents (tributylphosphate TBP and hydrogenated tetrapropylene HTP) representatives of the nuclear fuel recycling process. Cerium and ruthenium have been considered respectively as stable and volatile fission products and which could be eventually released as airborne particles during thermal degradation of contaminated and inflammable liquids. Airborne release fractions (ARF) and their experimental uncertainties have been determined. Considering fire involving contaminated organic solvents, higher ARF are reported for ruthenium Ru(+III) (0.99 +/- 1.20 %) in comparison with cerium (0.22 +/- 0.31 % and 0.20 +/- 0.28 % for Ce(+III) and Ce(+IV), respectively). This discrepancy is partially due to the volatility of ruthenium formed under these conditions. Considering configurations involving an aqueous nitric acid phase placed below contaminated solvents, boiling of this phase enhances the release of contaminant materials, 1.78 +/- 1.06 % and 1.01 +/- 1.31 % for Ce(+III) and Ce(+IV), respectively and 12.41 +/- 29.45 % for Ru(+III). Analysis of size distribution, morphology and chemical composition of released particles and droplets emitted during HTP/TBP bubble collapse are reported, highlighting the contribution of bubble bursting at the solvent surface to airborne release.

**Keywords:** aerosol released, PUREX, combustion, particle analysis, bubbles bursting.

## 1. Introduction

Nuclear fuel reprocessing is of prime importance to reduce volume of stored highly radioactive materials and to recycle valuable materials for further processing of mixed oxides. Among the different chemical elements composing nuclear used fuel, uranium and plutonium are critical and need to be purified by liquid-liquid extraction. Several methods have been developed to allow such extraction and among them, the Plutonium Uranium Reduction Extraction (PUREX) reprocessing technique is mainly used in the nuclear industry for specific extraction of Pu(+IV) and U(+VI) from nitric acid solutions <sup>1</sup>. Within this process, extraction is carried out using Tributylphosphate (TBP) in combination with diluents such as hydrogenated tetrapropylene (HTP) or kerosene. In France, the reprocessing plant at La Hague (UP2/UP3 reprocessing plants) has considered HTP diluent and reprocesses nearly 1 700 metric tonnes of heavy metal per year <sup>1</sup>. Due to high flammability of those organic solvents and past fire events reported in commercial nuclear industry <sup>2</sup>, special care regarding explosion and fire risks must be considered during safety analysis of nuclear fuel reprocessing facilities. Beyond the question of

53 direct consequences of fires on containment devices by soot emissions <sup>3,4</sup>, their transport in facility rooms and  
54 ventilation networks <sup>5,6</sup> and their direct contribution to clogging of high efficiency particulate air filters (HEPA)  
55 by emitted particles <sup>7-9</sup>, resuspension of radioactive material under aerosol form must be considered for estimating  
56 source terms potentially released <sup>10-14</sup>.

57 Prediction of consequences of fires within industrial facility handling hazardous materials is generally based on  
58 the airborne release fraction describing the ability of contaminants to be dispersed as airborne particles according  
59 to an external stress. For the specific hypothetic case of fire occurring during the PUREX process, the airborne  
60 release fraction ARF is defined as the ratio between the mass of hazardous material released in airborne phase  
61 ( $m_{\text{released}}$ ) and the mass of the same hazardous material initially dissolved within contaminated liquids ( $m_{\text{initial}}$ ):

$$62 \quad \text{ARF} = \frac{m_{\text{released}}}{m_{\text{initial}}} \quad (\text{Eq. 1})$$

63  
64  
65 For safety reasons, it is crucial to be able to predict the order of magnitude of ARF. Nevertheless, due to complexity  
66 of chemical processes induced by extraction in the PUREX process, but also during the pyrolysis of HTP/TBP  
67 solvents, current state of knowledge of the scientific community still remains limited from a phenomenological  
68 point of view.

69 Several studies have been conducted in the past regarding releases of radioactive materials from burning of  
70 HTP/TBP contaminated solutions. Table I presents a review of experimental conditions associated to previous  
71 works conducted both at an analytical scale, i.e. less than half a liter <sup>14-22</sup>) and at a larger scale, from several liters  
72 to pool fires with a surface lower than 1 m<sup>2</sup> <sup>15,16,19</sup> to nearly 200 L and pool surface reaching up to 5 m<sup>2</sup> <sup>16,19,20,23-25</sup>.  
73 Results obtained by Malet et al., (1983) <sup>19</sup> are also reported in Table I. Due to potential errors in the interpretation  
74 of data presented in this study (especially regarding the definition of “Transfer coefficient”), values reported in  
75 this study will not be considered in the rest of our analysis and discussion of literature.

76 Analysis of Table I highlights a significant variation, in terms of ARF, mainly due to different types and  
77 concentrations of contaminants (elements present in the nuclear fuel), but also to experimental protocols and  
78 scales.

79 Dealing with any potential scale effects, mean values of ARF could be computed by considering non-volatiles  
80 contaminants (and as a consequence by excluding values reported for Cs, Ru and I in Table I). Comparison of  
81 mean ARF values (associated to a confidence interval (CI) of 95% and presented hereafter by considering extended  
82 absolute standard deviation (k=2)) of 0.2 +/- 0.2 % <sup>14,16,18,26,27</sup> and 1.7 +/- 4.5 % <sup>16,24,25</sup> for small (< 0.4 m<sup>2</sup>) and  
83 large (> 0.4 m<sup>2</sup>) scale pool fires, respectively, do not highlight any statistical differences and, consequently, no  
84 influence of pool size on aerosol release fraction. Limit of 0.4 m<sup>2</sup> for characterizing small scale pool fires  
85 (corresponding to an effective pool diameter of 0.7 m) has been considered based on previous studies on scale  
86 effect on smoke yield <sup>28</sup> and mass loss rate <sup>29</sup>. One must notice that the reported order of magnitudes, for both  
87 small and large scales, are consistent with a conservative ARF value of 10 %, commonly recommended for this  
88 type of fire scenario <sup>10,30</sup>.

89 Considering the contaminants nature, obviously, their volatility has a significant effect on aerosol resuspension.  
90 In this context, the question of ruthenium volatility has been addressed by several authors <sup>15,16</sup> while the highest  
91 ARF was reported for gaseous iodine with a mean value of 77.2% +/- 18.2 % for a confidence interval of 95% <sup>23</sup>.  
92 Beyond the question of volatility, other non-volatile elements (Ce, Sr, Zr and U) are generally characterized by  
93 significantly smaller order of magnitude of ARF (from 0.002 % to 58.6 % with a mean value of 4.6% +/- 25.2%  
94 for a confidence interval of 95%) without any specific trend regarding the nature of elements. On the other hand,  
95 influence of several contaminant concentrations on ARF was investigated in the literature. While an increase of U  
96 concentration leads to an increase of ARF when using uranium nitrate (mainly associated to the contribution of  
97 nitrate to fuel mass loss rate and stronger boiling effect (Ballinger et al., 1988; Jordan & Lindner, 1984)), dispersion

98 and level of uncertainties associated to values reported in the literature do not allow to conclude on any direct  
99 effect of contaminant concentrations on ARF.

100 Beyond this wide range of variation of ARF reported in the literature, discussion on the relevance of the surrogate  
101 proposed to simulate the chemical and physical behaviour of plutonium complexes formed in the organic phase in  
102 terms of aerosol resuspension is limited. As far as we are concerned, no study was able to propose a justified  
103 surrogate of plutonium. In some cases, uranium was considered as a proxy of the plutonium to determine  
104 experimentally its ARF (Ballinger et al., 1988; Mishima & Schwendiman, 1973c; Nishio & Hashimoto, 1989).  
105 On the other hand, other authors have studied fission products under realistic fire conditions but discussion on the  
106 relevance of ARF reported for such elements is still missing. Thus, in the present study, both approaches will be  
107 considered. The first one will deal with cerium as a chemical surrogate of the plutonium complexes formed in the  
108 organic phase of the PUREX process. It is well known that plutonium(IV) forms a tetranitrate complex with the  
109 TBP in the form of  $(\text{Pu}(\text{NO}_3)_4(\text{TBP})_2)$ <sup>31</sup> and recent studies were devoted to propose a surrogate, in terms of  
110 extraction from an aqueous contaminated phase to a TBP/diluent organic phase of plutonium, to mainly perform  
111 experimental measurements of ARF<sup>31,32</sup> that could be used for predicting plutonium release. Despite the fact that  
112 cerium is a fission product encountered in the PUREX process, this element, in the form of  $\text{CeO}_2$ , is commonly  
113 considered as a surrogate of plutonium dioxide  $\text{PuO}_2$ <sup>33</sup> but also in complexed forms<sup>31</sup>. Dealing with the relevance  
114 of Ce(+IV) to mimic the behaviour of Pu(+IV) within the PUREX process, recent studies have highlighted some  
115 limitations in the use of cerium since additional hydrated complexes<sup>34</sup> could be formed in addition to tetranitrate-  
116 TBP complexes and that Ce(+IV) could be reduced to Ce(+III) form, when going from the organic to the aqueous  
117 phase<sup>32</sup>. Nevertheless, in this study and in the present state of the art, cerium was considered as a potential  
118 surrogate for plutonium since it is not possible to conduct ARF measurement for Pu due to its high radioactivity  
119 and specific handling installation requirements. Then, Cerium was mainly used to investigate release mechanisms  
120 and driving forces. On this subject, few studies were devoted to the phenomenological description of contaminant  
121 release during contaminated pool fire. Most experimental studies considered bubble bursting induced by pool  
122 boiling as the main driven mechanism in contaminant entrainment<sup>14,15</sup>. More recently, numerical modelling  
123 approach was introduced by Brown et al.<sup>35-37</sup>, confirming the significance of the boiling phenomena as one of the  
124 most influencing physical mechanism involved in aerosol release from contaminated pool fire. In such a situation,  
125 bubbles are expected to present a diameter close to 1-3 mm and their collapses are characterized by droplet  
126 emissions with diameter ranging from 1-100  $\mu\text{m}$  and 100-300  $\mu\text{m}$  for film breakup or jet regimes, respectively  
127<sup>36,38</sup>. Additional clues of the significance of bubble bursting on the overall airborne release were introduced by  
128 demonstrating the spherical shape of released uranium particles<sup>14</sup> within a size range of nearly 1-10  $\mu\text{m}$  in  
129 agreement with a droplet drying process. Nevertheless, and as far as we are concerned, limited number of studies  
130 attempted to specifically analyze the size and shape of released particles<sup>14,15</sup>, and concluded to the occurrence of  
131 optical and mass median aerodynamic diameters in the range 1-2  $\mu\text{m}$  and 1-10  $\mu\text{m}$ , respectively. Furthermore,  
132 both authors reported isolated and well separated particles, in terms of size, from soot particles emitted by the  
133 combustion of solvents. More recently, Hubbard et al.<sup>22</sup> reported the release of  $\sim 0.2 \mu\text{m}$  spherical lanthanide  
134 phosphate particles from 70% kerosene/30% TBP solutions highly contaminated (100 g/L) with hydrated  
135 lanthanide nitrates ( $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ).

136 To open the way to a phenomenological model of airborne release of particles from burning contaminated solvents,  
137 it is then crucial to characterize the shape and the size of emitted surrogate containing particles. Additional analysis  
138 of number and size of bubbles emitted at the surface of the burning liquid is also needed with special attention to  
139 the emission of droplets during bubble bursting.

140 The aim of the present study is to propose new experimental findings for linking the properties of released particles  
141 with those of bubbles and droplets suspected to be the main cause of contaminant resuspension in the aerosol  
142 phase. For this purpose, cerium(+IV) and ruthenium(+III) were both considered as contaminants. Despite  
143 previously mentioned limitations, cerium(+IV) will be used to mimic the behaviour of plutonium(+IV) in a  
144 complexed form. Ruthenium(+III) will be investigated to analyse the airborne release of an element known to  
145 produce volatile form ( $\text{RuO}_4$ ) during fire experiments<sup>16,39</sup>. In addition to cerium(+IV), and in order to investigate

146 the effect of chemical form of contaminant in the organic phase, cerium(+III) was also considered. ARF were then  
147 determined according to a qualified experimental protocol. Additional efforts were also devoted to investigate the  
148 nature, shape and size distribution of particles released from cerium and ruthenium contaminated solvents,  
149 respectively to support hypothesis both on bubbles bursting and volatile behaviour of ruthenium. In a last step,  
150 size of bubbles formed during the combustion of contaminated solvents was characterized prior to the analysis of  
151 number and size distribution of film and jet droplets emitted from bubbles generated at an air / liquid HTP-TBP  
152 interface under ambient non-flaming conditions.

153 Table I-part 1: analysis of airborne release fractions reported in the literature measured experimentally (white lines) or postulated (grey lines)

Fuel composition (in volume)	Contaminants	Combustion details	Pool size	Mean or range ARF (%) 95 % CI (number of test)	Comments	Reference
70% kerosene/30% TBP	Pu(NO <sub>3</sub> ) <sub>4</sub> 5.4 g/L + UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> 11.1 g/L + Th(NO <sub>3</sub> ) <sub>4</sub> 64 g/L + Fission products	100 L of organics air change 0.5–5 h <sup>-1</sup>	12.3 m <sup>2</sup>	0.12 +/- 0.06 (3)	Modelling approach, airborne release induced by airflow <sup>23</sup>	<sup>24</sup>
			24.5 m <sup>2</sup>	0.31 (3)		
70% HTP / 30% TBP	Dissolved contaminant	All range	All range	10	Recommendations from literature analysis	<sup>30, 40</sup>
70% normal paraffin hydrocarbon (NPH) / 30% TBP	Uranium 270 g U/L Cesium ~0.2 ppm Cerium ~0.2 ppm Zirconium ~0.2 ppm Iodine ~0.2 ppm	25 ml Forced ventilation	Small scale	U: 0.12 +/- 0.32 (3) Cs: 0.42 +/- 0.78 (4) Ce: 0.70 +/- 0.19 (4) Zr: 0.48 +/- 0.43 (3) I: 77.18 +/- 18.18 (6)	Study of air entrainment  Iodine: volatile fission product	<sup>23</sup>
70% normal paraffin hydrocarbon (NPH) / 30% TBP	Strontium ~0.2 g Sr/L	150 L	~2.5 m <sup>2</sup>	0.21 +/- 0.04 (2)		<sup>25</sup>
Kerosene + contaminated 5 M HNO <sub>3</sub>	Pu(NO <sub>3</sub> ) <sub>4</sub> in 5M HNO <sub>3</sub> , 160 g Pu / Kg solution)	< 100 ml kerosene	Small scale	0.026 (1)	No TBP, contamination only in HNO <sub>3</sub> .	<sup>21</sup>
70% kerosene/30% TBP	Cerium or Thorium at 0.55 g/L in organics (no mention of oxidation state of elements)	20-157 ml Free atmosphere	78 cm <sup>2</sup>	TC: 33.57 +/- 27.95 (7) FRF 0.015 (4)	No influence of pool size on ARF TC: transfer coefficient FRF: fraction reaching filter	<sup>19</sup> <i>Not considered in the present analysis</i>
	Cerium in organics (no mention of oxidation state of elements)	20 -250 L Free atmosphere	0.4 - 5 m <sup>2</sup>	TC: 58.60 +/- 60.97 (5) FRF: 0.017 (3)		
70% kerosene/30% TBP	Uranium nitrate, 1 g U /L to 84 g U/L	50 ml of organics	33 cm <sup>2</sup>	Mean: 1.17 +/- 0.80 (5) Range: 0.7 – 1.6	ARF increases with increasing [U].	<sup>20</sup>

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156 Table I-part 2: analysis of airborne release fractions reported in the literature measured experimentally (white lines) or postulated (grey lines)

Fuel composition (in volume)	Contaminants	Combustion details	Pool size	Mean or range ARF (%) 95 % CI (number of test)	Comments	Reference
70% normal paraffin hydrocarbon (NPH) / 30% TBP	Uranium nitrate, 1 g U /L to 84 g U/L	50 ml of organics	33 cm <sup>2</sup>	Mean: 1.86 +/- 1.11 (10) Range: 0.9 – 2.6	Sphere like U particles, 1-2 μm optical diameter, not connected to soot particles.  ARF increases in presence of HNO <sub>3</sub> .	14
70% normal paraffin hydrocarbon (NPH) / 30% TBP + 3M HNO <sub>3</sub> : ratio 3:1				Mean: 5.75 +/- 4.63 (6) Range: 3.5 – 9.3 (6)		
70% normal paraffin hydrocarbon (NPH) / 30% TBP + 3M HNO <sub>3</sub> : ratio 1:1				Mean: 6.25 +/- 7.56 (4) Range: 1.8 – 10.3		
70% normal paraffin hydrocarbon (NPH) / 30% TBP + 3M HNO <sub>3</sub> : ratio 1:1	Depleted uranium 101.2 g U/L in organics	100 ml of organics Free atmosphere	Small scale	0.47 +/- 0.16 (3)	Presence of fission products limit uranium migration to the acid from the organic phase	18
	Depleted uranium, 101.2 g U /L in organics / fission product in acid			2.61 +/- 0.26 (2)		
	Pure organics, depleted uranium 188 g U/L in acid			6.53 +/- 1.57 (2)		
70% normal paraffin hydrocarbon (NPH) / 30% TBP + 3M HNO <sub>3</sub> : ratio 1:2	Pure organics, depleted uranium 188 g U/L in acid + fission products	50 ml of organics Free atmosphere	Small scale	0.81 (1)		
70% normal paraffin hydrocarbon (NPH) / 30% TBP + 3M HNO <sub>3</sub> : ratio 1:3	Depleted uranium, 101.2 g U/L in organics / 188 g U/L in acid + fission products	50 ml of organics Free atmosphere		1.56 (1)		
	Pure organics, depleted uranium 188 g U/L in acid + fission products			0.17 (1)		

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158 Table I-part 3: analysis of airborne release fractions reported in the literature measured experimentally (white lines) or postulated (grey lines)

Fuel composition (in volume)	Contaminants	Combustion details	Pool size	Mean or range ARF (%) 95 % CI (number of test)	Comments	Reference
70% n-dodecane/30% TBP + water, ratio 1:1	Cerium 8 – 10 g Ce/L Cesium 39 – 64 g Cs/L Ruthenium 2 – 17 g Ru/L Strontium 45 – 118 g Sr/L		0.08 – 0.7 m <sup>2</sup>	Ce: 0.17 +/- 0.49 (15) Cs: 10.31 +/- 19.59 (15) Ru: 8.77 +/- 18.05 (18) Sr: 0.26 +/- 0.46 (10)	No influence of pool size on ARF excepted for Sr	16
70% n-dodecane/30% TBP + water with or without HNO <sub>3</sub>	Cerium, Cesium Ruthenium Strontium UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> (0.06 – 6 g U/L)	150 ml Air change 30 h <sup>-1</sup>	14 cm <sup>2</sup>	Cs: 12.54 +/- 16.65 (4) Ru: 7.62 +/- 27.66 (6) Sr: 2.73 +/- 5.87 (4) U: 0.031 +/- 0.046 (8) U w.out HNO <sub>3</sub> : 3.1E <sup>-3</sup> +/- 2.5E <sup>-3</sup> (7)	Ru volatility: RuO <sub>2</sub> (s) + O <sub>2</sub> (g) => RuO <sub>4</sub> (g) RuO <sub>4</sub> (g) + solvent vapor => RuO <sub>2</sub>	
70% HTP / 30 % TBP	~0.5–1 g Ru /L in organics	150 ml of organics Free atmosphere	Small scale	0.67 +/- 0.43 (4)	Slight decrease of ARF with increasing [Ru] No influence of pool size on ARF	15
	2–3.3 g Ru /L in organics	3 – 5 L of organics	0.16 m <sup>2</sup>	0.51 +/- 0.63 (4)		
	1.7 g Ru/L in organics	6 L of solvent	0.16 m <sup>2</sup>	0.31 (1)		
		Free atmosphere	0.63 m <sup>2</sup>	0.49 (1)		
70% HTP / 30 % TBP HNO <sub>3</sub> at 3M, ratio 1:1	3.3 g Ru /L in organics - pure acid	3 L of organics	0.16 m <sup>2</sup>	0.42 +/- 0.30 (2)	No influence of acid	
	~1 g Ru/L organics - ~3 g Ru/L acid	Free atmosphere		0.49 +/- 0.26 (2)		
70% Kerosene / 30 % TBP	100 g/L Lu(NO <sub>3</sub> ) <sub>3</sub> •6H <sub>2</sub> O 100 g/L Yb(NO <sub>3</sub> ) <sub>3</sub> •6H <sub>2</sub> O 100 g/L <sup>238</sup> U(NO <sub>3</sub> ) <sub>2</sub> •6H <sub>2</sub> O	25 ml of organics 42.5 m <sup>3</sup> /h of airflow in test chamber	Small scale	0.002 +/- 0.003 (3) 0.016 +/- 0.055 (3) 0.102 +/- 0.152 (3)	200 nm spherical Lu/Yb/U phosphates particles. Lu, Yb nitrates precipitation suspected.	22

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160 **II. Experimental procedure**

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162 **II.A. Contaminated materials**

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164 Experiments were conducted by burning previously contaminated 30% tributylphosphate TBP ( $C_{12}H_{27}O_4P$ ,  
165 reference A16084 from Alfa Aesar) diluted in 70% hydrogenated tetrapropylene HTP (Novasep Sas, France).  
166 Organics solutions were prepared by extraction from nitric acid aqueous solution ( $HNO_3$  at 65%, reference 20429  
167 from VWR) containing known concentration of element of interest as a dissolved phase. Concentration of aqueous  
168 phase is imposed according to dissolution of known mass of salts containing cerium (for Ce(+IV): Cerium(+IV)  
169 Ammonium Nitrate  $(NH_4)_2Ce(NO_3)_6$  or CAN, reference 39215.14 from Alfa-Aesar; for Ce(+III): Cerium nitrate  
170 hexahydrate  $Ce(NO_3)_3 \cdot 6(H_2O)$ , reference 218695000 from Acros Organics, for Ce(+III)) and ruthenium  
171 (Ruthenium nitrosyl nitrate  $RuNO(NO_3)_3$  known for its good extractability within the conditions of the PUREX  
172 process, reference 12175 from Alfa Aesar, for Ru(+III)). As previously mentioned, Ce(+IV) was considered as a  
173 potential surrogate of Pu(+IV). However, as reported by a previous study<sup>32</sup>, the reduction of Ce(+IV) into Ce(+III)  
174 and backextraction from the organic to the aqueous phase of cerium occurs during combustion. This point has  
175 been demonstrated as one the main limitation for the use of Ce(+IV) to mimic the complex behaviour of Pu(+IV)  
176 during the solvent combustion and to go further, Ce(+III) was also considered as a contaminant. Final  
177 concentrations of these specific elements (Ce or Ru) are then computed according to the composition and purity  
178 of these salts. Pure organic and contaminated aqueous phases are put in contact by mixing them in a borosilicate  
179 glass settling tank of 1 liter during 5 min when considering cerium solutions and 60 min for ruthenium which is  
180 longer due to its lower extractability at ambient temperature (close to 14% from<sup>41,42</sup>) compared to cerium (higher  
181 than 95% from<sup>32</sup>). Due to its low extractability and its cost, ruthenium concentration of contaminated solvents  
182 was voluntarily fixed at 0.6 Ru g/L (in agreement with the concentration considered in<sup>15</sup>). Contaminated organic  
183 and aqueous phases were finally separated by gravity. For all conditions, concentrations of Ce and Ru elements  
184 have been determined for organic phases by ICP-MS (Inductively Coupled Plasma Mass Spectrometry) analysis  
185 and corresponding values have been considered for each test used as reference for computing airborne release  
186 fraction. Table II presents experimental conditions for cerium and ruthenium contaminants.

187 Table II: Experimental conditions of different concentrations of cerium(+IV or +III) and ruthenium(+III) in  
188 HTP/TBP or HTP/TBP/ $HNO_3$  mixtures (absolute extended uncertainty for  $[C_{org}]$  at a CI of 95 %)

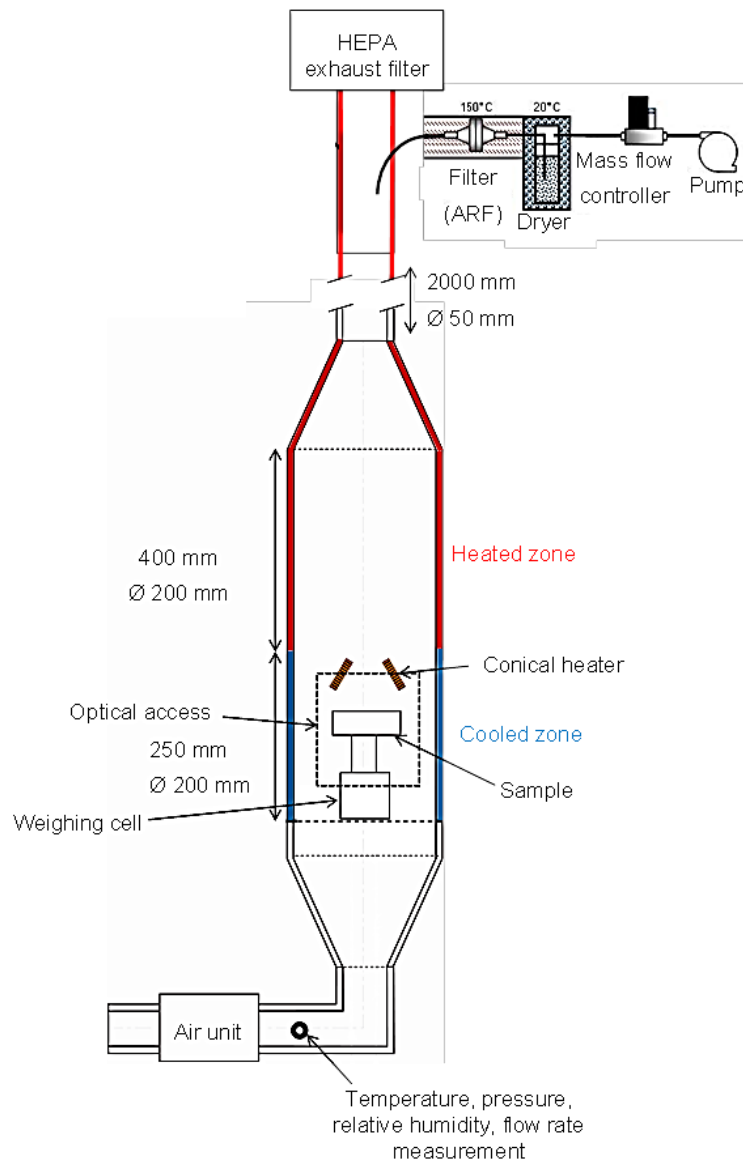
Fuel composition (in volume)	Element	Salt	Number of tests	$[C_{org}]$ (g/L)	$V_{org}$ (ml)	$V_{aq}$ (ml)
Contaminated 70% HTP / 30% TBP	Ce(+III)	Cerium(III) nitrate hexahydrate $Ce(NO_3)_3 \cdot 6(H_2O)$	3	0.2 +/- 0.01	30	-
			3	4.8 +/- 0.05		
			4	9.3 +/- 0.01		
Contaminated 70% HTP / 30% TBP + Pure $HNO_3$ 3M, Ratio 1:1			3	0.4 +/- 0.01	15	15
			2	8.6 +/- 0.03		
Contaminated 70% HTP / 30% TBP	Ce(+IV)	Cerium(IV) Ammonium Nitrate $(NH_4)_2Ce(NO_3)_6$	10	10 +/- 0.01	30	-
Contaminated 70% HTP / 30% TBP + Pure $HNO_3$ 3M, Ratio 1:1			10	10 +/- 0.01		
Contaminated 70% HTP / 30% TBP	Ru(+III)	Ruthenium(III) Nitrosylnitrate $RuNO(NO_3)_3$	3	0.6 +/- 0.1	30	-
Contaminated 70% HTP / 30% TBP + Pure $HNO_3$ 3M, Ratio 1:1			3	0.6 +/- 0.1		

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## II.B. Combustion test bench

Thermal degradation and ARF measurements were carried out on a specifically designed experimental test bench<sup>12</sup>. Figure 1 summarizes the main schematic route of the thermal degradation and sampling devices. A ventilation fan coupled to a calibrated diaphragm allows for the injection of air at a fixed flow-rate (40 m<sup>3</sup>/h for the present study) inside the degradation chamber including a radiant conical heater (not used in the present study). Particles are then extracted from this chamber inside an exhaust duct heated at 150°C before being sampled under well-mixed conditions 2 meters downstream from the inlet. Finally, particles are trapped on HEPA filter (pleated glass fiber filter reference 1505.40.00 from CAMFIL<sup>®</sup>) before releasing exhaust gases in the atmosphere. As reported in bibliographical analysis presented in the introduction of the present article, most of experimental test benches previously used were not optimized to reduce particle losses by walls or ducts deposition. In most cases, a lack of knowledge on particle transfer function within the test bench may partially explain disparities in terms of ARF values reported between different studies even for a given fuel or similar experimental conditions. As a consequence, and to avoid such disparities, our test bench was optimized for reducing particles losses in the combustion chamber and the exhaust duct. In addition, transport efficiency measurements and computational fluid dynamics calculations (CFD) were carried out for a range of aerodynamic diameters in agreement with those associated to released particles (more details could be retrieved in<sup>12</sup>).



208  
209  
210

Figure 1: Diagram of the combustion test bench

211 A small part (reported as  $P_{p(\%)}$  in this study and defined as the ratio between volumetric sampling flow rate and  
212 exhaust flow rate) of the overall exhaust flow was sampled on HEPA membrane (Cellulose acetate, SARTORIS  
213 11106-47-N, 47 mm diameter with 0.45  $\mu\text{m}$  pore diameter) with an isokinetic probe. The mass of cerium or  
214 ruthenium composing released particles sampled on membranes were then determined by ICP-MS/AES  
215 (Inductively Coupled Plasma Mass Spectrometry/Atomic Emission Spectroscopy) or X-Ray Fluorescence  
216 analyses, respectively.

217 Taking into account transport efficiency of particles in the combustion test bench and experimental sampling  
218 conditions, the definition of the airborne release fraction is:

$$219 \quad \text{ARF} = \frac{m_{\text{element}}^{\text{sampling}}}{m_{\text{element}}^{\text{initial}} \cdot P_{p(\%)} \cdot F_{p(\%)}} \quad (\text{Eq. 2})$$

220  
221 with:

- 222 •  $m_{\text{element}}^{\text{sampling}}$  the mass of released element (Ce or Ru) determined on sampling the membrane,
- 223 •  $m_{\text{element}}^{\text{initial}}$  the mass of element (Ce or Ru) initially diluted in the HTP/TBP solution,
- 224 •  $P_{p(\%)}$  the ratio between volumetric sampling flow rate and exhaust flow rate,
- 225 •  $F_{p(\%)}$  the penetration fraction of particles within the facility and depending on the aerodynamic diameter  
226 of released particles.

227  
228 For each element (Ce or Ru), it is then crucial, to compute the ARF, to determine the released aerosol size  
229 distribution and its corresponding penetration factor within the test bench from the emission point to the sampling  
230 point. As previously demonstrated <sup>12</sup>, particle losses in this test bench could be considered negligible for  
231 aerodynamic diameter lower than 5  $\mu\text{m}$ . In the present study, we will demonstrate that released particles are within  
232 this lower size range and we will assume, for easing ARF computation, the penetration factor  $F_{p(\%)}$  as equal to 1  
233 (or 100%).

### 234 **II.C. Experimental protocol and analysis of samples**

237 Contaminated solutions are prepared a few minutes before combustion experiments since stability of  
238 cerium or ruthenium within solvents could not be maintained for all conditions <sup>32</sup>. A small amount of solvent is  
239 then analysed by ICP-MS after the extraction protocol giving the initial concentration of the organic phase in terms  
240 of contaminant. This concentration is of main importance since it gives the initial mass contaminant mass in the  
241 liquid phase  $m_{\text{initial}}$  needed for computing ARF according to eq. 2.

242 Contaminated solvents are then placed in a cylindrical borosilicate glass container with an internal  
243 diameter of 48 mm and a volume of 50 mL. 30 mL of contaminated HTP/TBP and 15 mL of contaminated  
244 HTP/TBP + 15 mL  $\text{HNO}_3$  3M are respectively considered for mono and biphasic experiments. Borosilicate glass  
245 container is placed in the combustion chamber and ignited with a blowtorch during a short period (5 seconds) in  
246 order to avoid Ce(+IV) reduction to Ce(+III) as previously reported <sup>32</sup>. After ignition, extraction air flowrate (40  
247  $\text{m}^3/\text{h}$ ) is applied in the combustion chamber and emitted particles (soot and released cerium or ruthenium  
248 containing particles) are sampled on cellulose acetate membranes.

249 Special care was considered in quantification methods useful for measuring the mass of contaminant  
250 released during experiments. For this purpose, two different approaches were considered; ICP-MS for cerium-  
251 based particles and X-Ray Fluorescence for ruthenium-based particles.

252 Dealing with ICP-MS, key issue remains in digestion step and a specific calibration protocol was applied  
253 in terms of yield in agreement with protocol previously validated by our team <sup>12</sup>. For cerium samples, acid digestion  
254 has been considered for completing in an efficient way the dissolution of filters and sampled particles within a  
255 liquid medium suitable for ICP-MS analysis. For calibrating the overall ICP-MS procedure, reference filters

256 containing a known amount of cerium oxide powder (5  $\mu\text{m}$   $\text{CeO}_2$  powder, REacton®, 99.9% reference 215-150-4  
 257 from Alfa Aesar) were prepared and analysed. For this purpose, cerium oxide powder was aerosolized using a  
 258 vortex shaker unit and the deposited mass was determined by weighing the membrane before and after powder  
 259 dispersion. The digestion yield of ICP-MS analysis, mainly associated to the process of dissolution or digestion of  
 260 sample from solid to liquid phase, was then determined by comparing the mass of considered element obtained by  
 261 ICP-MS with the mass deposited on the reference membrane. More details on the determination of the digestion  
 262 yield are available in supplementary materials (SI-I). According to this protocol, the mass of particles composed  
 263 by the element Ce and sampled on membranes during experiments is defined by:

264

$$265 \quad m_{\text{Ce}}^{\text{sample}} = \frac{m_{\text{Ce}}^{\text{ICP-MS}}}{Y_{\text{detection ICP-MS}}^{\text{chemical form of Ce}} \cdot Y_{\text{digestion}}^{\text{chemical form of Ce}}}, \quad (\text{Eq. 3})$$

266 with:

- 267 •  $m_{\text{Ce}}^{\text{sample}}$  : mass of element Ce sampled on membrane (kg),
- 268 •  $m_{\text{Ce}}^{\text{ICP-MS}}$  : mass of element Ce quantified by ICP-MS analysis (kg),
- 269 •  $Y_{\text{detection ICP-MS}}^{\text{chemical form of Ce}}$  : ICP-MS's yield of detection of element Ce,
- 270 •  $Y_{\text{digestion}}^{\text{chemical form of Ce}}$  : yield of digestion of element Ce in its chemical form as sampled on membrane, as  
 271 determined according to the calibration protocol using reference membranes.

272 Similar qualification protocol was applied to ruthenium samples, using  $\text{RuO}_2$  powder (micron size  $\text{RuO}_2$   
 273 powder, 99.9% reference A10816 from VWR). Nevertheless, we were not able to identify digestion protocol able  
 274 to fully dissolve our reference samples and relevant for further ICP analysis. Direct analysis method by X-Ray  
 275 fluorescence was then preferred to ICP-MS and was calibrated according to the same reference membranes. For  
 276 this purpose, X-ray source (88 kV with a tungsten anode) and CdTe spectrometer (X-123 CdTe X-Ray  
 277 spectrometer from Amptek) were mounted on an exposure cell devoted to the analysis of membrane samples. More  
 278 details on this calibration are available in supplementary materials (SI-II). For this second analysis method, the  
 279 mass of ruthenium associated to our samples are computed according to:

$$280 \quad m_{\text{Ru}}^{\text{sample}} = a \cdot m_{\text{Ru}}^{\text{XRF}} + b, \quad (\text{Eq. 4})$$

281 with:

- 282 •  $m_{\text{Ru}}^{\text{sample}}$  : mass of element Ru sampled on membrane (kg),
- 283 •  $m_{\text{Ru}}^{\text{XRF}}$  : intensity associated to the integral of the Ru peak recorded by XRF (count per second),
- 284 • a, b: calibration factors of XRF spectrometer (see SI-II).

285 In parallel to ARF determination, Scanning Electronic Analysis of membranes was also performed for  
 286 determining elemental composition, morphology and size distribution of cerium and ruthenium released particles.  
 287 Imaging was conducted using a JEOL Scanning Electron Microscope (SEM) JSM 6010-LV and a ZEISS SEM-  
 288 FEG GEMINI associated to Energy-dispersive X-ray spectroscopy (EDS) for elemental composition analysis.  
 289 Projected area equivalent diameters of the considered particles were then determined directly on SEM  
 290 micrographs.

291

### 292 **III. Experimental results**

293

#### 294 **III.A. Physico-chemical properties of released particles**

295

296 Analysis of 60 to 2000 particles was conducted for both contaminant (Ce or Ru). SEM illustrations of  
 297 particles emitted from Ce(+III), Ce(+IV) and Ru(+III) contaminated solvents are presented in Table III. Circularity  
 298 (defined as  $4\pi \text{Area}/\text{Perimeter}^2$ ) of the particles was measured on each SEM image using the ImageJ software and  
 299 orders of magnitude of this shape descriptor are presented in Table III. Size distribution properties and elemental

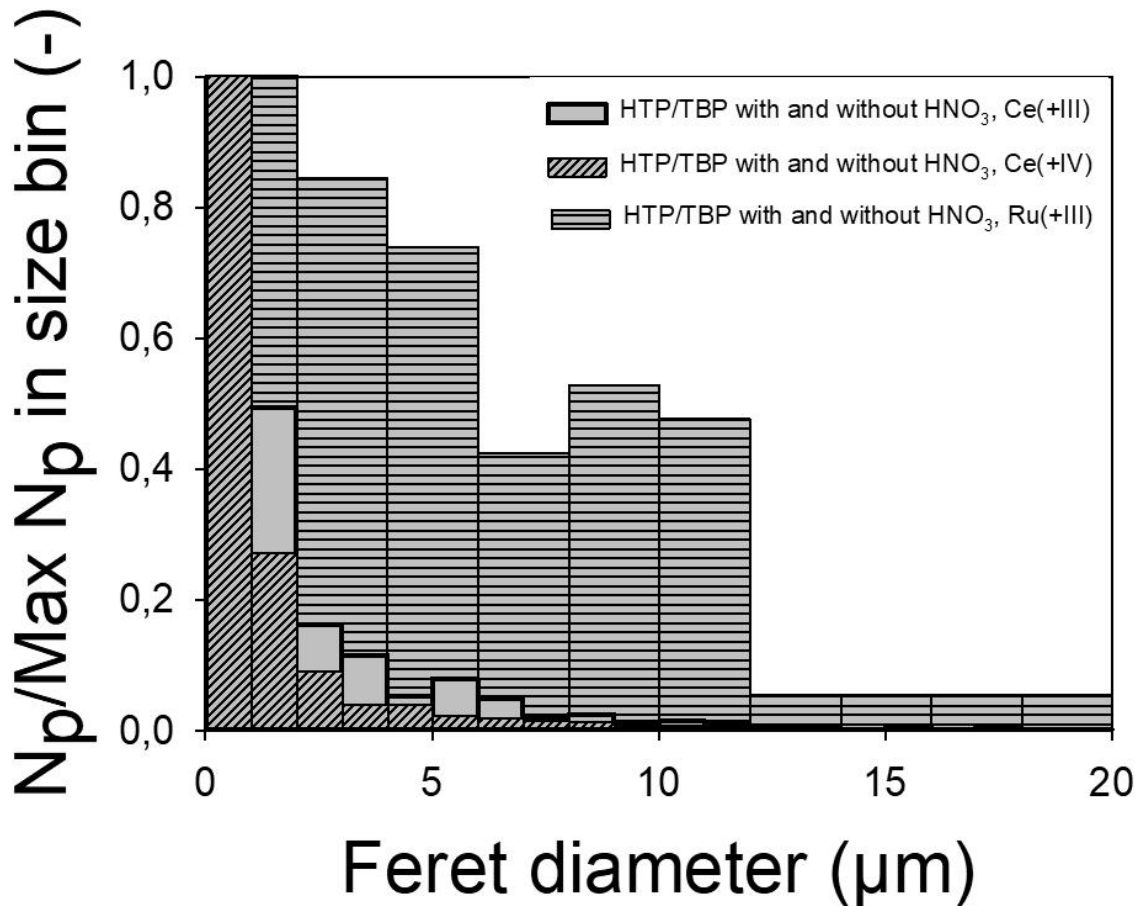
300 composition (performed by EDS analysis) are also presented in Table IV. Since a minimum number of particles is  
301 required for both size and shape statistical analysis, respectively 550 and 100 particles<sup>43</sup>, SEM pictures of particles  
302 emitted from organics and organics/nitric solutions were merged and considered in the same data set for each  
303 contaminant. One must notice that size analysis was limited to particle diameter larger than 0.2  $\mu\text{m}$  considering  
304 the SEM's resolution and corresponding Feret diameters (defined as the longest distance reported between any  
305 two pixels composing the particle). These data are then reported in Table III.

306 Figure 2 exhibits the size distribution in terms of Feret diameter of particles emitted for Ce(+III), Ce(+IV)  
307 and Ru(+III). Regarding particles shape, Table III presents illustrations of SEM images recorded for each  
308 contaminant and fuel composition (with and without  $\text{HNO}_3$ ). Since sampled particles could be characterized by a  
309 wide range of elongated or complex morphology, we introduced a circularity threshold to quantify contribution of  
310 "quasi perfect shape" spherical particles to other type of particles. For this purpose, a circularity criteria was fixed  
311 at a threshold of 0.995 and corresponding fraction of particles presenting a circularity higher than this threshold  
312 was computed. This threshold was determined according to a statistical analysis of 365 images of nearly perfect  
313 spherical reference polystyrene latex and glass particles (geometric diameter ranging from 2.5 to 10  $\mu\text{m}$ ).

314 Dealing with ruthenium, particles emitted and released during the combustion of HTP/TBP solutions  
315 contaminated by ruthenium nitrosyl nitrate are characterized by a wide range of particle morphology, composition  
316 and size distribution. Regarding particle shape, less than 10 % of particles fulfilled the 0.995 criteria for particle  
317 circularity, highlighting complex and variable particle shapes as it could be noticed on SEM images reported in  
318 table III. For this contaminant, particles present bimodal size distribution for both mono and biphasic conditions.  
319 Two peaks Gaussian fitting was applied to the size distribution obtained by merging mono and biphasic conditions,  
320 and modal Feret diameters of 1  $\mu\text{m}$  and 10  $\mu\text{m}$  were reported. Notice that this complex size distribution supports  
321 the hypothesis that airborne resuspension is due, for ruthenium, to two distinct mechanisms, bubble bursting and  
322 volatility, potentially occurring at the same time and with a prevalence of volatility.

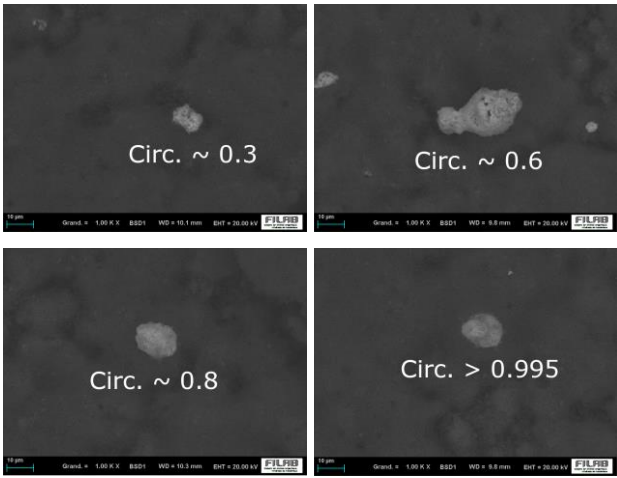
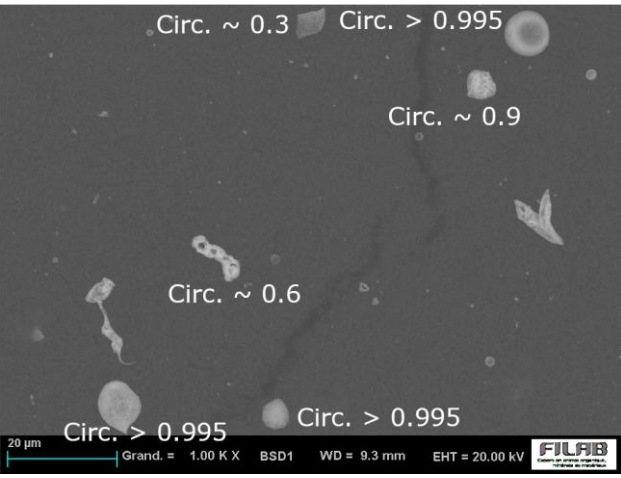
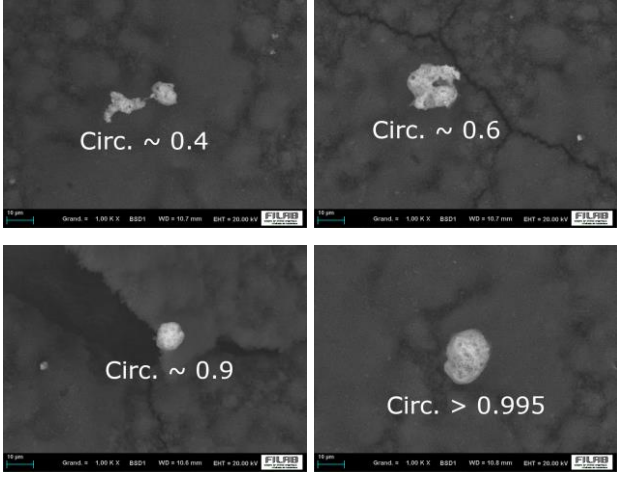
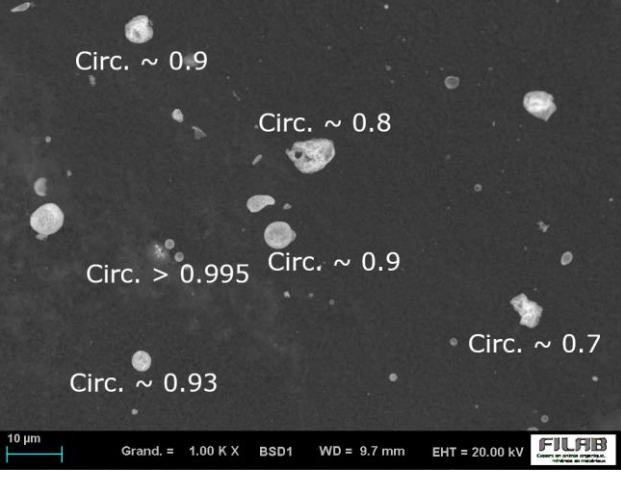
323 Concerning elemental composition of ruthenium particles, most of them are composed of pure ruthenium  
324 (57-71 % of all analysed particles). Nevertheless, a significant contribution of phosphorous and phosphorous-  
325 oxygen containing particles are also observed (11-13% and 17-32 %, respectively). As previously reported<sup>39</sup>,  
326 extracted ruthenium is present in the form of two main complexes in the organic phase ( $(\text{TBP})_3\text{RuNO}(\text{NO}_3)_3(\text{H}_2\text{O})_2$   
327 and  $(\text{TBP})_2\text{RuNO}(\text{NO}_3)_3(\text{H}_2\text{O})_2$  with a predominance of the tris-TBP complex for  $[\text{HNO}_3]$  concentration at 3 M).  
328 Lefebvre et al.<sup>44</sup> also reported that nitrosyl form of ruthenium complexes was maintained in the organic phase  
329 without TBP in the first coordination sphere of Ru, potentially linked through a water molecule. Furthermore,  
330 thermal degradation of ruthenium nitrosyl is also known as a route to produce  $\text{RuO}_2$  particles<sup>45</sup> under oxidative  
331 conditions. In the present study, evidence of metallic form of ruthenium, as the major form of released particles,  
332 supports the idea introduced by Bouilloux<sup>15</sup>, that reductive conditions are representative of those encountered  
333 within studied TBP/HTP flames. Under such non-oxidative conditions, Duvigneaud & Reinhard-Derie<sup>46</sup> reported  
334 emission of Ru(metal) and  $\text{RuO}_2$  from the thermal decomposition of Ru(+III) hydrate. This abundance release of  
335 Ru in metal form from the thermal degradation of Ru(+III) is in agreement with the presence of pure Ru particles  
336 released under our present experimental conditions. Nevertheless, and as reported by Duvigneaud & Reinhard-  
337 Derie<sup>46</sup>, Ru(metal) is not expected to be the predominant chemical form of emitted ruthenium under non-oxidative  
338 conditions. As mentioned by those authors<sup>46</sup>,  $\text{RuO}_2$  should be the most predominant ruthenium form, in strong  
339 dis-agreement with the absence, under the present experimental conditions, of released particles solely made of  
340 Ru and O in Table IV. To explain this discrepancy, one must keep in mind that in the present study, significant  
341 quantities of organophosphates and phosphoric acid are available in liquid<sup>47</sup> or gas phases<sup>3,26</sup>. Such abundance of  
342 phosphorus in organic or acid forms react<sup>48</sup> or be strongly adsorbed<sup>49</sup> with  $\text{RuO}_2$  to generate ruthenium  
343 organophosphates (Ru, P, O) that could further be reduced to Ru, P. In addition to this major contribution of  
344 ruthenium reactivity to the overall airborne release, bubble bursting release could be another mechanism for  
345 explaining the significant contribution of ruthenium organophosphates in the aerosol phase, as reported hereafter  
346 for the cerium contaminant. Nevertheless, further analysis are needed (as an example particle analysis by Raman  
347 spectroscopy) to confirm the chemical nature of particles made of Ru, P and O.

348 Considering cerium contaminated solvents, contribution of quasi perfect spherical particles (circularity  
 349 higher than 0.995) reaches 40 % and 58 % for Ce(+III) and Ce(+IV), respectively. This huge contribution of  
 350 spherical particles supports the assumption of airborne release mainly driven by bubble bursting and rapid droplet  
 351 drying in the flame <sup>38,50,51</sup> leading to the formation of dry particles containing the contaminant element, in close  
 352 agreement with recent findings <sup>22</sup>. Size distributions reported in Figure 2 show major distribution of particles with  
 353 a Feret diameter lower than 5  $\mu\text{m}$  with a count median diameter (determined by log-normal fitting on the size  
 354 distribution obtained by merging Ce(+III) and Ce(+IV)) of 0.8  $\mu\text{m}$  and a geometric standard deviation of 2.9.  
 355 These results are in good agreement with the “sphere like” shape particles with an optical diameter of nearly 1-2  
 356  $\mu\text{m}$  previously reported for uranium contaminated kerosene-TBP solutions <sup>14</sup> and more recently for lanthanides  
 357 nitrates (Lu, Yb and depleted uranium <sup>22</sup>). Under all our experimental conditions, released particles are composed  
 358 of cerium, phosphorus and oxygen. Due to the presence of soot in analysed samples, mainly composed of carbon,  
 359 phosphorus and oxygen <sup>3</sup>, we were not able to conduct a stoichiometric analysis of the elemental composition of  
 360 cerium based particles. Nevertheless, the homogeneous composition of cerium-based released particles supports  
 361 the assumption that they are mainly in the form of the most thermally stable cerium phosphate  $\text{CePO}_4$  <sup>52,53</sup> in  
 362 agreement with lutetium and ytterbium phosphates reported by Hubbard et al. <sup>22</sup>, highlighting a potential reduction  
 363 of Ce(+IV) into Ce(+III) during their airborne release.



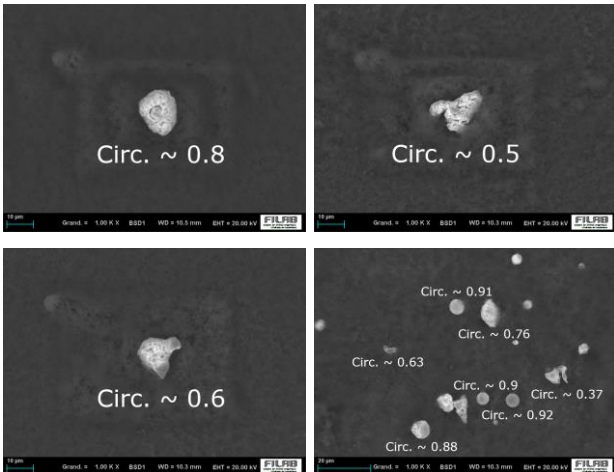

364 Figure 2: size distributions of particles released during combustion of contaminated organics with and without  
 365 HNO<sub>3</sub> at 3M  
 366  
 367

368 Table III - part 1: Scanning Electronic Microscopy images of released particles from cerium contaminated solutions

Fuel composition → Contaminant ↓	Contaminated organics 70% HTP / 30% TBP	Contaminated organics 70% HTP / 30% TBP Pure HNO <sub>3</sub> 3M, Ratio 1:1
Ce(+III) 10 g Ce/L		
Ce(+IV) 10 g Ce/L		

369

370 Table III - part 2: Scanning Electronic Microscopy images of released particles from ruthenium contaminated solutions

Fuel composition → Contaminant ↓	Contaminated organics 70% HTP / 30% TBP	Contaminated organics 70% HTP / 30% TBP Pure HNO <sub>3</sub> 3M, Ratio 1:1
Ru(+III) 0.6 g Ru/L		

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382 Table IV: elemental composition and size properties of released particles

Fuel composition (in volume)	Contaminant	Number of particles	Composition by EDS analysis	Min-Max projected diameters ( $\mu\text{m}$ )	Overall size distribution
Contaminated 70% HTP / 30% TBP	Ce(+III) at 10 g Ce/L	59	100% with Ce, O, P	-	CMD = 0.8 $\mu\text{m}$ $\sigma_g = 2.9$
Contaminated 70% HTP / 30% TBP + Pure HNO <sub>3</sub> 3M, Ratio 1:1	Ce(+III) at 10 g Ce/L	1109		1 – 6 $\mu\text{m}$	
Contaminated 70% HTP / 30% TBP	Ce(+IV) at 10 g Ce/L	114		3 – 4 $\mu\text{m}$	
Contaminated 70% HTP / 30% TBP + Pure HNO <sub>3</sub> 3M, Ratio 1:1	Ce(+IV) at 10 g Ce/L	2191		1 – 5 $\mu\text{m}$	
Contaminated 70% HTP / 30% TBP	Ru(+III) at 0.6 g Ru/L	237	71% pure Ru 17% Ru, O, P 13% Ru, P	1 – 23 $\mu\text{m}$ 1 – 12 $\mu\text{m}$ 7 – 17 $\mu\text{m}$	Two peaks Gaussian fit  Mode 1: 1.0 $\mu\text{m}$ Mode 2: 10 $\mu\text{m}$
Contaminated 70% HTP / 30% TBP + Pure HNO <sub>3</sub> 3M, Ratio 1:1	Ru(+III) at 0.6 g Ru/L	92	57% pure Ru 32% Ru, O, P 11% Ru, P	1 – 14 $\mu\text{m}$ 1 – 36 $\mu\text{m}$ 3 – 28 $\mu\text{m}$	

383

### III.B. Airborne release fractions

A set of 9 different experimental conditions were considered with at least 2 repetitions each. Corresponding values are reported in Tables SI-I to SI-III in Supplementary Information with corresponding experimental uncertainties. Mean values associated to each experimental condition are summarized in Table V including absolute uncertainties (within 95% confidence interval) computed by taking into account the absolute experimental uncertainties (see SI-3 for more detail) of each ARF and the standard deviation determined from the entire set of ARF reported for this condition.

Considering solutions contaminated with cerium at nearly 10 g/L (bold values in Table V), ARF mean values appear to be similar despite the oxidation state of cerium. Mean values of 0.22 % +/- 0.31 % and 0.20 % +/- 0.28 % are then reported for monophasic Ce(+III) and Ce(+IV) contaminated organic solutions, respectively. These results are in agreement, within the confidence interval, with values previously reported<sup>16,23</sup> for small scale experiments. Contribution of non-contaminated aqueous phase to ARF also appears significant with values 5 to 8 times higher for biphasic experimental conditions (1.78 % +/- 1.06 % and 1.01 % +/- 1.31 % for Ce(+III) and Ce(+IV), respectively). This promoting influence of aqueous phase confirms that resuspension is mainly driven by pool boiling and bubbles bursting as previously mentioned in the literature<sup>15,36</sup> and discussed in the present study. Beyond the contribution of aqueous phase to ARF, experiments were also conducted for Ce(+III) at several contamination levels (from 0.2 to 9.3 g/L of Ce(+III)). Nevertheless, extended uncertainties do not allow us to clearly identify a significant trend of ARF as a function of Ce concentration.

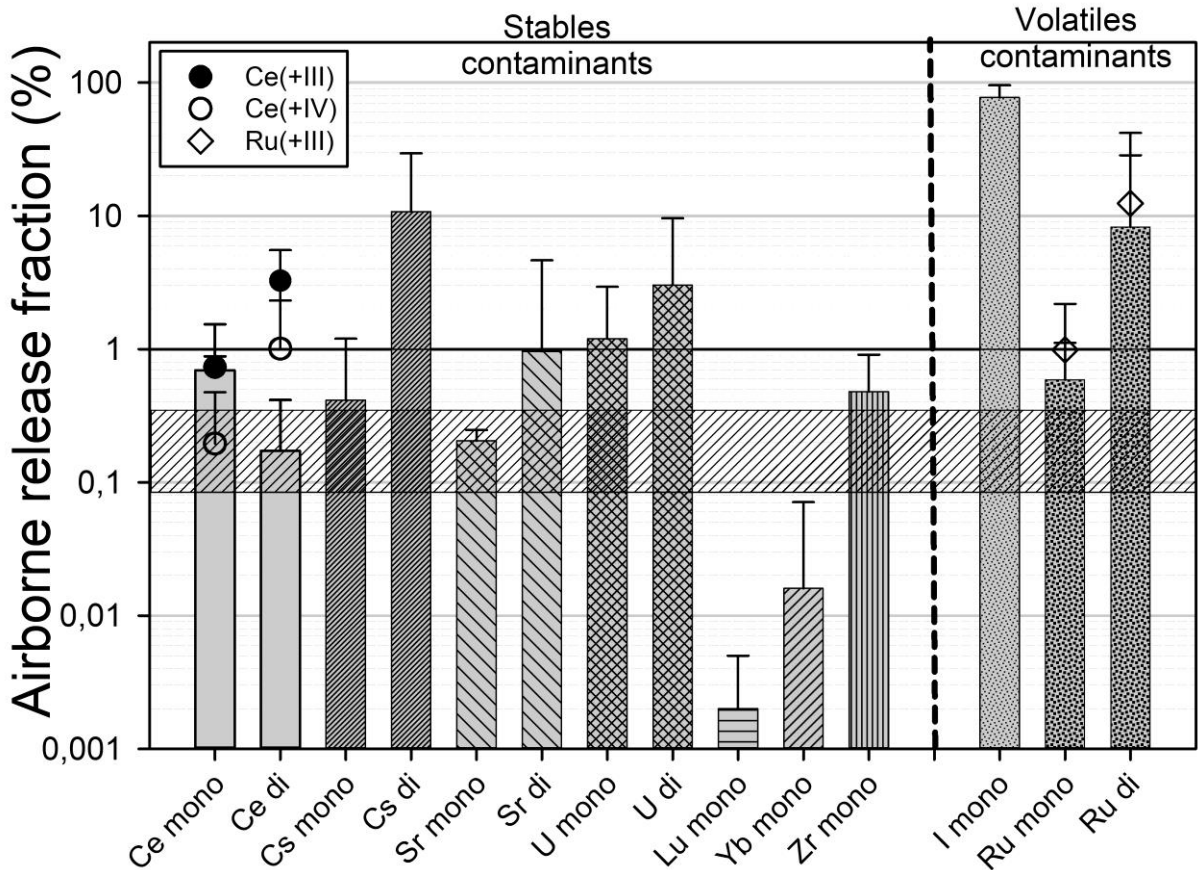
Regarding ruthenium Ru(+III) contaminated solutions, ARF appears significantly higher even for solutions contaminated at a lower level (0.6 g/L). Furthermore, high level of uncertainty is reported for biphasic conditions, supporting the volatile nature of ruthenium released suspected to be highly influenced by sampling conditions and potentially explaining this large level of experimental dispersion (see SI-3 for ARF values reported for each experimental repetitions).

Table V: mean Airborne Release Fractions (ARF) determined for each experimental condition (in bold, experiments conducted for surrogate concentrations close to 10 g/L)

Fuel composition (in volume)	Contaminant	Salt	[Cont <sub>org</sub> ] (g/L)	Mean ARF (%, extended uncertainty)
Contaminated 70% HTP / 30% TBP	Ce(+III)	Cerium(III) nitrate hexahydrate Ce(NO <sub>3</sub> ) <sub>3</sub> .6(H <sub>2</sub> O)	0.2	0.58 % +/- 0.62 %
			4.8	1.56 % +/- 1.57 %
			<b>9.3</b>	<b>0.22 % +/- 0.31 %</b>
Contaminated 70% HTP / 30% TBP + Pure HNO <sub>3</sub> 3M, Ratio 1:1			0.4	4.24 % +/- 2.12 %
			<b>8.6</b>	<b>1.78 % +/- 1.06 %</b>
Contaminated 70% HTP / 30% TBP	Ce(+IV)	Cerium(IV) Ammonium Nitrate (NH <sub>4</sub> ) <sub>2</sub> Ce(NO <sub>3</sub> ) <sub>6</sub>	<b>10</b>	<b>0.20 % +/- 0.28 %</b>
Contaminated 70% HTP / 30% TBP + Pure HNO <sub>3</sub> 3M, Ratio 1:1			<b>10</b>	<b>1.01 % +/- 1.31 %</b>
Contaminated 70% HTP / 30% TBP	Ru(+III)	Ruthenium(III) Nitrosylnitrate RuNO(NO <sub>3</sub> ) <sub>3</sub>	0.6	0.99 % +/- 1.20 %
Contaminated 70% HTP / 30% TBP + Pure HNO <sub>3</sub> 3M, Ratio 1:1			0.6	12.41 % +/- 29.45 %

A comparison of present results with values reported in the literature, summarized in Table I, is proposed in Figure 3. Present experimental results appear in agreement with previously reported values both for cerium and ruthenium contaminated HTP/TBP. Since we were not able to identify from the literature the experimental ARF values obtained for plutonium contaminated HTP/TBP, we also reported in Figure 3, through a dashed horizontal area, the range of ARF (from 0.0885 to 0.309 %) proposed by Ballinger et al.<sup>24</sup> from the FIRIN compartment fire code

418 for large scale solvent extraction fire including Pu(+IV) in the organic phase. It is worth noting that results obtained  
 419 for Ce(+IV) for monophasic condition are within the range of ARF introduced by Ballinger et al. (1985) for Pu.  
 420 Furthermore, values obtained for cerium in the present study appear in good agreement with mean values  
 421 determined for uranium, a contaminant generally considered as a surrogate of plutonium release in case of fires  
 422 involving fuels representative of the PUREX process. These conclusions support our main assumption that release  
 423 of stable contaminants is mainly driven by bubble bursting and that the chemical nature of the contaminants (Ce,  
 424 Cs, Sr, Zr and U) does not induce significant discrepancy in terms of ARF.



425  
 426 Figure 3: Comparison of results obtained in the present study (circular and diamond dots) with mean values  
 427 determined from values reported in the literature (from raw data extracted from each reference cited in Table I).  
 428 Volatile and stable contaminants are considered separately. Dashed horizontal bar corresponds to the range of  
 429 ARF associated to release of Pu as computed by Ballinger et al. <sup>24</sup>

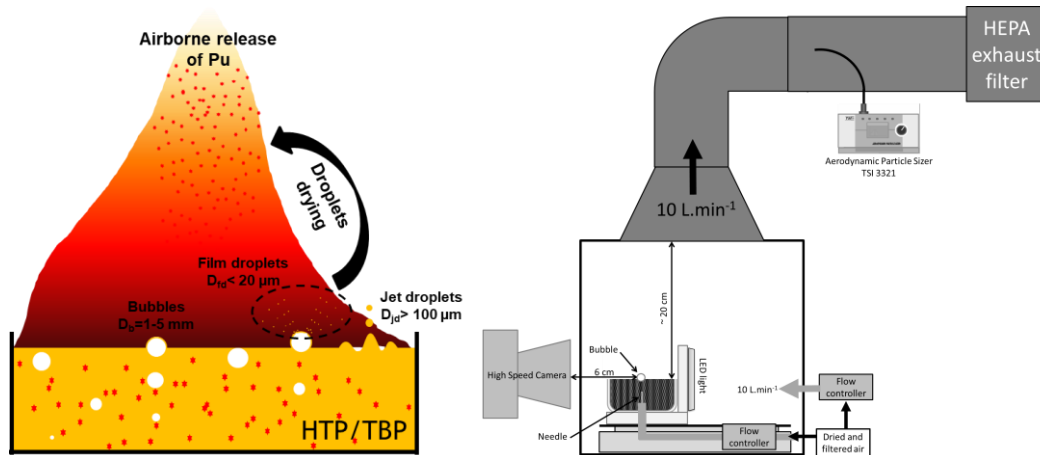
### 430 III.C. Phenomenological description

431  
 432 As demonstrated both by SEM analysis of cerium released particles and comparison of ARF measured for mono  
 433 and biphasic experimental configurations, bubble bursting is one of the main driven mechanism associated to  
 434 airborne release during contaminated liquid fuels fires. To go further on the theoretical description of this  
 435 mechanism, additional experiments were carried out firstly, to describe the size of bubbles formed in the organic  
 436 phase prior to bursting and secondly, to mimic bubble bursting under non-flaming conditions for analyzing number  
 437 and size of droplets finally formed. Figure 4 illustrates a simple phenomenological description of the contribution  
 438 of bubble bursting to the release of particles during complex pool fires. As reported by several authors, airborne  
 439 release associated to bubble bursting of aqueous salt solutions representative of seawater <sup>54-56</sup> or radionuclides  
 440 contaminated water pool <sup>38,57</sup> mainly occurs through the formation of two different types of droplets. The first  
 441 droplet emission process, mostly concerning small bubbles, is due to the breakage of the bubble cap, followed by  
 442 a sudden pressure drop. In this case, a jet is formed and droplets are emitted from the fragmentation of this jet. The  
 443 number  $N_{jd}$  and diameter  $D_{jd}$  of these droplets, named in the rest of this discussion as “jet droplet”, are inversely  
 444 proportional to the bubble diameter as pressure drop is expected to be higher for smaller bubbles. Diameter of  
 445 these droplets is generally one-tenth of the bubble diameter for seawater <sup>58</sup>. The second emission process identified  
 446 during bubble bursting is associated to droplets emitted from the rupture of the liquid film forming the interface  
 447 between the bubble cavity and the atmosphere. This release phenomenon is expected to be more efficient for  
 448 millimetric bubbles <sup>54</sup> with increasing number of “film droplets” per bubbles with increasing bubble diameter <sup>55</sup>.  
 449

450 The diameter  $D_{fd}$  of these droplets is reported to linearly increase with bubble diameter with an average diameter  
 451 of nearly 30-40  $\mu\text{m}$  for bubble diameter in the range 2-3 mm for seawater<sup>56,59</sup>. At the final stage of the release  
 452 process, dry residues are emitted as solid particles and are defined, in terms of diameter  $D_{geo, p}$ , according to the  
 453 following relationship:  
 454

$$D_{geo, p} = D_d \sqrt[3]{\frac{C_m}{\rho_p}}, \quad (\text{Eq. 5})$$

455 with  $D_d$  the droplet diameter (m),  $C_m$  the mass concentration ( $\text{kg}\cdot\text{m}^{-3}$ ) and  $\rho_p$  the dry particles density ( $\text{kg}\cdot\text{m}^{-3}$ ).  
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 457  
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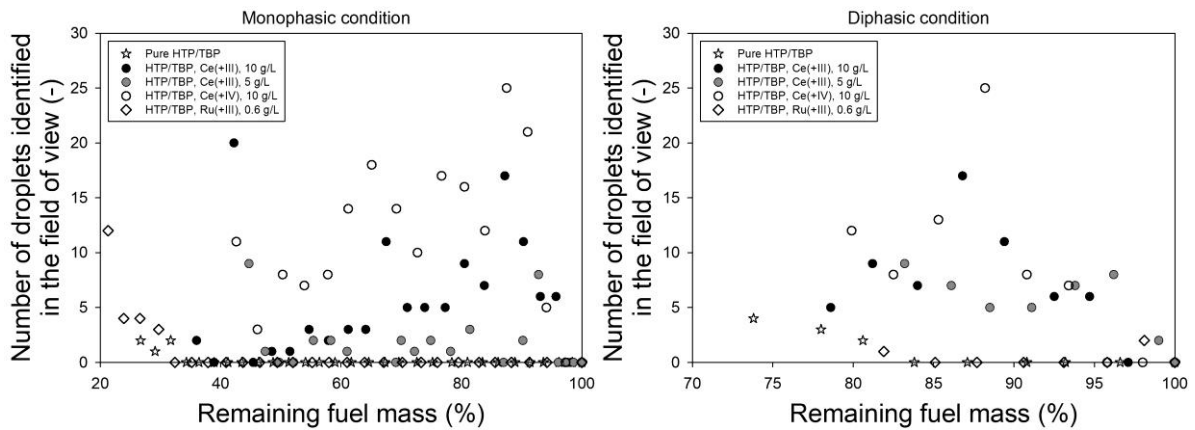


459  
 460  
 461 Figure 4: (left) phenomenological description of Pu particle released from bubble bursting during HTP/TBP pool  
 462 fire, (right) diagram of the facility used for the study of the bubble and jet/film droplets formation under non-  
 463 flaming condition  
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465 Beyond these numerous studies available for release and formation of salt particles from boiling or bursting water  
 466 contaminated solutions, as far as we are concerned, no experimental study is available regarding the properties of  
 467 bubbles and droplets formed during HTP/TBP combustion. To fill this lack of knowledge, and to bring  
 468 experimental analysis of bubbles and droplets emissions fundamental for simulation of contaminant release from  
 469 liquid fuel fire, the present study aims to characterize all these phenomena under as much representative conditions  
 470 as possible.

471 For this purpose, and to measure the size and number of bubbles emitted as a function of time for pure and Ce(+III),  
 472 Ce(+IV) or Ru(+III) contaminated HTP/TBP under mono or biphasic conditions, bubble bursting was  
 473 characterized using a High-Definition (HD) camera (SONY HDR-SR11) placed at 90° of the cylindrical  
 474 borosilicate glass container of the test bench. The optical focusing was carried out at the centre of the sample  
 475 holder with a corresponding field of view covering the entire diameter of the glass container. Optical depth of field  
 476 and focusing were fixed constant over the test in order to avoid any misinterpretation of millimetric bubble  
 477 diameter potentially present above or beyond the observation area. Scale was determined using a 30 mm ruler and  
 478 corresponding size resolution was of 30  $\mu\text{m}$  per pixel. Images recorded by HD camera were analyzed during 25  
 479 minutes after the ignition with a time period of 1 minute. Figure 5 presents the evolution of number and diameter  
 480 of droplets determined on each picture for monophasic (left part of Figure 5) and biphasic conditions (right part of  
 481 Figure 5) as a function of remaining mass of fuel. For pure and Ru(+III) contaminated solutions, no bubble was  
 482 reported during the major part of the experiments. This limited formation of bubbles during fire test could be  
 483 explained by limited abundance of “bubbles nuclei” within HTP/TBP for pure and low Ru(+III) contaminated  
 484 solutions (0.6 g/L). On the other hand, the slight increase of emission identified at the end of fire tests, at nearly  
 485 30 % of remaining fuel mass for monophasic condition is due to the formation of residues within pure solvent and  
 486 increase of Ru(+III) concentration within the residual solvent since major part of Ru(+III) still remains in the  
 487 organic phase (with relatively low ARF values reported in Table V). The low ability of Ru(+III) contaminated  
 488 solutions to produce bubbles prior to TBP combustion and formation of residues supports our previous assumption  
 489 that the ruthenium release is mainly ruled by its volatility rather than bubble bursting.

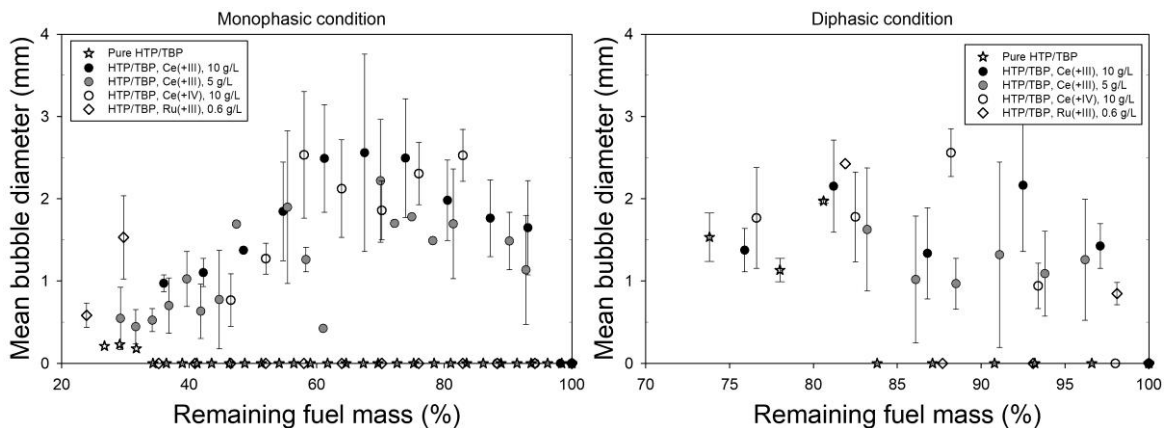
490 Regarding Ce(+III) and Ce(+IV) contaminated solutions at 10 g Ce/L, continuous emission of bubbles could be  
 491 noticed in Figure 5 with similar level of emission between both cerium oxidation state. Unlike the case of  
 492 ruthenium, comparison of results reported for lower contamination level (5 g Ce/L) for Ce(+III) does not allow to  
 493 draw any conclusion on the influence of concentration in the range 5 - 10 g/L. Consequently, the threshold  
 494 concentration of “bubbles nuclei” to reach continuous emission of bubbles must be in the range 0.6 - 5 g/L.



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Figure 5: Evolution, as a function of remaining fuel (HTP/TBP) mass, of number of bubbles formed at the liquid interface during fire experiments of (left) HTP/TBP monophasic pool fire and (right) biphasic HTP/TBP – 3M HNO<sub>3</sub> pool, both containing different cationic species (Ce(+III), Ce(+IV), Ru(+III)).

Figure 6 presents the evolution of mean diameter of bubbles as a function of time since ignition. In agreement with the evolution of number of bubbles, mean diameters reported for pure and Ru(+III) contaminated solvents confirm limited emission of bubbles for these solutions and for both mono and biphasic conditions. For solvents contaminated by cerium, mean bubble diameters are mostly ranging between 1 and 3 mm for both mono and biphasic conditions. Evolution of mean bubble diameter as a function of time appears more pronounced for monophasic with an increase of diameter from 90 % to 60 % of remaining fuel mass followed by a constant decrease of mean bubble diameter until flame extinction.



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Figure 6: Evolution, as a function of remaining fuel (HTP/TBP) mass, of mean bubble diameter at the liquid interface during fire experiments of (left) HTP/TBP monophasic pool fire and (right) biphasic HTP/TBP – 3M HNO<sub>3</sub> pool, both containing different cationic species (Ce(+III), Ce(+IV), Ru(+III)).

In a second time, this investigation of bubble diameter formed during HTP/TBP pool (containing different cationic species (Ce(+III), Ce(+IV), Ru(+III)) fire was considered to mimic synthetic bubbles under non-flaming conditions. This non-flaming study was carried out in order to analyse the number and the diameter of jet and film droplets formed during collapse of solvent bubbles. This experimental study does not aim to be fully representative of airborne release conditions (evolution of physical properties of solvent, drying/evaporating conditions) during HTP/TBP combustion but only to focus on the formation of droplet through bubble bursting and to demonstrate that this mechanism is the main driving force. For this purpose, an experimental test bench was designed as shown in Figure 4. Bubbles were formed in a square glass container presenting a glass tube in its centre for injecting dry and filtered pressurized air through needles with varying diameter. Experiments were conducted for pure HTP/TPB and contaminated HTP/TBP and in a range of bubbles diameter of 1 to 4 mm and jet droplets were identified and characterized using a High Speed Camera (NAC Hi-Dcam II).

Figure 7 presents the evolution of mean diameter and number of jet droplets emitted per bubble as a function of bubble mean diameter. Error bars correspond to standard deviation ( $k=1$ ) associated to mean values reported in this figure.

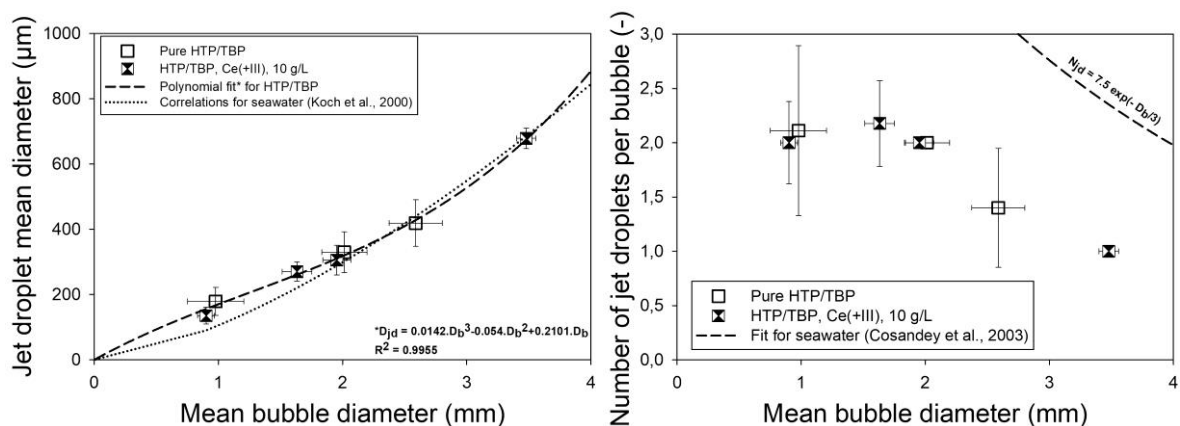


Figure 7: Evolution of mean jet droplet (left) diameter and (right) number emitted per bubble as a function mean bubble diameter

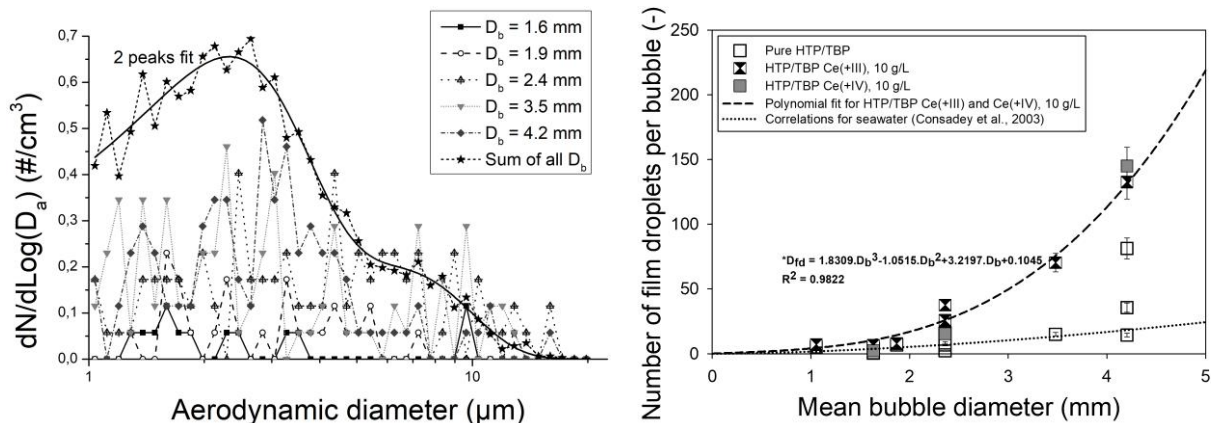
Considering jet droplet diameter, as reported in the literature<sup>38,57</sup>, mean diameters are within 200-800 µm and appear to increase with increasing bubble size. Correlations proposed by Koch et al.<sup>57</sup> for seawater is in good agreement with present results, especially for bubble diameters larger than 2 mm. Nevertheless, since seawater and TBP/HTP present different physico-chemical properties, we propose a new empirical correlation for the entire range of bubble diameters. Corresponding third order polynomial fit appears in good agreement with both HTP/TBP measurements. A close agreement is also reported between pure and contaminated solvents, highlighting that present contamination level (10 g/L of Ce(+III)) and nature of this contaminant does not influence the fragmentation process. Considering the dimensionless approach proposed by Russel & Singh<sup>60</sup> and based on the Bond-Eötvös number describing the balance between gravitational forces compared to surface tension forces, this poor influence of Ce(+III) concentration is potentially due to a limited evolution of density and surface tension of contaminated solvents.

Regarding the number of jet droplets emitted per bubble (right part of Figure 7), a peak of emission is identified for bubble diameters in the range of those experimentally reported for flaming conditions (1 - 3 mm). This peak of release does not agree with the empirical evolution reported by Cosandey et al.<sup>38</sup> for seawater based on a relatively limited number of experimental values. On the other hand, a close agreement could be identified with results obtained by Blanchard & Syzdek<sup>54</sup> for seawater with a peak of emission of jet droplets for a bubble diameter close to 2 mm. Beyond the dispersion of results reported in the literature for different experimental set-up and conditions, present results obtained for HTP/TBP confirm that the release of jet droplet is limited to less than 3 droplets per bubble and that 400 µm diameter droplets emitted from 2 mm bubbles will be hardly transported in the aerosol phase. This is an additional demonstration that jet droplet may not fully explain the overall airborne release of particles from the contaminated liquid pool fire.

Additional measurements were then carried out to describe the emission of droplets through film breakage. For this purpose, an aerodynamic particle sizer (TSI APS 3321) was used to determine number concentration of dry particles formed according to the evaporation of film droplets and expected to present diameters lower than 20 µm<sup>56</sup>. Dry and filtered air was injected in the test chamber and film droplets were transported from the emission point to sampling probe connected to the APS.

Left part of Figure 8 presents the size distributions of particles emitted for each mean bubble diameter (from 1.6 to 4.2 mm) over 3 hours of continuous bubbles bursting. As shown in Figure 8, the corresponding size distributions suffer from a lack of statistic and we were not able to propose any statistical analysis for each bubble diameter. Nevertheless, all experimental results were merged in order to build a mean size distribution (star symbols in Figure 8) of particles emitted during the bursting of bubbles presenting diameters from 1.6 mm to 4.2 mm. Two peaks Gaussian fitting procedures were applied (Origin Pro 8.6) to this mean size distribution and corresponding count modal aerodynamic diameter were respectively of 2.2 +/- 0.1 µm and 6.0 +/- 1.4 µm. This bi-modal size distribution confirms the influence of bubble diameter on the size of particles emitted<sup>61</sup> with largest particle diameters associated to the larger bubbles. It is worth noting that corresponding count modal diameters could not be fully considered as the film droplets diameter since we were not able to avoid evaporation of these droplets and particle emission was recorded even for pure HTP/TBP. In the present situation, we could only suppose that film droplets may present diameter in a size range defined by the diameter associated to dry residue formed through droplet evaporation, and film droplet diameter which could be computed from this dry residue diameter. Assuming a spherical dry particle residue mainly composed of CePO<sub>4</sub> ( $\rho_p = 5220 \text{ kg/m}^3$ ,<sup>32</sup>), the diameter of the film droplet emitted from a solution contaminated at 10 g Ce/L could be computed from equation 5. The geometric diameter  $D_{geo,p}$  in equation 5 is computed from count modal particles aerodynamic diameter  $D_{a,p}$ , determined in Figure 8,

576 and converted to geometric diameter  $D_{geo,p}$  according to  $D_{a,p} = D_{geo,p} \sqrt{\rho_p/\rho_0}$  (assuming spherical shape and  
577 reference density  $\rho_0$  of  $1000 \text{ kg/m}^3$ ). According to equation 5, geometric diameters of film droplets are expected  
578 to range between  $6.5 \text{ }\mu\text{m}$  and  $17.5 \text{ }\mu\text{m}$ , in agreement with values commonly considered in previous studies <sup>15,36</sup>  
579 from experimental measurements mainly carried out by Borkowski et al. <sup>62</sup>. Comparison of aerodynamic diameter  
580 of particles released from non-flaming bubble bursting (Figure 9) and from contaminated HTP/TBP pool fires (see  
581 part III.a) shows again a good agreement. Assuming that particles released during flaming conditions are mainly  
582 composed of monazite ( $\text{CePO}_4$ ), count median geometric diameter reported in Table III could be converted to  
583 aerodynamic diameter of  $1.9 \text{ }\mu\text{m}$ , in close agreement with values determined under non-flaming conditions.  
584 Right part of Figure 8 presents the evolution of number of film droplets emitted per bubble as a function of mean  
585 bubble diameter. For pure HTP/TBP, number of film droplets is not equal to zero, highlighting that film droplets  
586 are not fully evaporated at the sampling point. Surprisingly, a good agreement is noticed between correlation  
587 proposed by Cosandey et al. <sup>38</sup> for seawater and pure HTP/TBP. On the other hand, bubbles produced by  
588 contaminated solvents appear more efficient to release film droplets than seawater. This higher tendency of  
589 solvents to release more droplets than water could be mainly explained by lower surface tensions reported for  
590 kerosene/TBP or HTP/TBP mixtures <sup>15,63</sup>, close to  $25 \text{ mN/m}$  compared to seawater surface tensions of nearly  $72$   
591  $\text{mN/m}$  <sup>60</sup>. As recently observed experimentally <sup>61</sup>, bubbles formed from lowest surface tension liquids produced  
592 more particles with larger diameters. For predictive purpose, the evolution of the number of film droplets per  
593 bubble could be correlated with the mean bubble diameter from a third order polynomial fit (see Figure 8). In the  
594 range of bubble diameter reported under flaming conditions ( $1\text{-}3 \text{ mm}$ ), the number of film droplets per bubble is  
595 reported between 10 and 50, in reasonable agreement with the value of 10 particles emitted per  $5 \text{ mm}$  seawater  
596 bubbles reported by Ke et al. <sup>61</sup>. This larger amount of film droplets emitted per bubbles in comparison with jet  
597 droplets confirms our first assumption, based on SEM analysis of released particles that ARF is mainly due to film  
598 droplets rather than jet ones. Despite the mass balance in favour of jet contaminated droplets, it is worth noting  
599 that such large droplets (from  $200$  to  $800 \text{ }\mu\text{m}$ ) could not be transported by the convective flux of the pool fire flame  
600 and are too influenced by the gravity and subject to settling (settling velocity ranging from  $0.7$  to  $3 \text{ m/s}$  <sup>64</sup> for  $200$   
601  $\text{-}800 \text{ }\mu\text{m}$  HTP/TBP droplets with a density of  $827 \text{ kg/m}^3$  under ambient conditions <sup>15</sup>), to be finally released in the  
602 aerosol phase.  
603



604  
605 Figure 8: (left) mean film droplets size distribution formed during bursting of bubbles with different diameters  
606 within HTP/TBP contaminated at 10 g Ce(+III)/L and (right) evolution of the number of film droplets emitted  
607 per bubble as a function of mean bubble diameter  
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#### 609 IV. Conclusions

610  
611 The aim of this study was to enhance our state of knowledge on airborne release during contaminated pool fires  
612 from a phenomenological point of view. For this purpose, experiments were conducted for three different  
613 contaminants, cerium in two state of oxidation states (Ce(+III) and Ce(+IV)) and ruthenium (Ru(+III)). The  
614 observed Airborne Release Fractions confirm the significant contribution of bubble bursting involved during  
615 organic and aqueous boiling and for solutions contaminated by cerium in both oxidation states. ARF reported for  
616 cerium are in good agreement with values previously determined, demonstrating a limited influence of the nature  
617 of thermally stable contaminant (within the range of experimental uncertainty) on the final ARF and highlighting  
618 the contribution of bubble bursting to the release phenomenon. On the other hand, higher ARF values reported for  
619 ruthenium could only be explained by the volatility of chemical forms of this element emitted during HTP/TBP  
620 pool fires.

621 To support these assumptions, scanning electronic microscopy analysis of released particles was performed. This  
622 analysis has shown homogeneous composition and shape of particles emitted during combustion of cerium  
623 contaminated solutions. On the other hand, wide variety of chemical composition and shape of ruthenium particles  
624 confirms the volatile origin of these particles suspected to explain higher ARF values obtained for this element.  
625 Additional analysis of size and number of bubbles produced during contaminated pool fires was conducted and  
626 has confirmed, for pure or poorly contaminated organic solutions (Ru(+III) et 0.6 g/L), a limited formation of  
627 bubbles. Considering highest level of contamination (from 5 to 10 g/L of cerium), significant emission of 1-3 mm  
628 bubbles was reported. This bubble characterization, conducted under fire conditions, was used to conduct non-  
629 flaming experiments to describe for the first time jet and film droplets emitted for different HTP/TBP bubbles  
630 diameters. Jet droplets diameters, in the range 200 – 800  $\mu\text{m}$  and number of film droplets (less than 20  $\mu\text{m}$  in terms  
631 of diameter) emitted per bubbles are closely linked to bubble diameter. Empirical correlations were proposed for  
632 predictive purpose. Finally, a good agreement was demonstrated between diameters of particles released during  
633 pool fire of cerium contaminated solvents and particles produced during drying/evaporation of film droplets  
634 emitted during non-flaming bubble bursting experiments. This result finally confirms that bubble bursting is the  
635 main driving mechanism explaining the airborne release of non-volatile contaminant during this type of hazardous  
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- 793

794 **Supplementary information SI-1: yield of digestion associated to ICP analysis**

795  
 796 Figure SI-1 presents the evolution of ICP-MS detection yield  $Y_{ICP}$  of cerium as a function of mass of  $CeO_2$  particles  
 797 ( $5 \mu m$   $CeO_2$  powder, REacton®, 99.9% reference 215-150-4 from Alfa Aesar) deposited on reference samples.  
 798 For this purpose, cellulose acetate membranes similar to those used for sampling during HTP/TBP pool fire  
 799 experiments were considered.  $CeO_2$  powder were aerosolized using a vortex shaker device<sup>1</sup> and mass of deposited  
 800 particles was determined by weighing according to NF ISO 15767<sup>2</sup>. ICP-MS analysis was carried out by Intertek  
 801 laboratory using previously qualified digestion protocol. The detection yield  $Y_{ICP}$  both includes digestion and  
 802 detection yields and is defined as the ratio between the mass of cerium determined by ICP analysis  $m_{ICP}^{Ce}$  and the  
 803 mass of cerium deposited on the reference membrane  $m_{ref}^{Ce}$   
 804

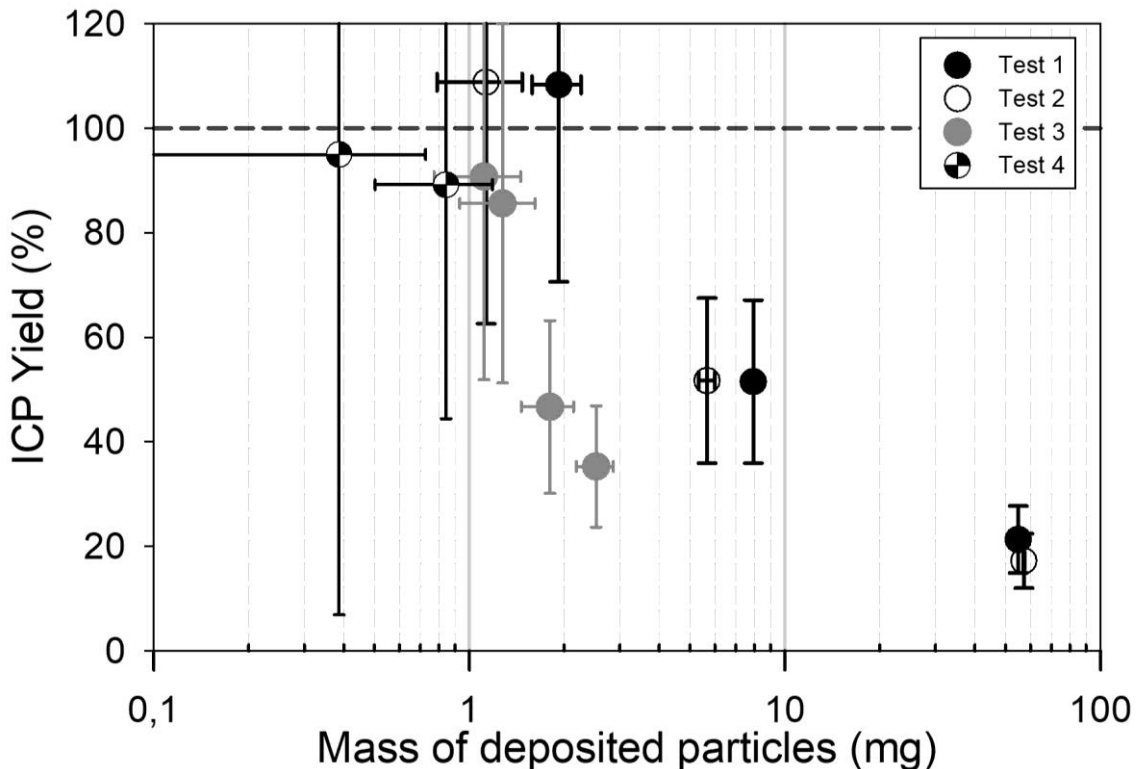
805 
$$Y_{ICP}^{chemical\ form\ of\ Ce} = Y_{detection\ ICP-MS}^{chemical\ form\ of\ Ce} \cdot Y_{digestion}^{chemical\ form\ of\ Ce} = \frac{m_{ICP}^{Ce}}{m_{ref}^{Ce}}$$

806  
 807 The corresponding uncertainty is defined as:  
 808

809 
$$u(R_m) = \sqrt{\left(\frac{1}{m_{ref}^{Ce}}\right)^2 \cdot u^2(m_{ICP}^{Ce}) + \left(\frac{-m_{ICP}^{Ce}}{(m_{ref}^{Ce})^2}\right) \cdot u^2(m_{ref}^{Ce})}$$

810  
 811 with  $u(m_{ICP}^{Ce})$  and  $u(m_{ref}^{Ce})$  the uncertainties associated to the ICP and reference masses, determined according to  
 812 NF ISO 15767.

813 It is worth noting that ICP yields are close to 100 % for reference mass lower than 2 mg and decreases for larger  
 814 deposited mass. This decrease is not relevant for our fire samples since, according to the initial mass and ARF,  
 815 less than 0.1 mg of cerium particles is expected on membranes. Mean ICP yield of 89.3 % +/- 6.5 % was determined  
 816 for deposited mass in the range 0.4 – 2 mg and was considered as a correction factor in the computation of ARF.  
 817



818  
 819  
 820 Figure SII-1: digestion yield of cerium reference samples  
 821

<sup>1</sup> Gensdarmes, F., & Roynette, A. (2013). French patent: W02013092816.

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822 **Supplementary information SI-2: calibration of XRF for samples containing ruthenium**

823

824 Figure SI-2 presents the experimental calibration curve between mass of ruthenium and number of events recorded  
 825 for an X-ray energy of 19.279 keV corresponding to the  $K_{\alpha}$  emission ray of Ruthenium.  $RuO_2$  particles were  
 826 deposited on acetate cellulose membrane using a vortex shaker<sup>3</sup>. Mass of deposited Ruthenium particles was  
 827 determined by weighing according to NF ISO 15767<sup>4</sup>. Mass of ruthenium is then linked to number  $Nb_{events\ K_{\alpha}}$  of  
 828  $K_{\alpha}$  events according to the following relation and a calibration factor  $C_f$ :

829

$$830 \quad m_{Ru} = C_f \cdot Nb_{events\ K_{\alpha}}$$

831

832 The corresponding uncertainty is defined as:

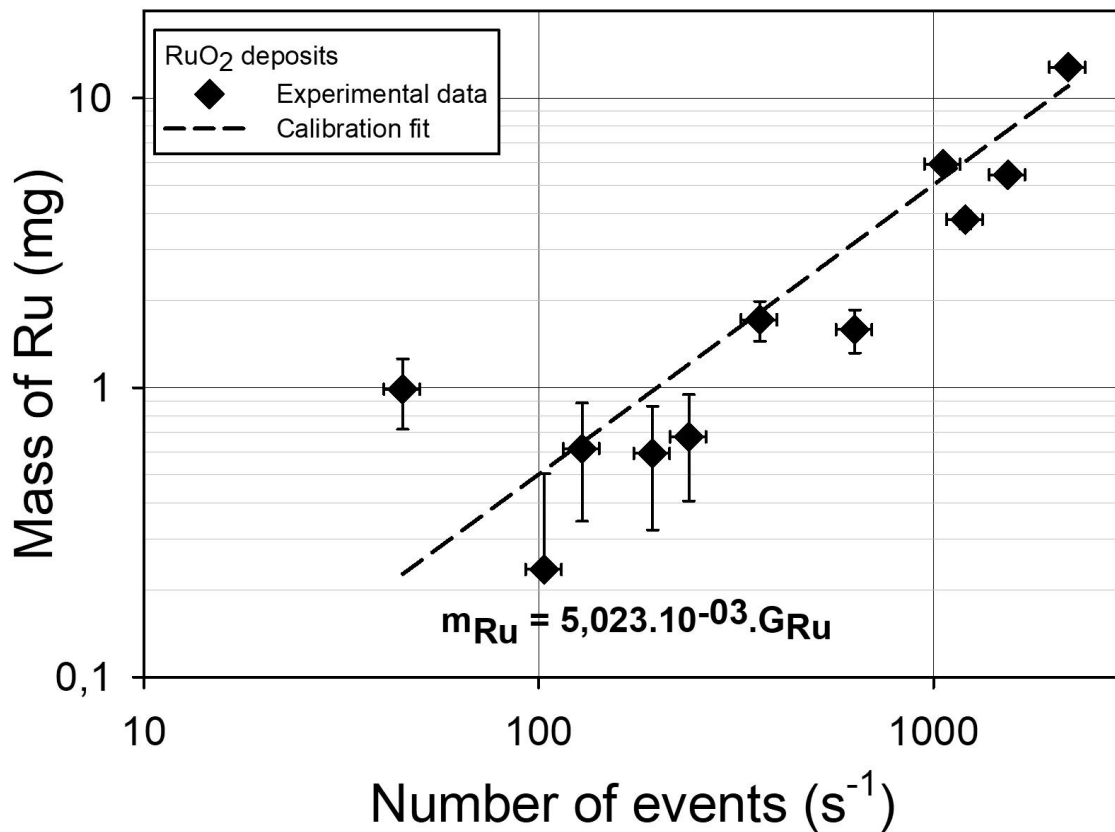
833

$$834 \quad u(m_{Ru}) = \sqrt{Nb_{events\ K_{\alpha}}^2 \cdot u^2(C_f) + C_f^2 \cdot u^2(Nb_{events\ K_{\alpha}})},$$

835

836 with  $u(C_f)$  and  $u(Nb_{events\ K_{\alpha}})$  the uncertainties associated to the calibration factor (determined from the linear fit)  
 837 and number of events according to the spectrometer specifications.

838



839

840 Figure SI2-1: experimental calibration curve linking mass of ruthenium with number of events recorded by X-  
 841 ray spectrometer for the  $K_{\alpha}$  Ruthenium energy (19.279 keV<sup>5</sup>)

842

<sup>3</sup> Gensdarmes, F., & Roynette, A. (2013). French patent: W02013092816.

<sup>4</sup> AFNOR. (2008). NF ISO 15767. Atmosphères des lieux de travail - Contrôle et caractérisation des erreurs de pesée des aérosols collectés.

<sup>5</sup> <http://xdb.lbl.gov/>

843 **Supplementary information SI-3: computation of ARF experimental uncertainties associated**

844

845 Airborne release fraction ARF is defined as:

846 
$$ARF = \frac{m_{\text{element}}^{\text{sampling}}}{m_{\text{element}}^{\text{initial}} \cdot P_{P(\%)} \cdot F_{P(\%)}}$$

847 Corresponding uncertainty could be computed according to:

848 
$$u(ARF) = \sqrt{\left(\frac{\partial ARF}{\partial m_{\text{element}}^{\text{sampling}}}\right)^2 u^2(m_{\text{element}}^{\text{sampling}}) + \left(\frac{\partial ARF}{\partial m_{\text{element}}^{\text{initial}}}\right)^2 u^2(m_{\text{element}}^{\text{initial}}) + \left(\frac{\partial ARF}{\partial P_{P(\%)}}\right)^2 u^2(P_{P(\%)}) + \left(\frac{\partial ARF}{\partial F_{P(\%)}}\right)^2 u^2(F_{P(\%)})}$$

849 Uncertainty associated to the sampled mass of element of interest  $u(m_{\text{element}}^{\text{sampling}})$  is determined for cerium according  
850 to ICP measurement uncertainty (see SI-1) and for ruthenium according to X-Ray Fluorescence measurement  
851 uncertainty (see SI-2).

852 Uncertainty associated to initial mass of element of interest  $u(m_{\text{element}}^{\text{initial}})$  is determined according to the preparation  
853 protocol of contaminated solvents. First, a known mass of salt containing the element of interest  $m_{\text{aqueous}}^{\text{initial}}$  was first  
854 dissolved in a known volume of aqueous  $\text{HNO}_3$  solution. The corresponding mass of element in the aqueous phase  
855 is then defined from the mass of dissolved salt  $m_{\text{salt}}$  and the contribution of the element of interest to the  
856 composition of this salt  $\%_{\text{element/salt}}$ :

857

858 
$$m_{\text{element}}^{\text{aqueous}} = m_{\text{salt}} \cdot \%_{\text{element/salt}}$$

859

860 Uncertainty associated to the composition of the salt was assumed negligible and uncertainty associated to the  
861 mass of salt was only considered to compute the uncertainty corresponding to the mass of element of interest in  
862 the aqueous phase:

863 
$$u(m_{\text{element}}^{\text{aqueous}}) = u(m_{\text{salt}}) \cdot \%_{\text{element/salt}}$$

864

865 The mass of element of interest in HTP/TBP is defined as a function of the mass of this element in the aqueous  
866 phase  $m_{\text{element}}^{\text{aqueous}}$  in contact with the organic phase during the extraction protocol presenting an extraction coefficient  
867  $C_{\text{ext, element}}$  for this element:

868 
$$u(m_{\text{element}}^{\text{initial}}) = m_{\text{element}}^{\text{aqueous}} \cdot C_{\text{ext, element}}$$

869

870 Uncertainty of this initial mass of element in the organic phase is computed according to:

871

872 
$$u(m_{\text{element}}^{\text{initial}}) = \sqrt{\left(\frac{\partial m_{\text{element}}^{\text{initial}}}{\partial m_{\text{element}}^{\text{aqueous}}}\right)^2 u^2(m_{\text{element}}^{\text{aqueous}}) + \left(\frac{\partial m_{\text{element}}^{\text{initial}}}{\partial C_{\text{ext, element}}}\right)^2 u^2(C_{\text{ext, element}})}$$

873 Uncertainty associated to the extraction coefficient was determined for cerium from experimental determination  
874 of this coefficient<sup>32</sup> and for ruthenium by considering mean values and corresponding standard deviation computed  
875 from experimental values reported in previous studies (TBP in contact, under ambient conditions, during 60  
876 minutes with  $\text{HNO}_3$  3 M aqueous phase containing dissolved Ruthenium Nitrosyl Nitrate salt<sup>15,41</sup>).

877 The volume fraction of gas sampled through the membrane  $P_{P(\%)}$  is defined as the ratio between the volumetric  
878 flow rate sampled  $Q_{\text{sampled}}$  and the volumetric flow rate within the test bench exhaust duct  $Q_{\text{exhaust}}$ :

879

879 
$$P_{P(\%)} = Q_{\text{sampled}} / Q_{\text{exhaust}}$$

880 Mass flow regulator was used to maintain the sampled flow rate then uncertainty associated to this flowrate was  
881 assumed negligible. The exhaust duct flow rate was manually regulated during each test and a mean exhaust flow  
882 rate was then computed and considered. Corresponding standard deviation associated to this mean exhaust flow  
883 rate was considered as the  $Q_{\text{exhaust}}$  uncertainty  $u(Q_{\text{exhaust}})$ . Finally, the  $P_{P(\%)}$  uncertainty is defined as follow:

884 
$$u(P_{P(\%)}) = \sqrt{\left(-\frac{Q_{\text{sampled}}}{Q_{\text{exhaust}}^2}\right) u^2(Q_{\text{exhaust}})}$$

885

886 Finally, penetration fraction  $F_{P(\%)}$  was fixed, according to computations reported in our previous study<sup>12</sup>, at a  
887 value of 1 (no losses of particles in the test bench) for aerodynamic diameter lower than 5  $\mu\text{m}$ .

888 **Supplementary information SI-4: values of airborne release fractions measured for each experimental**  
 889 **conditions**  
 890

891 Table SI-I: ARF values determined for each Ce(+III) contaminated HTP/TBP solutions

Fuel composition (in volume)	Contaminant	Salt	V <sub>org</sub> / V <sub>aq</sub> (ml)	[Cont <sub>org</sub> ] (g/L)	ARF (%)
Contaminated 70% HTP / 30% TBP	Ce(+III)	Cerium nitrate hexahydrate Ce(NO <sub>3</sub> ) <sub>3</sub> .6(H <sub>2</sub> O)	30 / 0	0.2	0.30 +/- 0.10
					0.79 +/- 0.21
					0.67 +/- 0.17
				4.8	0.70 +/- 0.06
					3.07 +/- 0.24
					0.92 +/- 0.07
				9.5	0.12 +/- 0.01
					0.04 +/- 0.004
					0.06 +/- 0.01
				8.6	0.66 +/- 0.05
Contaminated 70% HTP / 30% TBP + Pure HNO <sub>3</sub> 3M, Ratio 1:1			15 / 15	0.4	5.32 +/- 0.66
					3.81 +/- 0.47
					3.59 +/- 0.45
				8.6	1.35 +/- 0.17
					2.21 +/- 0.28

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902 Table SI-II: ARF values determined for each Ce(+IV) contaminated HTP/TBP solutions

Fuel composition (in volume)	Contaminant	Salt	V <sub>org</sub> / V <sub>aq</sub> (ml)	[Cont <sub>org</sub> ] (g/L)	ARF (%)
Contaminated 70% HTP / 30% TBP	Ce(+IV)	Cerium(IV) Ammonium Nitrate (NH <sub>4</sub> ) <sub>2</sub> Ce(NO <sub>3</sub> ) <sub>6</sub>	30 / 0	9.7	0.01 +/- 0.001
					0.05 +/- 0.01
					0.03 +/- 0.004
				10.2	0.12 +/- 0.03
					0.28 +/- 0.06
					0.20 +/- 0.04
					0.20 +/- 0.04
					0.18 +/- 0.04
					0.33 +/- 0.07
					0.55 +/- 0.12
Contaminated 70% HTP / 30% TBP + Pure HNO <sub>3</sub> 3M, Ratio 1:1	Ce(+IV)	Cerium(IV) Ammonium Nitrate (NH <sub>4</sub> ) <sub>2</sub> Ce(NO <sub>3</sub> ) <sub>6</sub>	15 / 15	9.7	0.27 +/- 0.03
					0.16 +/- 0.02
					0.19 +/- 0.02
				10.2	0.45 +/- 0.06
					0.58 +/- 0.08
					1.18 +/- 0.15
					2.28 +/- 0.49
					1.97 +/- 0.43
					1.32 +/- 0.29
					1.69 +/- 0.37

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908 Table SI-III: ARF values determined for each Ru(+III) contaminated HTP/TBP solutions

Fuel composition (in volume)	Contaminant	Salt	V <sub>org</sub> / V <sub>aq</sub> (ml)	[Cont <sub>org</sub> ] (g/L)	ARF (%)
Contaminated 70% HTP / 30% TBP	Ru(+III)	Ruthenium(III) Nitrosylnitrate RuNO(NO <sub>3</sub> ) <sub>3</sub>	30 / 0	0.6	0.63 +/- 0.18
					1.81 +/- 0.40
					0.53 +/- 0.18
Contaminated 70% HTP / 30% TBP + Pure HNO <sub>3</sub> 3M, Ratio 1:1			15 / 15		10.35 +/- 7.49
					19.58 +/- 16.04
					7.29 +/- 1.16

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