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# Direct determination of $^{237}\text{Np}$ in nuclear effluent by ICP-MS/MS

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## Keywords

Neptunium 237, nuclear effluent, direct measurement, ICP-MS/MS

## Abstract

A new method for the rapid quantification of neptunium 237 in nuclear effluent was developed. This method is based on the direct measurement of neptunium 237 by ICP-MS/MS on mass-shift mode as  $\text{NpO}$  and using 20% of  $\text{CO}_2$  as a reaction gas. These measurement conditions allowed the obtention of the best signal to noise ratio at  $m/z$  253 ( $^{237}\text{Np}^{16}\text{O}$ ) by the efficient elimination of the interferences due to sensitivity abundance of uranium 238 and hydrides of uranium 235 and uranium 236 while minimizing the elemental fractionation between neptunium and plutonium. Moreover, plutonium 242 can be used as a tracer for neptunium 237 isotopic dilution-based quantification. After an optimization of the measurement parameters, excellent figures of merit were obtained. Indeed, this protocol allows an accurate direct measurement of neptunium 237 in various nuclear effluent containing up to  $2 \mu\text{g.L}^{-1}$  ( $2.4 \text{ Bq.L}^{-1}$ ) of uranium 236 and up to  $20 \text{ mg.L}^{-1}$  ( $250 \text{ Bq.L}^{-1}$ ) of uranium 238 with an excellent accuracy and uncertainties lower than 15%, for sample containing  $10^{-5}$  to  $10^{-1} \mu\text{g.L}^{-1}$  ( $10^{-3}$  to  $13 \text{ Bq.L}^{-1}$ ), and a limit of detection for  $^{237}\text{Np}$  as low as  $4 \text{ pg.L}^{-1}$  ( $10^{-4} \text{ Bq.L}^{-1}$ ).

## Introduction

Neptunium 237 is produced in nuclear reactors following neutron captures of uranium 235 and uranium 236, (n, 2n) reactions when rapid neutrons eject neutrons from uranium 238 and, in lesser extent, neptunium 237 is produced by alpha decay of americium 241<sup>1</sup>. This radionuclide could then be found in nuclear power plants and fuel reprocessing plants releases<sup>2,3</sup>. Neptunium 237 is also present in nuclear effluent where its mass represents only 4-5% of plutonium alpha emitter isotopes. Neptunium 237 is nonetheless of interest due to its longer half-life and its higher mobility than the other transuranic elements. In fact, under most effluent (and environmental) conditions, Np (V) is the most stable oxidation state and forms  $\text{Np(V)O}_2^+$ . The single charge of the double oxide gives then to neptunium its mobility and prevents the formation of stabilized complexes with large ligands<sup>4</sup>.

Neptunium 237 ( $2.14 \times 10^6 \text{ y}$ )<sup>1</sup> quantification is complicated due to the lack of an isotopic tracer. Neptunium has actually only two other isotopes with a half-life higher than 4.5 d (e.g.,  $^{235}\text{Np}$  396.1 d and  $^{236}\text{Np}$   $1.54 \times 10^5 \text{ y}$ )<sup>4-6</sup>. These isotopes couldn't be used to quantify neptunium 237 since neptunium 236 is not commercially available and neptunium 235 solutions often contain neptunium 237 since prepared by bombarding uranium 236 with protons.

Neptunium 237 is often determined by alpha spectrometry or neutron activation analysis (NAA)<sup>2</sup>. These methods require however a long chemical treatment to have thin alpha sources which generates an important sample turnaround time (up to several days). When neptunium 237 is quantified by alpha spectrometry, plutonium chemical protocol is realized and plutonium 236 is used as a tracer to quantify not only neptunium but also plutonium alpha emitters isotopes. The usual tracer e.g., plutonium 242 (4 858 keV)<sup>7,8</sup> can't be used due to energy interference with neptunium 237 (4 788 keV). Plutonium 236 solutions often contain plutonium isotopes as impurities and the use of a chemical analogous as a tracer with such a

complicated radiochemical protocol generates a bias on neptunium 237 determined activity<sup>9</sup>. The generated bias has been estimated to be ~ 30%<sup>8</sup>.

NAA method is 500 times more sensitive than alpha spectrometry and provides very consistent results. This method is however not suitable for the quantification of neptunium 237 in nuclear effluent. In fact, in NAA, <sup>237</sup>Np is formed following the beta emission of <sup>237</sup>U generated by the (n, 2n) reaction on <sup>238</sup>U. This contribution becomes significant in case of an important amount of uranium which is the case of nuclear effluent<sup>10</sup>.

Neptunium 237 can also be quantified by mass spectrometry e.g., AMS<sup>11</sup> and ICP-MS<sup>12,13</sup>. Accelerator Mass Spectrometry (AMS), although could present several advantages, is not accessible due to its cost. When neptunium 237 is quantified by ICP-MS, plutonium 242 can be used as a tracer since there is no interference with neptunium 237. Indeed, when analyzing neptunium 237, the most important interference in ICP-MS is due to uranium isotopes e.g., uranium 238 peak tailing and hydrides of uranium 235 and 236. Some polyatomic compounds could also interfere in lesser extent (e.g., <sup>197</sup>Au<sup>40</sup>Ar<sup>+</sup>, <sup>199</sup>Hg<sup>38</sup>Ar<sup>+</sup>, <sup>201</sup>Hg<sup>36</sup>Ar<sup>+</sup>, <sup>206</sup>Pb<sup>31</sup>P<sup>+</sup>, <sup>203</sup>Tl<sup>34</sup>S<sup>+</sup>, <sup>205</sup>Tl<sup>32</sup>S<sup>+</sup>, <sup>200</sup>Hg<sup>37</sup>Cl<sup>+</sup>, <sup>202</sup>Hg<sup>35</sup>Cl<sup>+</sup>, <sup>205</sup>Tl<sup>16</sup>O<sub>2</sub><sup>+</sup>). The detection limit achieved with ICP-MS is of 0.02 pg.mL<sup>-1</sup> with a conventional quadrupole<sup>14</sup> and as low as fg.mL<sup>-1</sup> or fg.mL<sup>-1</sup> with SF-ICP-MS<sup>15,16</sup> after a chemical treatment<sup>17</sup> which allows reaching a decontamination factor of uranium up to 10<sup>7</sup>. This decontamination factor is however not sufficient when analyzing samples containing a high amount of uranium which is the case of nuclear effluent.

ICP-MS/MS could represent an excellent alternative to quantify neptunium 237 in samples containing a large amount of uranium (e.g., <sup>235</sup>U, <sup>236</sup>U and <sup>238</sup>U)<sup>17-20</sup>. In fact, the MS/MS mode drastically decreases the overlap of uranium 238 peak on neptunium 237 peak due to the sensitive abundance performance (< 10<sup>-10</sup>)<sup>21</sup>. Studies using collision reaction cell (CRC) capabilities to eliminate hydride interferences (e.g., <sup>235</sup>U<sup>1</sup>H<sub>2</sub> and <sup>236</sup>U<sup>1</sup>H) are however

limited<sup>21-23</sup>. Besides, none of these works studied plutonium behavior or the potential element fractionation under the measurement conditions when analyzing complex matrix and using plutonium 242 as a tracer.

The objective of this work is to develop a new method to quantify neptunium 237 by ICP-MS/MS in nuclear effluent containing a high concentration of uranium isotopes. This method aims to be based on the direct measurement of neptunium 237, without any previous chemical treatment, by using MS/MS and CRC capabilities. Indeed, unlike the quantification by alpha spectrometry, any elemental fractionation between neptunium and plutonium must be avoided since the quantification will be based on the isotopic dilution technique using plutonium 242 as a tracer. The limit of detection (LOD) usually obtained by alpha spectrometry when 500 mL of sample are analyzed and the counting time is 48h ( $\sim 10^{-4}$  Bq.L<sup>-1</sup>) has nonetheless to be reached with this new method in order to maintain a high level of analytical performance.

## **Reagents and instrumentation**

### **Reagents**

Nitric, hydrochloric and hydrofluoric acids were prepared from Suprapur-grade acid (Merck, Inc.). Rinsing nitric acid was prepared from Ultrapur-grade acid (Merck, Inc.). All the solutions were prepared with Milli-Q water (18.2 M $\Omega$  cm). For this study, concentration certified <sup>237</sup>Np, <sup>236</sup>U and <sup>242</sup>Pu reference materials are from the NATIONAL PHYSICAL LABORATORY (UK). Uranium reference materials are from SCP SCIENCE (FR) and NEW BRUNSWICK LABORATORY (USA) (e.g., CRM U030 – A). While only uranium concentration is certified in the reference material provided by SCP SCIENCE, the NEW BRUNSWICK LABORATORY provides an isotopic reference material (<sup>235</sup>U/<sup>238</sup>U = 0.031367 (atom/atom)  $\pm$  0,1%), used for the mass bias correction during the measurement step.

High-purity NH<sub>3</sub>, O<sub>2</sub> and CO<sub>2</sub> (>99.99%) used in the CRC are from AIR PRODUCTS (FR).

## Instrumentation

Measurements were performed using an Agilent 8900 ICP-MS/MS from AGILENT TECHNOLOGIES (JPN). This ICP-MS/MS is equipped with a CRC with four gas lines to which four different gases could be connected. During the present study, NH<sub>3</sub> was introduced in the 3<sup>rd</sup> gas line while O<sub>2</sub> and CO<sub>2</sub> were independently introduced in the 4<sup>th</sup> gas line.

To improve the sensitivity by up to 10 times, a high sensitivity desolvating system (APEX  $\Omega$ ) with an included additional desolvating membrane from ELEMENTAL SCIENTIFIC (FR) was used as sample introduction system.

ICP-MS/MS and APEX  $\Omega$  parameters are daily optimized using a solution containing natural U (1  $\mu\text{g.L}^{-1}$ ) and Np (0.1  $\mu\text{g.L}^{-1}$ ). Optimization criteria are the maximization of Np sensitivity and the minimization of U hydrides formation. The experimental parameters of the Apex  $\Omega$  and the ICP-MS/MS are listed in table 1.

**Table 1 - Experimental parameters of the Apex  $\Omega$  and the ICP-MS/MS.**

<b>APEX-<math>\Omega</math></b>	
Sample uptake rate	0.1 mL.min <sup>-1</sup>
Nitrogen	2.66 mL.min <sup>-1</sup>
Argon	4.55 mL.min <sup>-1</sup>
Spray Chamber temperature	140 °C
Peltier Cooler temperature	3 °C
Desolvator temperature	155 °C
Peripump flow	0.6 mL.min <sup>-1</sup>
<b>ICP-MS/MS</b>	
RF power	1520 W
RF matching	1.85 V
Sampling depth	8 mm
Nebulizer gas flow rate	1.34 L.min <sup>-1</sup>
Extraction lens 1; 2	-28 V; -250 V
Deflect	11 V
Energy discrimination	-8 to -4 V
Axial acceleration	0 V
Plate bias	-60 V
Octupole bias	-24.5 V
Cell entrance	-85 V
Cell exit	-93 V

For each analytical session, monitored m/z in MS mode (single quad) are 234 – 242. In MS/MS mode, monitored m/z depend on the injected gas in the CRC and whether the detection is performed in on-mass or mass-shift mode. For each sample injection, 5 replicates are performed with 300 sweeps and 1 point per peak.

To avoid any cross contamination, the introduction system is rinsed after each sample using three solutions and the same measurement parameters, successively: HNO<sub>3</sub>/HCl/HF suprapur-grade (2%/1%/0.2%, Wt/Wt), HNO<sub>3</sub> suprapur-grade (2%, Wt/Wt) and HNO<sub>3</sub> ultrapur-grade (2%, Wt/Wt). Counts on m/z 237 after the rinse procedure are lower than 5 cps.

## **Samples**

For the method development, spiked acidic solution (HNO<sub>3</sub> 2%) were prepared. To verify the accuracy of the method, eight nuclear effluents from various installations with and without <sup>237</sup>Np spike were used as reference materials.

## **Results and discussion**

### Results interpretation method

Obtained results interpretation is based on Signal/Noise (S/N) comparison, where S is the signal obtained at m/z 237 when measuring the Np solution (<sup>237</sup>Np) and N is the signal obtained at m/z 237 when measuring the U solutions. In this later case the signal obtained at m/z 237 in MS/MS mode is mainly due to <sup>236</sup>U<sup>1</sup>H. The LOD is in fact directly related to the measured S/N ratio since determined using eq. 1.

#### **Eq. 1 – Limit of detection**

$$LOD = n \times N + 3 \times N_{STD}$$

*Where n is repetition number and N<sub>STD</sub> is N standard deviation for n measurement (n is at least = 3)*

Measurement parameters selection will be based not only on the parameters which allow having the highest S/N ratio and so the lowest LOD but also allow minimizing the elemental



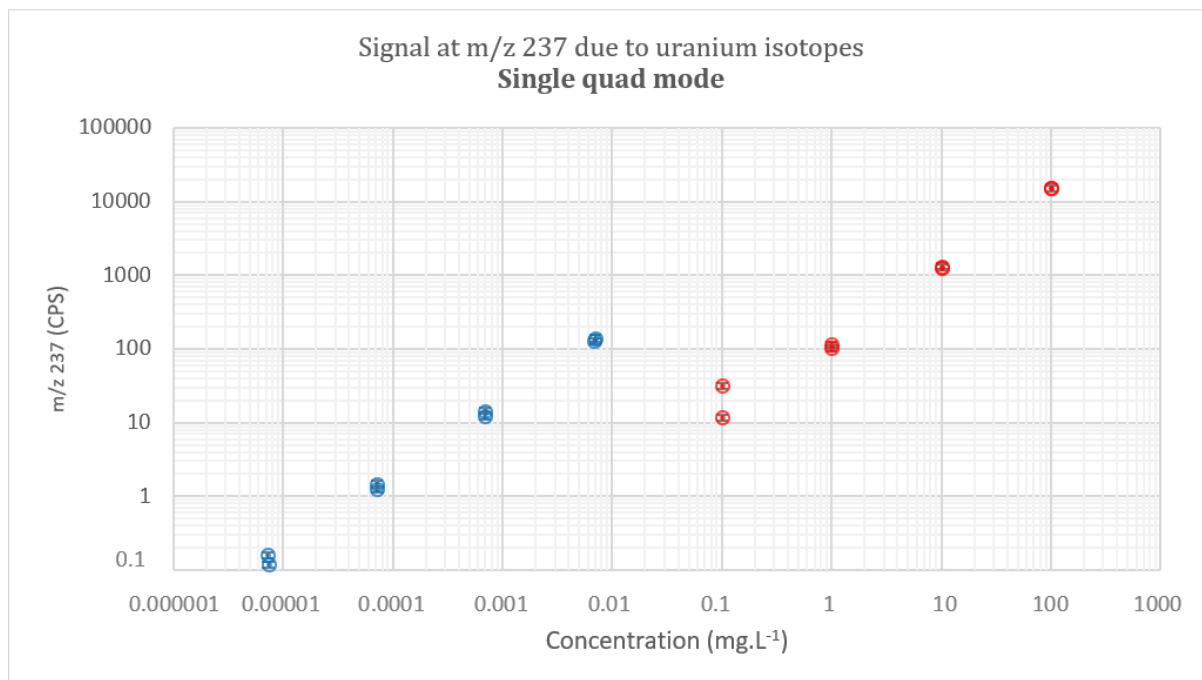
fractionation between neptunium and plutonium since  $^{242}\text{Pu}$  will be used as a tracer for the isotopic dilution-based quantification of  $^{237}\text{Np}$ . Indeed, minimizing this elemental fractionation is necessary to avoid any bias on the determined  $^{237}\text{Np}$  concentration and any shift due to matrix effect.

#### Sensitivity abundance induced interference

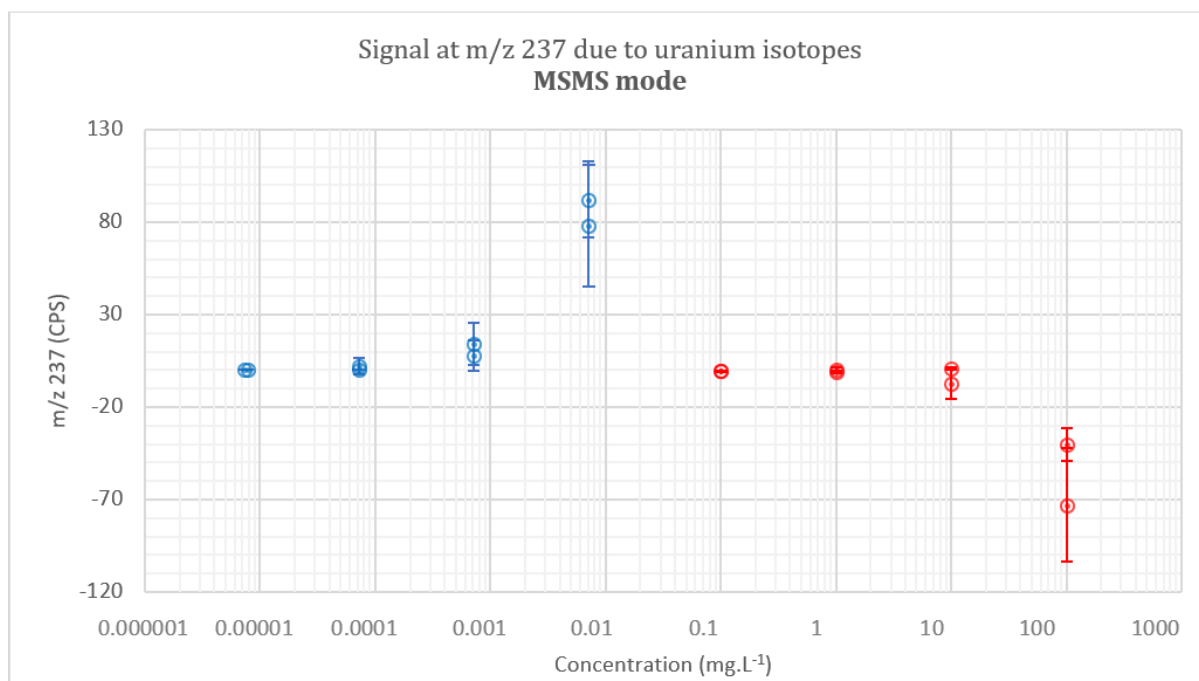
Analyzed nuclear effluent in France usually contain a high concentration of uranium isotopes. These concentrations can reach  $2 \mu\text{g.L}^{-1}$  of  $^{236}\text{U}$  and  $20 \text{mg.L}^{-1}$  of  $^{238}\text{U}$ .

Figure 1 shows signal (cps) generated at m/z 237 when an acidic solution ( $\text{HNO}_3$  2%) containing only  $^{236}\text{U}$  (blue curve) or uranium with a naturally occurring isotopic composition (red curve) are analyzed. Signal at m/z 237 represented by the blue curve is generated by  $^{236}\text{U}$  hydrides ( $^{236}\text{U}^1\text{H}$ ) while the signal represented by the red curve could be due to  $^{235}\text{U}$  double hydride formation ( $^{235}\text{U}^1\text{H}_2$ ) but mainly due to the abundance of  $^{238}\text{U}$  and the overlap of its peak on m/z 237. This latter interference is easily eliminated when using the MS/MS mode. Indeed, figure 2 highlights the MS/MS capabilities since the counts at m/z 237 due to  $^{238}\text{U}$  peak overlap are eliminated, for counts to  $10^{12}$  at m/z 238 (red curve). These results point up that the interference due to  $^{235}\text{U}^1\text{H}_2$  is negligible since solutions of  $^{238}\text{U}$  contain up to  $10^8$  counts of  $^{235}\text{U}$ , signal at m/z 237 is nonetheless undetectable. Even if the counts at m/z 237 due to  $^{236}\text{U}$  hydride are lowered in the MS/MS measurement mode, this interference is not effectively eliminated. Indeed, 20 counts are generated at m/z 237 when  $^{236}\text{U}$  concentration is  $2 \mu\text{g.L}^{-1}$ , which is the typical  $^{236}\text{U}$  concentration measured in the analyzed effluent. This interference could reach 90 cps if samples containing  $9 \mu\text{g.L}^{-1}$  are analyzed (figure 2). With measurement conditions detailed in table 1, 20 counts at m/z 237 correspond to a concentration of  $\approx 7.7 \times 10^{-4} \mu\text{g.L}^{-1}$  ( $\approx 0.02 \text{Bq.L}^{-1}$ ). This concentration is much higher than the target LOD usually obtained when the quantification is performed by alpha spectrometry ( $\approx 5 \times 10^{-4} \text{Bq.L}^{-1}$ ). The objective is to eliminate the interference caused by the peak overlap

of  $^{238}\text{U}$  as well as the interference caused by  $^{236}\text{U}^1\text{H}$  while maintaining a sensitivity high enough to be able to reach the target LOD usually obtained by alpha spectrometry.



**Figure 1 - signal generated at m/z 237 when  $^{236}\text{U}$  (blue) and  $^{238}\text{U}$  (red) solutions are measured in single quad mode - Uncertainties are extended with a coverage factor of 2. Presented uncertainties could be very small since only related to the measurement; on some occasions included in the size of the dot.**



**Figure 2 - signal generated at m/z 237 when  $^{236}\text{U}$  (blue) and  $^{238}\text{U}$  (red) solutions are measured in MS/MS mode - Uncertainties are extended with a coverage factor of 2. Presented uncertainties could be very small since only related to the measurement; on some occasions included in the size of the dot.**

### $^{236}\text{U}$ hydride interference

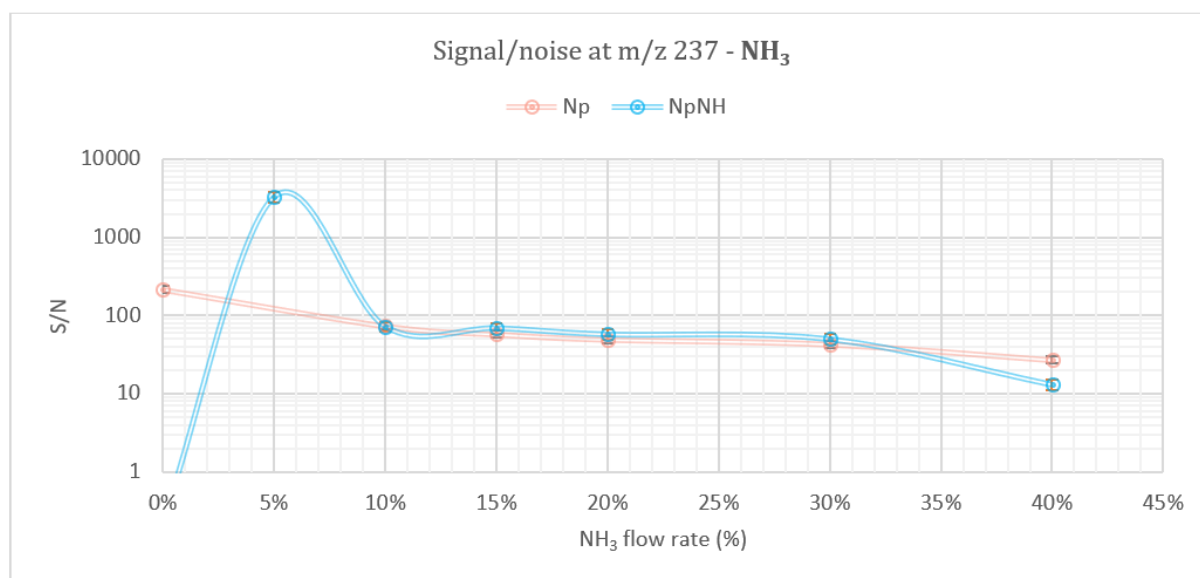
To eliminate the interference at m/z 237 due to  $^{236}\text{U}$  hydride, CRC capabilities was used with three different gases (e.g.,  $\text{O}_2$ ,  $\text{NH}_3$  and  $\text{CO}_2$ ). To determine the optimal measurement conditions, 3 solutions (e.g.,  $^{238}\text{U}$  at  $100\ \mu\text{g}\cdot\text{L}^{-1}$ ,  $^{236}\text{U}$  at  $2\ \mu\text{g}\cdot\text{L}^{-1}$  and  $^{237}\text{Np} + ^{242}\text{Pu}$  at  $0.1\ \mu\text{g}\cdot\text{L}^{-1}$  and  $0.1\ \text{ng}\cdot\text{L}^{-1}$  respectively) were measured.

Figures 3, 4 and 5 show S/N ratios obtained when  $\text{NH}_3$ ,  $\text{O}_2$  and  $\text{CO}_2$  are introduced respectively in the CRC.

$\text{NH}_3$  proved its efficiency for an accurate determination of Pu isotopes in samples containing a high concentration of uranium isotopes<sup>24</sup>. According to Xu *et al.* study, the interference due to uranium hydride ( $^{238}\text{U}^1\text{H}$  and  $^{238}\text{U}^1\text{H}_2$ ) is eliminated by shifting uranium to  $\text{U}(\text{NH}_m)_n^+$  and  $\text{UH}(\text{NH}_m)_n^+$  while Pu is measured on on-mass mode.

When  $\text{NH}_3$  is introduced in the CRC (figure 3), neptunium has the same behavior as plutonium and remains at 90% under the form of Np while 8% of neptunium is under the form of  $\text{NpNH}$ . Other minority  $\text{NpN}_x\text{H}_y$  clusters are also formed but the formed fractions remain negligible. At such uranium concentrations, even if the interference (e.g.,  $^{236}\text{U}^1\text{H}$ ) is minimized when Np is quantified in on-mass mode, it remains significant, and the highest S/N ratio is obtained when the quantification is performed in mass-shift mode when introducing 5% of  $\text{NH}_3$ . In fact, at this  $\text{NH}_3$  flow rate, a fraction of Np is already under the form of  $\text{NpNH}$  while uranium hydrides (e.g.,  $^{236}\text{U}^{15}\text{N}^1\text{H}_2$ ) formation is still insignificant. In this case, when quantifying Np in mass-shift mode as  $^{237}\text{Np}(^{15}\text{N}^1\text{H})$ , the determined LOD is  $3 \times 10^{-3}\ \text{Bq}\cdot\text{L}^{-1}$

which is one order of magnitude higher than the LOD obtained when the quantification is performed by alpha spectrometry.



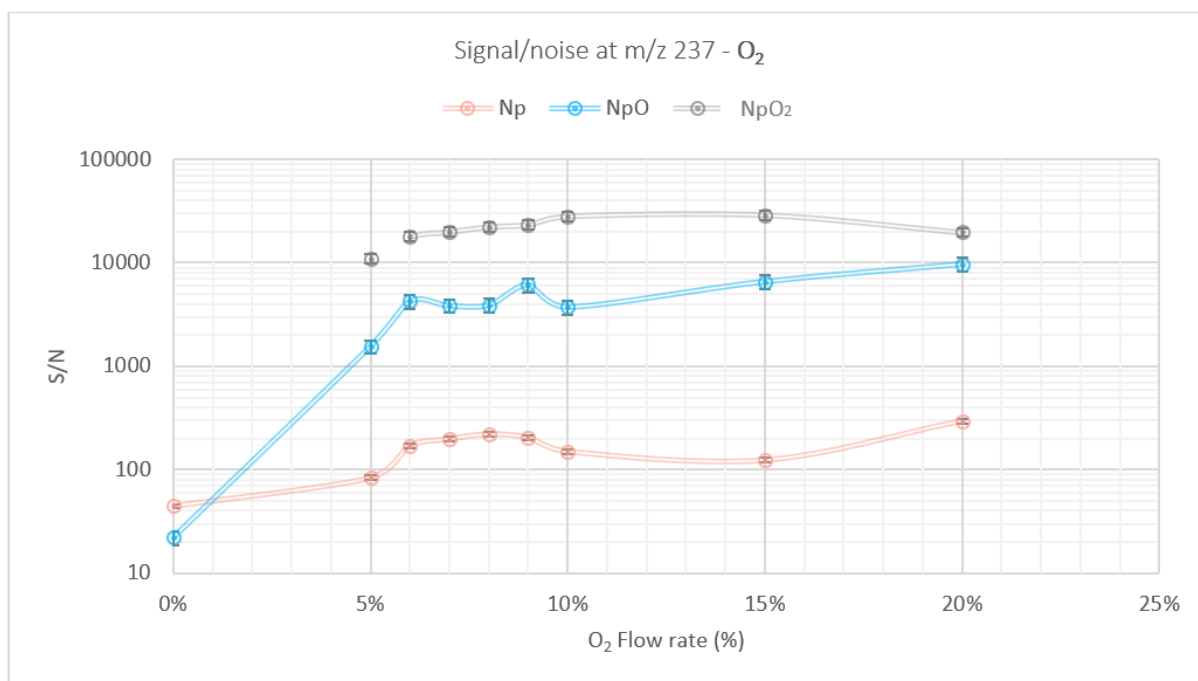
**Figure 3 - S/N at m/z 237 when NH<sub>3</sub> is used as a reaction gas - Uncertainties are extended with a coverage factor of 2. Presented uncertainties could be very small since only related to the measurement; on some occasions included in the size of the dot.**

Results presented figure 3 highlighted the fact that NH<sub>3</sub> is not suitable for this application.

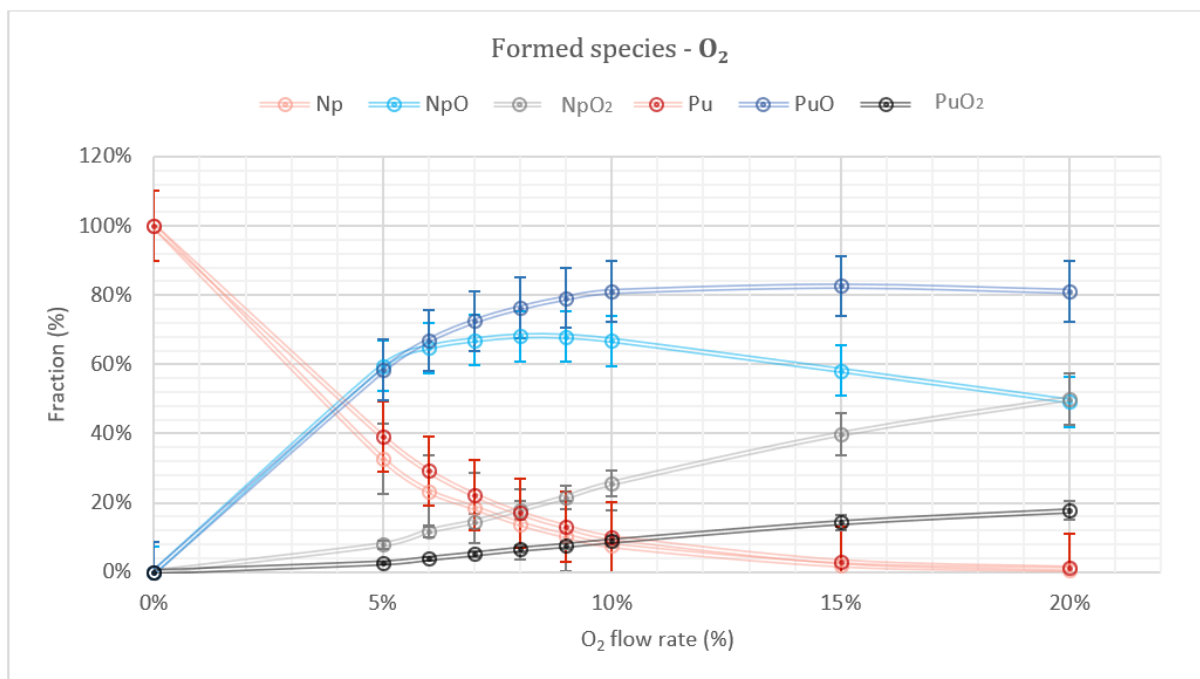
The introduction of oxidizing gases in the CRC (e.g., O<sub>2</sub>, NO<sub>2</sub>...) has proven its efficiency to form uranium oxides (UO and UO<sub>2</sub>) and to significantly decrease uranium polyatomic interferences such as hydrides<sup>20</sup>.

Figure 4 shows S/N ratios obtained for different flow rates of O<sub>2</sub> when the quantification of neptunium is based on the measurement of Np (on-mass mode), NpO and NpO<sub>2</sub> (mass-shift mode). When using O<sub>2</sub> as a reaction gas, the highest S/N is obtained for NpO<sub>2</sub> mass-shift mode quantification. This S/N ratio, when O<sub>2</sub> flow rate is between 10 and 15%, is even 10 times higher than the one obtained at NH<sub>3</sub> 5% for NpNH mass-shift mode quantification. Furthermore, figure 6 shows that whether the O<sub>2</sub> flow rate is between 5 and 20%, the

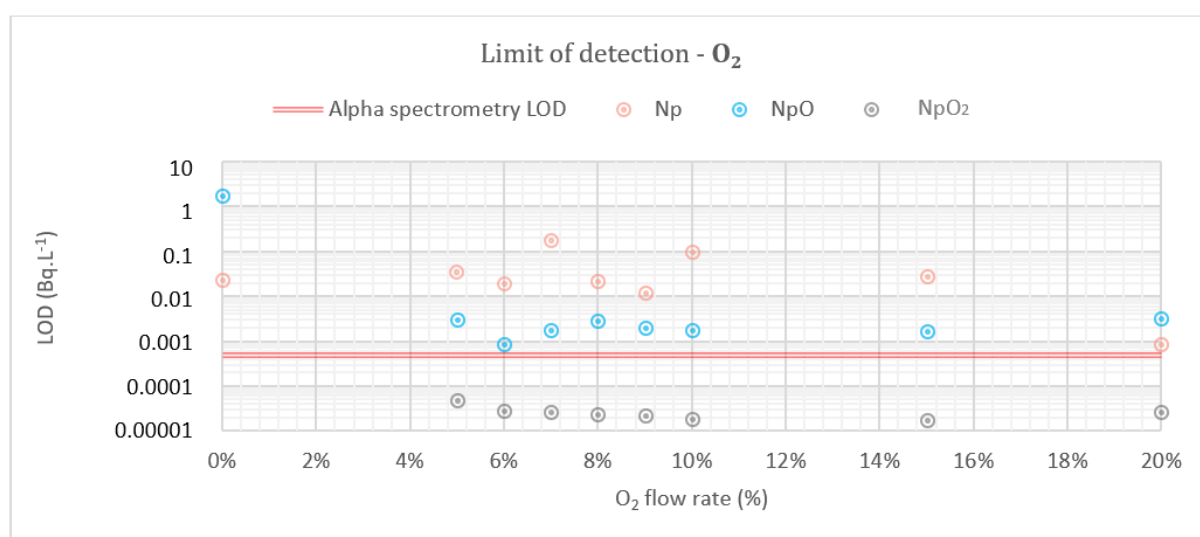
experimental LOD, when the quantification is performed on mass-shift mode for  $\text{NpO}_2$ , is lower than the LOD obtained by alpha spectrometry. Indeed, more the flow rate of  $\text{O}_2$  increases, more the fraction of neptunium under the form of  $\text{NpO}_2$  is important and reach 50% for a flow rate of 20% (figure 5). The S/N (and so the LOD) don't proportionally increase due to both the gas-induced dilution and the increase of the fraction of  $\text{UO}_2$  and so  $\text{UO}_2\text{H}$ . Figure 5 also shows that under the same conditions, plutonium is hardly double oxidized and remains under the form of  $\text{PuO}$  (80% at 20% of  $\text{O}_2$ ). A fractionation is then observed between neptunium and plutonium which will induce a bias on  $^{237}\text{Np}$  quantification when this later is based on isotopic dilution with  $^{242}\text{Pu}$  as a tracer. This bias could reach 60% for  $\text{O}_2$  flow rate of 20% (figure 5) and could be higher when analyzing complex matrix.



**Figure 4 - S/N at m/z 237 when  $\text{O}_2$  is used as a reaction gas - Uncertainties are extended with a coverage factor of 2. Presented uncertainties could be very small since only related to the measurement; on some occasions included in the size of the dot.**



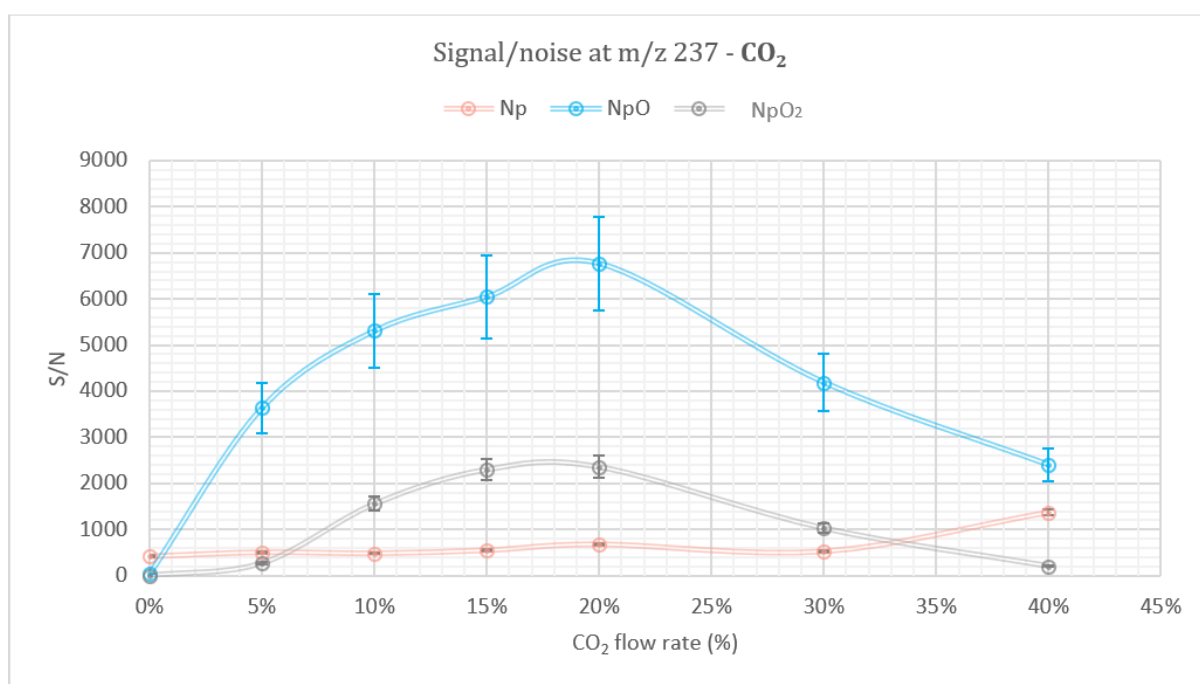
**Figure 5 - Np and Pu detected species when O<sub>2</sub> is used as a reaction gas - Uncertainties are extended with a coverage factor of 2. Presented uncertainties could be very small since only related to the measurement; on some occasions included in the size of the dot.**



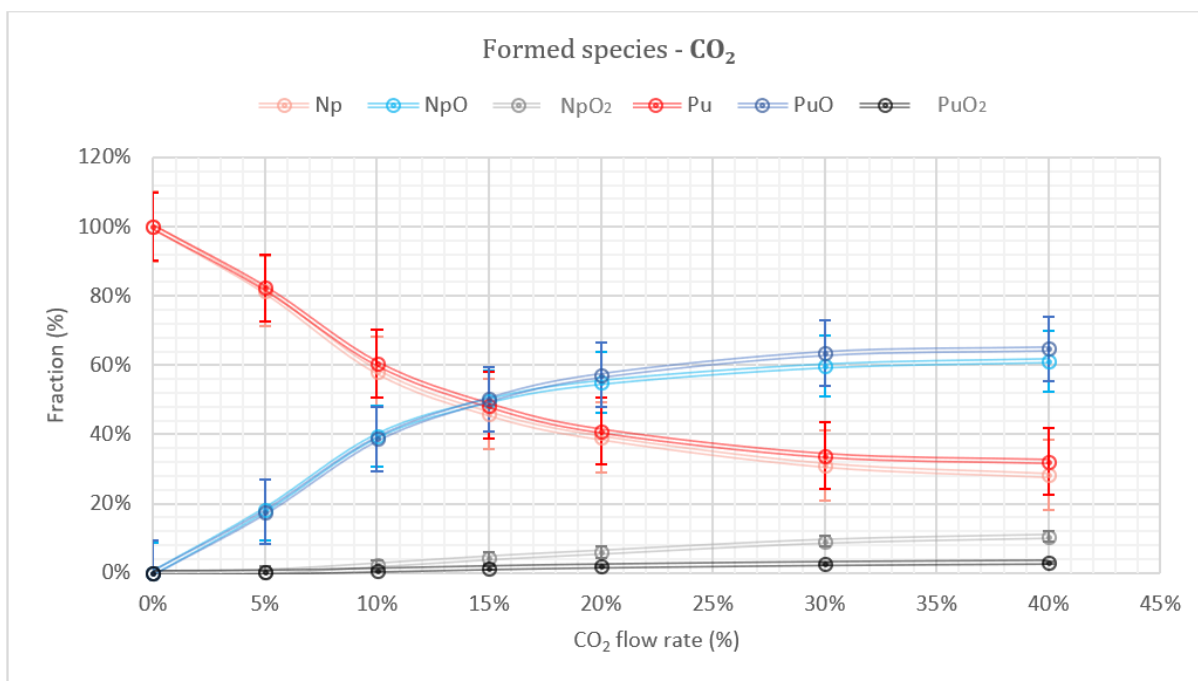
**Figure 6 - limit of detection of <sup>237</sup>Np when O<sub>2</sub> is used as a reaction gas - Uncertainties are extended with a coverage factor of 2.**

CO<sub>2</sub> was then used in the CRC as a less oxidizing gas<sup>25</sup> with the aim of maintaining Np under the form of NpO and thus avoid the double oxidation of neptunium. In this case, at 20% of CO<sub>2</sub>, the S/N is almost 7000 (figure 7). This S/N is lower than all those obtained by O<sub>2</sub> but the fact that a less oxidizing gas is used allows minimizing the formation of NpO<sub>2</sub> and

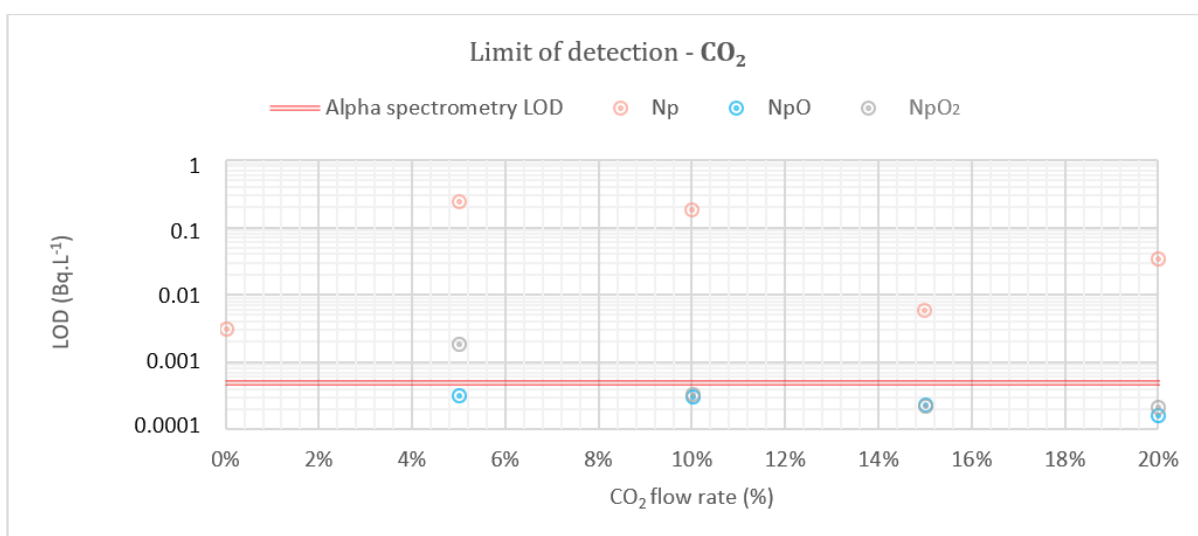
maximizing NpO fraction (figure 8). The advantage of CO<sub>2</sub>, especially 20% of flow rate, is double. First, the S/N at 20% is sufficient to obtain an LOD ( $1.6 \times 10^{-4}$  Bq.L<sup>-1</sup>) lower than the one obtained in alpha spectrometry (figure 9). This is due to not only the maximization of <sup>237</sup>Np<sup>16</sup>O formation but also to the minimization of <sup>236</sup>U<sup>16</sup>O<sup>1</sup>H formation. Furthermore, the CRC conditions in mass-shift mode (CO<sub>2</sub> 20%, KED -10 V and axial acceleration 2 V) allows having very similar behavior between plutonium and neptunium (figure 8). Pu and Np fractionation is then avoided.



**Figure 7 - S/N at m/z 237 when CO<sub>2</sub> is used as a reaction gas - Uncertainties are extended with a coverage factor of 2. Presented uncertainties could be very small since only related to the measurement; on some occasions included in the size of the dot.**



**Figure 8 - Np and Pu detected species when CO<sub>2</sub> is used as a reaction gas - Uncertainties are extended with a coverage factor of 2. Presented uncertainties could be very small since only related to the measurement; on some occasions included in the size of the dot.**



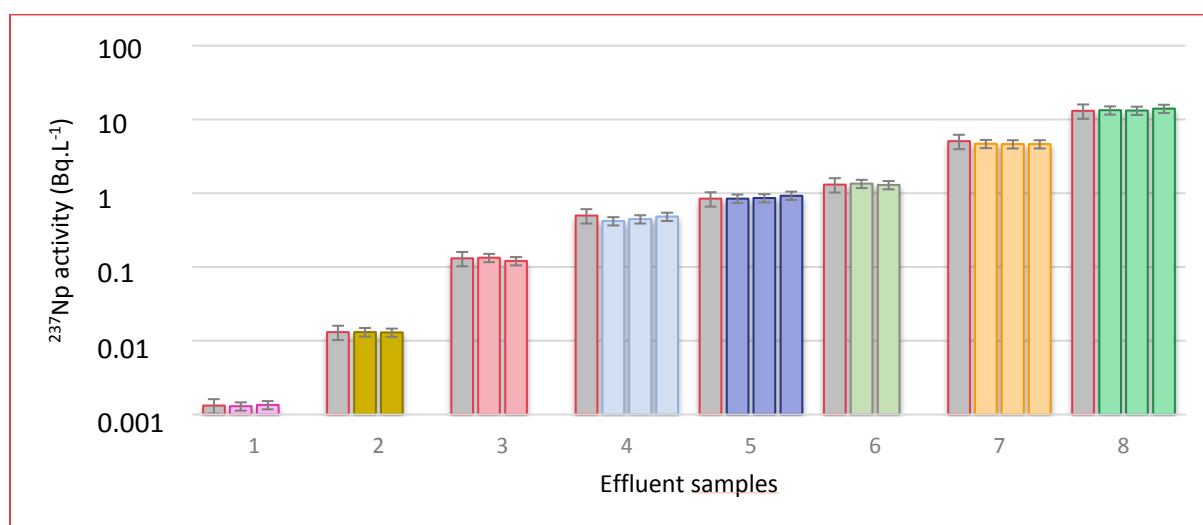
**Figure 9 - limit of detection of <sup>237</sup>Np when CO<sub>2</sub> is used as a reaction gas.**

### Method validation with nuclear effluent samples

The newly developed method with CO<sub>2</sub> gas was then applied to various effluent samples, containing 2 µg.L<sup>-1</sup> of <sup>236</sup>U and 20 mg.L<sup>-1</sup> of <sup>238</sup>U, to quantify <sup>237</sup>Np (figure 10). These samples have been spiked with ≈ 0.02 Bq of <sup>242</sup>Pu and directly introduced in the ICP-MS/MS, without any previous chemical treatment. For samples 1, 2 and 3, <sup>237</sup>Np reference activities



were obtained by the analysis of 3 replicates of each sample by alpha spectrometry. Samples 4 to 8 are spiked nuclear effluent samples in which  $^{237}\text{Np}$  activities are initially below the limit of detection of the developed method. Spiked activities are 0.5, 0.85, 1.3, 5.1 and 13.1  $\text{Bq}\cdot\text{L}^{-1}$ ). In addition to the measurement conditions summarized in table 1,  $\text{CO}_2$  at a flow rate of 20% was introduced in the CRC and the quantification was performed in mass-shift mode and based on the isotopic dilution with Np and Pu under the form of  $\text{NpO}$  and  $\text{PuO}$ .



**Figure 10 - effluent samples analyzed with the newly developed method – reference activities in gray – Each color represents the replicate measurement for each activity level - Uncertainties are extended with a coverage factor of 2.**

Excellent figures of merit have been obtained with the new method. Indeed, figure 10 shows that results obtained using the ICP-MS/MS mass-shift mode are repeatable (at least 2 replicates for each sample) with relative standard deviations (RSD) lower than 6%. Furthermore, measured activities are in accordance with the reference values (in gray) with calculated relative deviations (Eq. 2) from 0.2% to 11%. Due to the direct quantification based on isotopic ratios, uncertainties obtained with the newly developed method ( $\approx 10\%$ ) are two times lower than those of the reference activities ( $\approx 20\%$ ).

## Eq. 2 – Relative deviation

$$R_d(\%) = |\text{reference activity} - \text{measured activity}| / \text{reference activity}$$

### Conclusion

A new measurement method was developed to quantify  $^{237}\text{Np}$ , using  $^{242}\text{Pu}$  as tracer, in effluent samples with a high amount of uranium isotopes (e.g.,  $^{236}\text{U}$  and  $^{238}\text{U}$ ). This method is simple and robust since the measurement is performed with ICP-MS/MS without any previous chemical treatment. The measurement procedure is based on mass-shift mode quantification where  $\text{CO}_2$  (20%) is used as a reaction gas. In these conditions, interferences of uranium hydrides and peak tailing from  $^{238}\text{U}^+$  are successfully eliminated. Furthermore, this quantification procedure minimizes the elemental fractionation of Pu and Np,  $^{242}\text{Pu}$  can thus be used as a tracer. The reliability, repeatability, and stability of the method were validated through the analysis of several effluent samples with known  $^{237}\text{Np}$  activities. This new method allows reaching a limit of detection for  $^{237}\text{Np}$  of  $4 \text{ pg.L}^{-1}$  ( $10^{-4} \text{ Bq.L}^{-1}$ ).

### Conflicts of interest

There are no conflicts to declare.

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