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# Quantifying the accurate content of $^{107}\text{Pd}$ in a radioactive effluent using the isotope dilution technique and multi-collector ICP-MS

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## ABSTRACT

The radionuclide  $^{107}\text{Pd}$  is a long-lived fission product that decays to  $^{107}\text{Ag}$  by  $\beta^-$  emission. The accurate quantification of the  $^{107}\text{Pd}$  content in nuclear waste is essential in compliance with international regulations on the long-term storage of radioactive waste. Moreover, fission-produced Pd holds an economic interest through its recycling for industrial purposes. The accurate quantification of  $^{107}\text{Pd}$  is presently problematic due to the absence of a commercial reference material certified for  $^{107}\text{Pd}$  content, and because of the scarcity of  $^{107}\text{Pd}$ -concentrated materials. In this study, we accurately characterize a purified radioactive effluent for its  $^{107}\text{Pd}$  content using multicollector (MC)-ICP-MS and the isotope dilution technique. The developed isotope-dilution method is based on the preparation and calibration of a  $^{108}\text{Pd}$ -enriched commercial spike solution. The repeatability of Pd isotope ratios in the radioactive effluent as obtained by MC-ICP-MS was on the order of 0.05 % (2\*standard deviation of  $n = 15$  measurements). The  $^{107}\text{Pd}$  content in the radioactive effluent was accurately quantified with an expanded uncertainty of 0.7 % at  $k = 2$ . The results obtained from the radioactive effluent are metrologically traceable to the International System of Units (SI). Lastly, the sources of uncertainty and their relative contribution on the final expanded uncertainty were determined and evaluated.

## 1. Introduction

Stable and radiogenic palladium isotopes are both present in spent nuclear fuel, and therefore in the acidic high-level liquid waste and high-level solid waste [1]. Among the palladium isotopes,  $^{107}\text{Pd}$  is a long-lived radionuclide produced from the fission of  $^{235}\text{U}$  and  $^{239}\text{Pu}$  [2,3; and references therein].  $^{107}\text{Pd}$  has a half-life of  $6.5 \pm 0.3$  million years and disintegrates to  $^{107}\text{Ag}$  by  $\beta^-$  decay [4]. There is thus the obligation to evaluate the radioactivity contribution of  $^{107}\text{Pd}$  for the long-term storage of radioactive waste, in compliance with the strict regulations and safety evaluations [5]. A better knowledge of  $^{107}\text{Pd}$  is essential as dismantling and decommissioning (D&D) of nuclear facilities are increasing worldwide. It is noteworthy that the D&D activities also require the characterization of other long-lived radionuclides such as  $^{93}\text{Zr}$ . Furthermore, the recycling of fission-produced Pd holds an economic interest for its high value in industrial fields such as the locomotive, electronic, and catalysis industries [1,6,7]. Consequently, it is necessary to quantify accurately the  $^{107}\text{Pd}$  content in radioactive waste.

$^{107}\text{Pd}$  must be purified prior to analyses regardless of the

measurement technique. The measurement of  $^{107}\text{Pd}$  using radiochemical methods has been historically difficult due to its radiochemical and radiological properties. As a  $\beta^-$  emitter,  $^{107}\text{Pd}$  can be quantified by liquid scintillation counting (LSC) but it must be isolated from the other radiation emitters, in particular the low-energy  $\beta$  emitters. Additionally, the detection efficiency with LSC is quite low due to the low-energy  $\beta$ -rays emitted by  $^{107}\text{Pd}$  (34 KeV; [8]), rendering it difficult to detect with this technique [9,10]. As  $^{107}\text{Pd}$  has a low specific activity due to its long half-life, mass spectrometry (MS) techniques have been considered to quantify  $^{107}\text{Pd}$  with a better sensitivity in comparison to radiometric techniques [3,11].

Few recent studies have quantified  $^{107}\text{Pd}$  in radioactive samples using MS instruments. Asai et al. [11] measured  $^{107}\text{Pd}$  using a single quadrupole ICP-MS following the selective extraction of Pd from a spent nuclear fuel solution using photoreduction induced by laser irradiation. Further studies quantified  $^{107}\text{Pd}$  using ICP-MS in zirconium radioactive hulls [12], in radioactive waste from the Fukushima Daiichi Nuclear Power Plant [13], and in irradiated  $^{107}\text{Pd}$ -concentrated samples [14]. Recently, Weller et al. [3] measured  $^{107}\text{Pd}$  in contaminated

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environmental samples by purifying the samples with ion-exchange resins and using the collision-reaction cell (CRC) technology with ICP-MS/MS. Palladium-107 ( $m/z$  107) was measured by “mass-shift” as  $^{107}\text{PdC}_2\text{H}_4^+$  and  $^{107}\text{PdC}_3\text{H}_6^+$  ( $m/z$  135 or 149). The “mass-shift” reaction was achieved using propane/He gases in the CRC, and the reported  $^{107}\text{Pd}$  detection limit was  $<2$  ng/kg. This method allowed to eliminate known interferences on the  $m/z$  107, such as those isobaric ( $^{107}\text{Ag}$ ) and polyatomic (oxides,  $^{91}\text{Zr}^{16}\text{O}^+$ ; hydrides,  $^{106}\text{PdH}^+$ ), for a Pd:Ag ratio not exceeding 10:1.

However, for all aforementioned studies, the  $^{107}\text{Pd}$  quantification methods could not be validated due to the absence of a commercial reference material for the  $^{107}\text{Pd}$  content. Indeed,  $^{107}\text{Pd}$ -concentrated materials are scarce and expensive and above all, did not undergo a standardization process according to metrological specifications in order to be used as reference materials [14,15]. Moreover, as regulations are becoming more restrictive on radioactive waste storage, high accuracy is required for the quantification of  $^{107}\text{Pd}$  in radioactive materials. This demonstrates the need for a certified Pd reference material with a certified isotopic composition and total  $^{107}\text{Pd}$  content, which could be utilized by nuclear analysis laboratories for calibration purposes.

Thus, the objective of this study is to characterize accurately a radioactive effluent for its isotopic composition and total Pd content, such that this sample can be used as a  $^{107}\text{Pd}$  concentration standard to validate quantification measurements in other study cases. Consequently, we developed a method to quantify accurately (at per-mil level) the atomic abundance of  $^{107}\text{Pd}$  and the total Pd content using the isotope dilution technique. The isotope dilution technique employs the measurement of isotopic ratios using multi-collector (MC)-ICP-MS, and is considered as a quantitative method of high metrological standing [16,17]. Accordingly, the analytical strategy consisted in well-constraining the isotopic measurement method using MC-ICP-MS, followed by accurately quantifying the total Pd content in a  $^{108}\text{Pd}$ -enriched spike solution using “reverse” isotope dilution. Then, the total  $^{107}\text{Pd}$  content in the radioactive effluent was accurately quantified using the isotope dilution technique and the  $^{108}\text{Pd}$ -enriched spike solution. Lastly, using the isotope dilution technique, the sources of uncertainty and their percentage contribution on the quantified Pd contents were well constrained and evaluated.

## 2. Materials and methods

The materials utilized such as Savillex™ PFA vials and Teflon™ FEP bottles were cleaned with concentrated HCl acid, whereas Sarstedt<sup>KG</sup> PP tubes were cleaned with HCl 9 %. All materials were then rinsed using Milli-Q® water (Merck) and dried before use. The nitric and hydrochloric acids are of high purity (PlasmaPURE Plus, SCP SCIENCE). The blank level was also controlled in all vials and bottles beforehand by measuring the Pd and Ag concentrations using ICP-MS (iCAP™ RQ, Thermo Scientific™) in HNO<sub>3</sub> 2 % solution. All Pd and Ag blank concentrations quantified were less than 10 pg/mL. The concentration of Ag has to be controlled because it has two naturally occurring isotopes  $^{107}\text{Ag}$  ( $51.839 \pm 0.008$  %,  $k = 2$ ; [18]) and  $^{109}\text{Ag}$  ( $48.161 \pm 0.008$  %,  $k = 2$ ), the former is an isobar of  $^{107}\text{Pd}$  and interferes on its mass during isotopic analysis. Furthermore, the Pd NIST 3138 standard reference material (SRM®, Lot No. 090629) was used in this study. The NIST 3138 certificate analysis shows a certified Pd mass fraction at  $10.004 \pm 0.016$  mg/g ( $k = 2$ ), conditioned in HCl 10 % for solution stability.

Laboratory preparations for the isotope dilution technique as well as isotopic measurements were done at the Laboratoire de développement Analytique Nucléaire, Isotopique et Élémentaire (LANIE) of the French Alternative Energies and Atomic Energy Commission (CEA) at Paris-Saclay in France. The dilution of the radioactive effluent and its radiochemical purification were performed at the Laboratoire d'Analyse en Soutien aux Exploitants (LASE) of the CEA at Paris-Saclay in France.

### 2.1. Radioactive effluent

The radioactive effluent containing  $^{107}\text{Pd}$  originated from a concretion of precipitates formed in the piping of a nuclear facility [19]. For this study, the effluent was initially acquired as a solution conditioned in HCl 2 %, at an approximate total Pd content of 280 µg/g. The effluent solution was purified beforehand by liquid-liquid extraction with dimethylglyoxime and anion-exchange chromatography using the AG1-X8 resin (100–200 mesh) [20]. A working solution was prepared at approximately 28 µg/g total Pd by sampling 2 mL from the effluent solution and diluting the taken volume in a total volume of 20 mL with HCl 2 %.

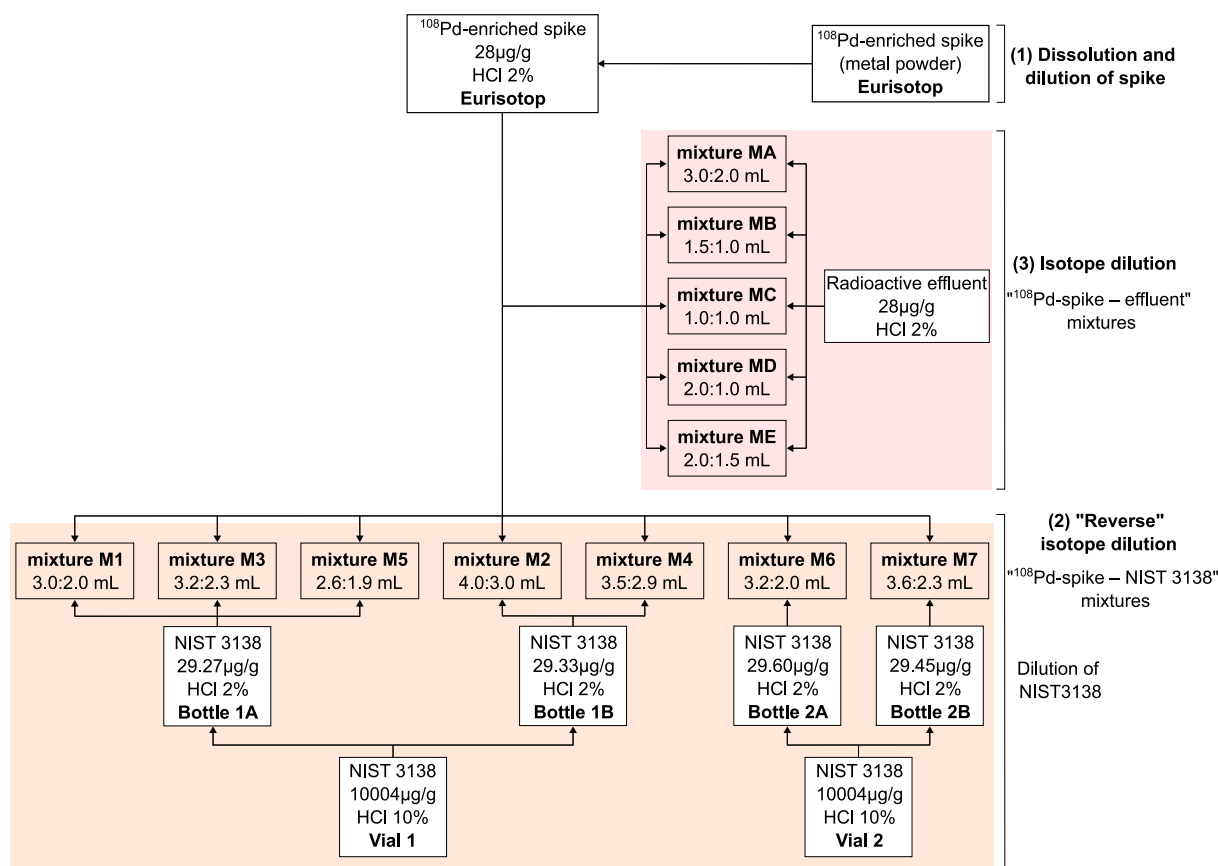
Moreover, the working solution was further purified by an additional chromatography purification step on Ni-resin® bearing dimethylglyoxime molecules [20]. Following the method developed by Dulanská et al. [10], Ni-resin® conditioning, sample loading and washing were performed with 0.5 M HCl, and Pd was eluted using 15 M HNO<sub>3</sub>. Both solutions, before and after the additional chemical purification, were analyzed for their Pd isotopic composition in order to quantify the total Pd content in the radioactive effluent by the isotope dilution technique. The additional chemical purification of the radioactive effluent allows verifying the absence of  $^{107}\text{Ag}$  (isobar) upon the reception of the effluent solution.  $^{107}\text{Ag}$  could have originated from a natural contamination or from the decay of  $^{107}\text{Pd}$  [4].

### 2.2. $^{108}\text{Pd}$ -enriched spike

The  $^{108}\text{Pd}$ -enriched spike was bought from Eurisotop (France), and was provided in the form of a metal powder (reference: MPD108M, Lot W2981). The  $^{108}\text{Pd}$ -enriched spike was chosen for the isotope dilution because  $^{108}\text{Pd}$  is not very abundant in the radioactive effluent, as initially estimated from a semi-quantitative analysis using ICP-MS. Approximately 60 mg of the spike metal powder was dissolved in a Savillex™ vial with a concentrated solution of HNO<sub>3</sub>:HCl (5:1). The concentrated acid solution was heated at 120 °C for a few days until complete dissolution was visually verified. Afterwards, the concentrated acid solution was evaporated, and the residue was conditioned in 10 mL HCl 10 % ( $\approx 6378$  µg/g) for storage. Subsequently, a working solution was prepared at an approximate Pd content of 28 µg/g diluted in HCl 2 % (Fig. 1). The matrix ( $\approx 28$  µg/g Pd content; HCl 2 %) was chosen so that all working solutions are at approximately similar Pd contents and acid concentrations.

### 2.3. Analytical strategy

The total Pd content in the working solution of the  $^{108}\text{Pd}$ -enriched spike was accurately quantified using the “reverse” isotope dilution technique. The Pd NIST SRM® 3138 (Lot No. 090629;  $10.004 \pm 0.016$  mg/g,  $k = 2$ ) was used for the “reverse” isotope dilution mixtures, since there is no commercial Pd isotopic reference material. The representative Pd isotopic abundances from Meija et al. [18] were considered for the NIST 3138, and are shown in the Supplementary material 1 (Supplementary table 1). For this purpose, two different vials of NIST 3138 (Lot No. 090629) were used to prepare four working solutions of NIST 3138 (Bottles 1A, 1B, 2A, and 2B; Fig. 1) gravimetrically diluted to approximately 28 µg/g in HCl 2 % such that all working solutions are intended to be at roughly similar matrices ( $\approx 28$  µg/g Pd content; HCl 2 %). The resulting values for the total Pd content (µg/g) in the NIST 3138 working solutions, following the gravimetric dilution calculations, are shown in Fig. 1. The expanded uncertainty ( $U$ ) on the total Pd content (µg/g) in the NIST 3138 working solutions is calculated at  $\pm 0.09$  µg/g ( $k = 2$ ) (Fig. 1). This expanded uncertainty ( $U$ ) was calculated following the Kragten method [21,22] by propagating the uncertainty of the weighing measurements (described below) along with the uncertainty of the Pd concentration in the NIST 3138 vials as obtained from the analysis certificate ( $\pm 16$  µg/g,  $k = 2$ , Lot No. 090629).



**Fig. 1.** Analytical strategy of this study: (1) dissolution and dilution of the  $^{108}\text{Pd}$ -enriched spike, bought from Eurisotop (France); (2) “reverse” isotope dilution mixtures “ $^{108}\text{Pd}$ -spike – NIST 3138”; and (3) isotope dilution mixtures “ $^{108}\text{Pd}$ -spike – radioactive effluent”. The volumes (mL) taken for the isotopic mixtures are also shown. The reported total Pd content for the radioactive effluent and  $^{108}\text{Pd}$ -enriched spike correspond to the initial approximated values. The reported total Pd content for the NIST 3138 working solutions (Bottles 1A, 1B, 2A, and 2B) are calculated from gravimetric dilutions; and the respective expanded uncertainty ( $U$ ) is calculated at  $\pm 0.09 \mu\text{g/g}$  ( $k = 2$ ) (refer to section 2.3 for more information). The uncertainty for the NIST 3138 vials (Vial 1 and Vial 2) is obtained from the analysis certificate (Lot No. 090629) at  $\pm 16 \mu\text{g/g}$  ( $k = 2$ ).

The gravimetric weighing were done using a precision balance (Mettler-Toledo®, XPE504) characterized with a resolution of 0.0001 g. The balance accuracy was verified using a reference weight (50 mg) at the beginning of each weighing series. The average of three measurements for the reference weight (50 mg) was consistently within the balance resolution of 0.0001 g at  $k = 2$ . Moreover, a static eliminator (Mettler Toledo®, Haug EN SL LC) was used to prevent electrostatic effects. Lastly, the average of three repeated weight measurements was used for the dilution of the NIST 3138 working solutions and for the preparation of the isotope mixtures (Fig. 1). The uncertainty of all weight measurements in this study is systematically considered at 0.001 g ( $k = 2$ ). This uncertainty value is based on the calibration certificate of the balance obtained in accordance with the COFRAC (French Accreditation Committee) technical accreditation guide for the calibration of weighing instruments [23].

Afterwards, seven mixtures were prepared by mixing varying volumes of the  $^{108}\text{Pd}$ -enriched spike and NIST 3138 (Fig. 1). All “reverse” isotope dilution mixtures were prepared at various dates over a period of 3 months in order to verify the absence of precipitation, and that the working solutions did not undergo any significant evaporation. The spiking ratios (mixed volumes) were varied such that the resulting isotope ratio  $^{106}\text{Pd}/^{108}\text{Pd}$ , which will be used for the quantification of the total Pd content, follows two criteria: (1) the beamline intensities measured by MC-ICP-MS on  $^{106}\text{Pd}$  and  $^{108}\text{Pd}$  allow the measurement of the  $^{106}\text{Pd}/^{108}\text{Pd}$  ratio at  $<0.01\%$  uncertainty, and (2) is distinctive from the natural  $^{106}\text{Pd}/^{108}\text{Pd}$  ratio in the NIST 3138. The  $^{106}\text{Pd}/^{108}\text{Pd}$  ratio in the NIST 3138 is calculated at  $1.033 \pm 0.004$  ( $U$ ,  $k = 2$ ), as described in

the Supplementary material 1 (Supplementary table 1). Thus, following the spiking ratios shown in Fig. 1, the theoretical  $^{106}\text{Pd}/^{108}\text{Pd}$  ratio in the “reverse” isotope dilution mixtures was expected to vary between 0.159 and 0.200.

Subsequently, for the isotope dilution scheme, five mixtures were prepared from varying volumes of the radioactive effluent and the  $^{108}\text{Pd}$ -enriched spike (Fig. 1). The number of mixtures prepared and the volumes collected from the radioactive effluent were reduced due to the limited available volume of the radioactive effluent. The isotope ratio of interest ( $^{107}\text{Pd}/^{108}\text{Pd}$ ) in the isotope dilution mixtures was theoretically expected to be between 0.069 and 0.132, as per the spiking ratios shown in Fig. 1. These isotope ratios can be measured at  $<0.01\%$  uncertainty by MC-ICP-MS, and are distinctive from the initially expected  $^{107}\text{Pd}/^{108}\text{Pd}$  ratio ( $\approx 1.499$ ) in the radioactive effluent. The contribution of the uncertainty of the isotope ratios in the mixtures is evaluated and discussed in the following sections. Such analytical strategy is similar to that applied in previous isotope dilution studies done at the CEA for the determination of  $^{93}\text{Zr}$  and  $^{151}\text{Sm}$  [24,25].

#### 2.4. Palladium isotopic measurements

Isotope ratio measurements ( $^{102}\text{Pd}/^{108}\text{Pd}$ ,  $^{104}\text{Pd}/^{108}\text{Pd}$ ,  $^{105}\text{Pd}/^{108}\text{Pd}$ ,  $^{106}\text{Pd}/^{108}\text{Pd}$ ,  $^{107}\text{Pd}/^{108}\text{Pd}$ , and  $^{110}\text{Pd}/^{108}\text{Pd}$ ) were performed on a multi-collector (MC)-ICP-MS (Neptune Plus™, Thermo Scientific™). The utilized cage configuration and resistors are shown in Table 1. For the analysis of the radioactive effluent and all isotope dilution mixtures, the  $10^{11} \Omega$  resistors were used for all cages except for  $^{102}\text{Pd}$  (cage L3) which

**Table 1**

Cage configuration and resistors coupled for measuring Pd isotope ratios ( $^{102}\text{Pd}/^{108}\text{Pd}$ ,  $^{104}\text{Pd}/^{108}\text{Pd}$ ,  $^{105}\text{Pd}/^{108}\text{Pd}$ ,  $^{106}\text{Pd}/^{108}\text{Pd}$ ,  $^{107}\text{Pd}/^{108}\text{Pd}$ , and  $^{110}\text{Pd}/^{108}\text{Pd}$ ) using the MC-ICP-MS (Neptune Plus™, Thermo Scientific™) in the radioactive effluent, isotopic mixtures, and  $^{108}\text{Pd}$ -enriched spike.

Faraday cage	Isotope	Coupled resistor ( $\Omega$ )	
		radioactive effluent and isotopic mixtures	$^{108}\text{Pd}$ -enriched spike
L3	$^{102}\text{Pd}$	$10^{13}$	$10^{13}$
L2	$^{104}\text{Pd}$	$10^{11}$	$10^{12}$
L1	$^{105}\text{Pd}$	$10^{11}$	$10^{12}$
C	$^{106}\text{Pd}$	$10^{11}$	$10^{11}$
H1	$^{107}\text{Pd}$	$10^{11}$	$10^{11}$
H2	$^{108}\text{Pd}$	$10^{11}$	$10^{11}$
H3	$^{110}\text{Pd}$	$10^{11}$	$10^{11}$

**Table 2**

Analyses conditions and parameters used for measuring Pd isotope ratios with the MC-ICP-MS (Neptune Plus™, Thermo Scientific™).

Analyses conditions and parameters (MC-ICP-MS)	
Plasma	Wet
Nebulizing chamber	Cyclonic/Scott dual spray chamber
Nebulizer	PFA micronebulizer (100 $\mu\text{L}/\text{min}$ )
Aspiration	Free
Sampler and skimmer cones	Nickel
Acquisition	1 block/25 cycles (1 block/15 cycles for blanks)
Integration time	4 s

was linked to a  $10^{13} \Omega$  resistor due to the very low intensity recorded on this isotope ( $< 0.01$  mV). For the analysis of the  $^{108}\text{Pd}$ -enriched spike, the available  $10^{12} \Omega$  and  $10^{13} \Omega$  resistors were used for the lowest intensities measured (Table 1):  $^{102}\text{Pd}$  (cage L3) was linked to a  $10^{13} \Omega$  resistor, while  $^{104}\text{Pd}$  (cage L2) and  $^{105}\text{Pd}$  (cage L1) were linked to  $10^{12} \Omega$  resistors. Lastly, the “reverse” isotope dilution mixtures were measured using only the  $10^{11} \Omega$  resistors.

Measurements were acquired at a total Pd concentration of 200 ng/mL diluted in  $\text{HNO}_3$  2 %, which provided a total sensitivity of approximately 81 V/ppm using the analyses conditions and parameters presented in Table 2. Inter-sample rinsing was done for around 20 min using two separate solutions (HCl 9 % then  $\text{HNO}_3$  2 %) in order to return to the blank background level for all Pd isotopes ( $< 1$  mV). A laboratory blank was prepared for each analytical session and was measured before each sample and standard (NIST 3138) to correct for the blank contribution. The average intensities and their respective blank contributions are shown in the Supplementary material 1 (Supplementary table 2). The blank contribution is on average  $< 0.05$  % for intensities  $> 0.3$  V,  $< 0.7$  % for intensities  $> 0.03$  V, and  $< 8.0$  % for intensities  $> 0.0004$  V. Only the  $^{102}\text{Pd}$  in the radioactive effluent had a higher average blank

**Table 3**

Average Pd isotope ratios of the NIST 3138 as obtained from all analytical sessions of this study and measured over a period of 8 months (1 \*standard deviation;  $n = 86$ ); per mil (‰) standard deviation is also shown. The Pd isotope ratios are corrected for mass bias by iteration and using different normalization values: internal correction using the IUPAC representative isotopic abundances (natural Pd) [18], and external correction using the normalization values mentioned in the bibliography [28–31]. In addition, the absolute % difference with the natural Pd isotope ratios [18] are shown.

Normalization value	$^{102}\text{Pd}/^{105}\text{Pd}$	‰	$^{104}\text{Pd}/^{105}\text{Pd}$	‰	$^{106}\text{Pd}/^{105}\text{Pd}$	‰	$^{108}\text{Pd}/^{105}\text{Pd}$	‰	$^{110}\text{Pd}/^{105}\text{Pd}$	‰
IUPAC [18]	0.045679 (1)	0.02	0.498882 (5)	0.01	1.22391 (1)	0.01	1.18495 (4)	0.04	0.52485 (2)	0.05
$^{108}\text{Pd}/^{105}\text{Pd}$ : 1.18899 [28,29]	0.045387 (8)	0.2	0.49694 (2)	0.04	1.22283 (8)	0.07	1.18899 (4)	0.04	0.5265 (1)	0.3
$^{108}\text{Pd}/^{106}\text{Pd}$ : 0.97238 [30]	0.04538 (1)	0.3	0.49693 (4)	0.08	1.2229 (1)	0.1	1.1891 (1)	0.09	0.5266 (2)	0.4
$^{110}\text{Pd}/^{104}\text{Pd}$ : 1.0604 [31]	0.045369 (3)	0.07	0.49688 (1)	0.03	1.22300 (3)	0.02	1.1895 (2)	0.2	0.52688 (3)	0.06

Normalization value	Absolute % difference with IUPAC isotope ratios				
IUPAC [18]	0.001	0.0002	0.0004	0.0003	0.002
$^{108}\text{Pd}/^{105}\text{Pd}$ : 1.18899 [28,29]	0.6	0.4	0.09	0.3	0.3
$^{108}\text{Pd}/^{106}\text{Pd}$ : 0.97238 [30]	0.6	0.4	0.09	0.3	0.3
$^{110}\text{Pd}/^{104}\text{Pd}$ : 1.0604 [31]	0.7	0.4	0.08	0.4	0.4

contribution (70 %) due to the very low intensity measured (0.00007 V). The blank contribution possibly originating from inter-measurement carryover and/or polyatomic interferences (e.g.,  $\text{ZrO}^+$ ,  $\text{NiAr}^+$ ,  $\text{ZnAr}^+$ ). In addition, potential Pd hydride formation rate at  $m/z$  107 ( $^{106}\text{Pd}^1\text{H}^+ / ^{106}\text{Pd}^+$ ) was  $< 0.004$  % on average, as measured from the NIST 3138 solution.

The measured palladium isotope ratios were corrected for mass bias by bracketing each sample with the Pd NIST 3138 standard and using the exponential law [26]. The NIST 3138 was measured as a standard to correct internally for mass bias relative to the IUPAC representative isotopic abundances [18] and IUPAC atomic mass units [27] (Supplementary material 1 – Supplementary table 1). It is noteworthy that a certified Pd isotopic reference material does not exist.

### 3. Results and discussion

#### 3.1. Mass bias correction

The mass bias correction factors ( $\beta_{\text{NIST 3138}}$ ) resulting from each NIST 3138 measurement throughout all analytical sessions of this study are shown in the Supplementary material 1 (Supplementary tables 3–7). Previous studies measuring Pd isotope ratios applied mass-bias correction by standard-sample bracketing with the NIST 3138 as standard, and using the exponential law with an external normalization value of  $^{108}\text{Pd}/^{105}\text{Pd}$ : 1.18899 [28,29] or  $^{108}\text{Pd}/^{106}\text{Pd}$ : 0.97238 [30]. Both of these values originate from the reported isotope ratios on a natural Pd solution measured by Kelly and Wasserburg [31] and normalized to  $^{110}\text{Pd}/^{104}\text{Pd}$ : 1.0604 using the power law. Indeed, the authors in Kelly and Wasserburg [31] did not discuss the origin of the normalization ratio  $^{110}\text{Pd}/^{104}\text{Pd}$ : 1.0604, and traceability to the International System of Units (SI) is not established. The results (measured Pd isotope ratios) obtained in our study on the NIST 3138 are normalized to the different aforementioned ratios for comparison with the previous studies (Table 3). The resulting average Pd isotope ratios on the NIST 3138 measurements of our study are similar at  $< 0.7$  % difference regardless of the applied normalization value (Table 3). Nonetheless, the isotope ratios normalized to the IUPAC representative isotopic abundances [18] demonstrate higher precision for all Pd isotope ratios and are traceable to the International System of Units (SI) (Table 3). Such traceability is presented by the greater similarity of the NIST 3138 isotope results with the IUPAC representative isotopic abundances (Table 3). Furthermore, and similarly to our study, Miyake et al. [14] used the IUPAC representative isotopic abundances of Pd to perform mass-bias correction in order to quantify  $^{107}\text{Pd}$  using ICP-MS in irradiated  $^{107}\text{Pd}$ -concentrated samples.

The mass bias correction factor for the radionuclide  $^{107}\text{Pd}$  ( $\beta_{\text{NIST 3138}}^{107\text{Pd}}$ ) was calculated for each analysis session as the average  $\beta_{\text{NIST 3138}}$  of all



other isotope ratios ( $^{102}\text{Pd}/^{108}\text{Pd}$ ,  $^{104}\text{Pd}/^{108}\text{Pd}$ ,  $^{105}\text{Pd}/^{108}\text{Pd}$ ,  $^{106}\text{Pd}/^{108}\text{Pd}$ , and  $^{110}\text{Pd}/^{108}\text{Pd}$ ; Supplementary material 1 – Supplementary tables 5–7). The results from the two analytical sessions on the radioactive effluent provided an average  $\beta_{\frac{^{107}\text{Pd}}{^{108}\text{Pd}}}$  value of  $-2.4 \pm 0.3$ , the uncertainty being two times the standard deviation ( $2^*\text{SD}$ ) of  $n = 17$  NIST 3138 measurements.

### 3.2. Palladium isotope ratios

The palladium isotope ratios, those measured and corrected for mass bias, are shown in the Supplementary material 1 (Supplementary tables 3–7) for all analyzed solutions: radioactive effluent,  $^{108}\text{Pd}$ -enriched spike, and all isotope dilution mixtures.

#### 3.2.1. $^{108}\text{Pd}$ -enriched spike

The average isotope ratios of the  $^{108}\text{Pd}$ -enriched spike are shown in the Supplementary material 1 (Supplementary table 3). The repeatability of isotope ratio measurements varies between 0.3 and 5.5 %, the repeatability being two times the standard deviation ( $2^*\text{SD}$ ) of  $n = 31$  measurements obtained from three separate analytical sessions. The relatively high standard deviations ( $> 1$  %,  $2^*\text{SD}$ ,  $n = 31$ ) correspond to the very low isotope ratios (e.g.,  $^{102}\text{Pd}/^{108}\text{Pd}$ :  $0.000026 \pm 0.000001$ ) measured in the  $^{108}\text{Pd}$ -enriched spike. Whereas, the lower standard deviations ( $< 1$  %,  $2^*\text{SD}$ ,  $n = 31$ ) correspond to the higher isotope ratios (e.g.,  $^{110}\text{Pd}/^{108}\text{Pd}$ :  $0.00582 \pm 0.00002$ ).

#### 3.2.2. Isotope dilution mixtures

The standard deviation of the  $^{106}\text{Pd}/^{108}\text{Pd}$  ratio measured in the “reverse” isotope dilution mixtures (M1 to M7) is  $< 0.03$  % ( $2^*\text{SD}$ ,  $n = 3$ –4 independent measurements per mixture; Supplementary material 1 – Supplementary table 4). The  $^{107}\text{Pd}/^{108}\text{Pd}$  ratio measured in the isotope dilution mixtures (MA to ME) demonstrates a standard deviation  $< 0.02$  % ( $2^*\text{SD}$ ,  $n = 3$ –4 independent measurements per mixture; Supplementary material 1 – Supplementary table 7).

$$[\text{Pd}]_{\text{spike}} = [\text{Pd}]_{\text{NIST 3138}} \times \frac{\text{mass}_{\text{NIST 3138}}}{\text{mass}_{\text{spike}}} \times \frac{\text{Atomic weight}_{\text{spike}}}{\text{Atomic weight}_{\text{NIST 3138}}} \times \frac{\text{Atomic Ab. } ^{108}\text{Pd} (\text{NIST 3138})}{\text{Atomic Ab. } ^{108}\text{Pd} (\text{spike})} \times \frac{\left(\frac{^{106}\text{Pd}}{^{108}\text{Pd}}\right)_{\text{NIST 3138}} - \left(\frac{^{106}\text{Pd}}{^{108}\text{Pd}}\right)_{\text{mixture}}}{\left(\frac{^{106}\text{Pd}}{^{108}\text{Pd}}\right)_{\text{mixture}} - \left(\frac{^{106}\text{Pd}}{^{108}\text{Pd}}\right)_{\text{spike}}} \quad (1)$$

#### 3.2.3. Radioactive effluent

The Pd isotope ratios of the radioactive effluent are obtained with a standard deviation (SD) lower than 0.05 % ( $2^*\text{SD}$ ,  $n = 15$ ; Table 4). Only the isotope ratio  $^{102}\text{Pd}/^{108}\text{Pd}$  ( $0.000020 \pm 0.000006$ ,  $2^*\text{SD}$ ,  $n = 15$ ) has a high standard deviation of 29.5 % due to the very low abundance of  $^{102}\text{Pd}$  in the radioactive effluent. Furthermore, the isotope ratios of the

**Table 4**

Palladium isotope ratios of the radioactive effluent measured by MC-ICP-MS (Neptune Plus™, Thermo Scientific™). The average isotope ratios are obtained from two separate analytical sessions, done before and after an additional chemical purification by extraction chromatography. The repeatability ( $2^*\text{SD}$ ) corresponds to two times the standard deviation of  $n$  independent measurements. The shown percentage difference is between the isotope ratios before and after the additional purification.

Radioactive effluent							
Isotope ratios	Before chemical purification ( $n = 10$ )		After chemical purification ( $n = 5$ )		Percentage difference	Final average ( $n = 15$ )	
	Average ( $\pm 2^*\text{SD}$ )	%	Average ( $\pm 2^*\text{SD}$ )	%		Average ( $\pm 2^*\text{SD}$ )	%
$^{102}\text{Pd}/^{108}\text{Pd}$	0.000020 (6)	29.1 %	0.000019 (6)	30.0 %	8.0 %	0.000020 (6)	29.5 %
$^{104}\text{Pd}/^{108}\text{Pd}$	1.6416 (6)	0.04 %	1.6422 (5)	0.03 %	0.03 %	1.6418 (8)	0.05 %
$^{105}\text{Pd}/^{108}\text{Pd}$	2.9226 (8)	0.03 %	2.9234 (7)	0.02 %	0.03 %	2.923 (1)	0.04 %
$^{106}\text{Pd}/^{108}\text{Pd}$	2.6364 (6)	0.02 %	2.6369 (4)	0.01 %	0.02 %	2.6366 (7)	0.03 %
$^{107}\text{Pd}/^{108}\text{Pd}$	1.4994 (2)	0.01 %	1.4993 (1)	0.01 %	0.007 %	1.4994 (2)	0.01 %
$^{110}\text{Pd}/^{108}\text{Pd}$	0.31407 (7)	0.02 %	0.31404 (6)	0.02 %	0.01 %	0.31405 (2)	0.02 %

radioactive effluent are very similar when compared between before and after the additional chemical purification by extraction chromatography. Percentage difference is lower than 0.03 % for all isotope ratios and even lower (0.007 %) for the ratio  $^{107}\text{Pd}/^{108}\text{Pd}$  (Table 4). However, the percentage difference is higher (8.0 %) for the ratio  $^{102}\text{Pd}/^{108}\text{Pd}$ , similarly due to the very low abundance of  $^{102}\text{Pd}$  in the radioactive effluent. The unchanged isotopic composition of the radioactive effluent before and after an additional chemical purification demonstrates the absence of  $^{107}\text{Ag}$  upon its reception as well as the repeatability of isotopic measurements, and validates the overall obtained isotopic results.

### 3.3. Accurate quantification of atomic abundances and total Pd contents

#### 3.3.1. $^{108}\text{Pd}$ -enriched spike

The percentage atomic abundance of  $^{108}\text{Pd}$  in the isotopically-enriched spike is accurately quantified in this study at  $98.775 \pm 0.007$  % ( $U$ ,  $k = 2$ ; Table 5). The expanded uncertainty ( $U$ ) is calculated by propagating the repeatability of isotope ratios following the Kragten method [21,22]. It is noteworthy that the enrichment value obtained in this study for  $^{108}\text{Pd}$  ( $98.775 \pm 0.007$  %) has a much lower uncertainty compared with the analysis certificate value ( $98.40 \pm 1.5$  %), yet both values overlap within the uncertainties.

The total Pd content in the working solution of the  $^{108}\text{Pd}$ -enriched spike is quantified using the “reverse” isotope dilution Eq. (1), providing a value of  $28.1 \pm 0.2$   $\mu\text{g/g}$  ( $U$ ,  $k = 2$ , 0.7 % uncertainty; Table 5). The expanded uncertainty ( $U$ ,  $k = 2$ ) is calculated from the “reverse” isotope dilution mixtures ( $n = 7$ ) by propagating the standard deviations of all the variables in Eq. 1, following the Kragten method [21,22]. Nonetheless, the repeatability among the “reverse” isotope dilution mixtures ( $n = 7$ ) provides a lower standard deviation on the total Pd content in the working solution of the  $^{108}\text{Pd}$ -enriched spike, at  $28.05 \pm 0.05$   $\mu\text{g/g}$  ( $k = 2$ , 0.2 % repeatability; Supplementary material 1 – Supplementary table 8).

Where,  $[\text{Pd}]_{\text{spike}}$  is the total Pd content in the  $^{108}\text{Pd}$ -enriched spike working solution,  $[\text{Pd}]_{\text{NIST 3138}}$  is the total Pd content in the NIST 3138 working solution,  $\text{mass}_{\text{NIST 3138}}$  and  $\text{mass}_{\text{spike}}$  are the weights of the mixed volumes of the  $^{108}\text{Pd}$ -enriched spike and the NIST 3138, “Atomic weight” corresponds to the atomic weight of Pd in the spike and NIST

**Table 5**

Atomic and mass abundances (%) of Pd isotopes as well as the total Pd content ( $\mu\text{g/g}$ ) in the  $^{108}\text{Pd}$ -enriched spike and radioactive effluent. The mass abundances were calculated using the IUPAC atomic mass units [27] (Supplementary material 1 – Supplementary table 1) and the atomic weight of Pd measured in each solution (section 3.3). The uncertainty  $U$  ( $k = 2$ ) of atomic and mass abundances corresponds to the expanded uncertainty calculated by propagating the repeatability of isotope ratios following the Kragten method [21,22]. The expanded uncertainty  $U$  ( $k = 2$ ) on the total Pd content is calculated by propagating the standard deviations of the variables in Eq. 1 and Eq. 2 for the  $^{108}\text{Pd}$ -enriched spike and radioactive effluent, respectively.

Isotope	$^{108}\text{Pd}$ -enriched spike		$U$ ( $k = 2$ , %)	Radioactive effluent		$U$ ( $k = 2$ , %)
	% atomic abundance	% mass abundance		% atomic abundance	% mass abundance	
$^{102}\text{Pd}$	0.0026	0.0024	$\pm 0.0002$ (7.1 %)	0.00019	0.00019	$\pm 0.00002$ (11.8 %)
$^{104}\text{Pd}$	0.043	0.041	$\pm 0.002$ (4.6 %)	16.394	16.107	$\pm 0.007$ (0.04 %)
$^{105}\text{Pd}$	0.189	0.184	$\pm 0.004$ (2.0 %)	29.186	28.951	$\pm 0.008$ (0.03 %)
$^{106}\text{Pd}$	0.417	0.409	$\pm 0.005$ (1.1 %)	26.327	26.363	$\pm 0.006$ (0.02 %)
$^{107}\text{Pd}$	–	–	–	14.971	15.133	$\pm 0.003$ (0.02 %)
$^{108}\text{Pd}$	98.775	98.779	$\pm 0.007$ (0.007 %)	9.985	10.188	$\pm 0.001$ (0.01 %)
$^{110}\text{Pd}$	0.574	0.585	$\pm 0.002$ (0.4 %)	3.136	3.259	$\pm 0.001$ (0.02 %)
Total Pd content ( $\mu\text{g/g}$ )	28.1 $\mu\text{g/g}$		$\pm 0.2$ (0.7 %)	27.3 $\mu\text{g/g}$		$\pm 0.2$ (0.7 %)

3138, “Atomic Ab.” is the percentage atomic abundance, and “mixture” corresponds to the “reverse” isotope dilution mixtures.

The atomic weight of Pd in the spike was calculated using the measured isotope ratios and atomic weights from De Laeter et al. [27], which provided a value of 107.8995 atomic mass unit (amu)  $\pm 0.0006$  ( $k = 2$ ). Whereas, the atomic weight of Pd in the NIST 3138 solution was taken from De Laeter et al. [27] at 106.42  $\pm 0.01$  amu ( $k = 2$ ).

### 3.3.2. Radioactive effluent

The radioactive effluent is characterized in this study for its Pd isotopic composition (percentage atomic and mass abundances) with an uncertainty lower than 0.04 % ( $U$ ,  $k = 2$ ; Table 5). The atomic abundance of the radionuclide  $^{107}\text{Pd}$  in the effluent is accurately quantified at 14.971  $\pm 0.003$  %. The uncertainty on the abundance of  $^{102}\text{Pd}$  is high (11.8 %) due to its very low abundance (0.00019 %  $\pm 0.00002$  %) in the radioactive effluent (Table 5). The expanded uncertainty ( $U$ ) is calculated by propagating the repeatability of isotope ratios following the Kragten method [21,22].

The total palladium content in the radioactive effluent is quantified at 27.3  $\pm 0.2$   $\mu\text{g/g}$  ( $U$ ,  $k = 2$ , 0.7 % uncertainty; Table 5), using the isotope dilution Eq. (2). The expanded uncertainty ( $U$ ,  $k = 2$ ) is calculated from the isotope dilution mixtures ( $n = 5$ ) by propagating the standard deviations of all the variables in Eq. 2, and following the Kragten method [21,22]. However, the repeatability among the isotope dilution mixtures ( $n = 5$ ) provides a lower standard deviation on the total Pd content in the radioactive effluent, at 27.34  $\pm 0.02$   $\mu\text{g/g}$  ( $k = 2$ , 0.1 % repeatability; Supplementary material 1 – Supplementary table 8).

$$[\text{Pd}]_{\text{sample}} = [\text{Pd}]_{\text{spike}} \times \frac{\text{mass}_{\text{spike}}}{\text{mass}_{\text{sample}}} \times \frac{\text{Atomic weight}_{\text{sample}}}{\text{Atomic weight}_{\text{spike}}} \times \frac{\text{Atomic Ab. } ^{108}\text{Pd} (\text{spike})}{\text{Atomic Ab. } ^{108}\text{Pd} (\text{sample})} \times \frac{\left(\frac{^{107}\text{Pd}}{^{108}\text{Pd}}\right)_{\text{mixture}}}{\left(\frac{^{107}\text{Pd}}{^{108}\text{Pd}}\right)_{\text{mixture}} - \left(\frac{^{107}\text{Pd}}{^{108}\text{Pd}}\right)_{\text{sample}}} \quad (2)$$

Where,  $[\text{Pd}]_{\text{sample}}$  is the total Pd content in the radioactive effluent working solution,  $\text{mass}_{\text{spike}}$  and  $\text{mass}_{\text{sample}}$  are the weights of the mixed volumes of the  $^{108}\text{Pd}$ -enriched spike and the radioactive effluent, “Atomic weight” corresponds to the atomic weight of Pd in the sample and spike, “Atomic Ab.” is the percentage atomic abundance, and “mixture” corresponds to the isotope dilution mixtures.

The atomic weight of Pd in the radioactive effluent was similarly calculated using the measured isotope ratios and atomic weights from De Laeter et al. [27], which provided a value of 105.75947  $\pm 0.0002$

amu ( $k = 2$ ).

Lastly, the accurate total  $^{107}\text{Pd}$  content in the radioactive effluent is evaluated at 4.13  $\pm 0.03$   $\mu\text{g/g}$  ( $U$ ,  $k = 2$ , 0.7 % expanded uncertainty) using Eq. (3):

$$[^{107}\text{Pd}]_{\text{sample}} = [\text{Pd}]_{\text{sample}} \times \text{Mass Ab. } ^{107}\text{Pd} (\text{sample}) \quad (3)$$

With,  $[^{107}\text{Pd}]_{\text{sample}}$  is the total content of  $^{107}\text{Pd}$  in the radioactive effluent working solution,  $[\text{Pd}]_{\text{sample}}$  is the total Pd content in the radioactive effluent working solution, and “Mass Ab.” is the percentage mass abundance from Table 5.

### 3.4. Evaluation of the expanded uncertainty

An advantage of the isotope dilution technique is that sources of uncertainty on the quantified total Pd content are well understood and controlled. It is thus interesting to evaluate the relative contribution of the standard deviation of the variables in Eq. 1 and Eq. 2 to the expanded uncertainty on the total Pd content.

#### 3.4.1. $^{108}\text{Pd}$ -enriched spike

The 0.7 % expanded uncertainty ( $k = 2$ ) on the total Pd content of the  $^{108}\text{Pd}$ -enriched spike (28.1  $\pm 0.2$   $\mu\text{g/g}$ ) mainly originates from the standard deviation of three variables (Table 6 and Supplementary Fig. 1): (1) 47.9 % from the standard deviation of the natural Pd isotope ratio  $\left(\frac{^{106}\text{Pd}}{^{108}\text{Pd}}\right)_{\text{NIST 3138}}$  ( $\pm 0.002$ ,  $k = 1$ ); (2) 25.5 % from the standard deviation of the total Pd content in the NIST 3138 working solution ( $\pm$

0.05  $\mu\text{g/g}$ ,  $k = 1$ ); and (3) 25.4 % from the standard deviation of the IUPAC representative isotopic abundance of  $^{108}\text{Pd}$  ( $\pm 0.045$  %,  $k = 1$ ). The remaining 1.3 % comes from the other variables in Eq. 1 (Table 6).

The natural Pd isotope ratio  $\left(\frac{^{106}\text{Pd}}{^{108}\text{Pd}}\right)_{\text{NIST 3138}}$  is calculated relative to the IUPAC representative isotopic abundances, and its uncertainty corresponds to the expanded uncertainty ( $k = 1$ ) calculated by propagating the uncertainty of atomic abundances from Meija et al. [18] (Supplementary material 1 – Supplementary table 1). Additionally, the standard deviation on the  $\left(\frac{^{106}\text{Pd}}{^{108}\text{Pd}}\right)_{\text{spike}}$  was independently calculated by

**Table 6**

Standard deviations ( $k = 1$ ) of the variables in Eq. 1 and Eq. 2 and their percent contribution on the expanded uncertainty of the total Pd content in the  $^{108}\text{Pd}$ -enriched spike and radioactive effluent (sample). Refer also to section 3.4 for more information about the standard deviations of  $\left(\frac{^{106}\text{Pd}}{^{108}\text{Pd}}\right)_{\text{NIST 3138}}$ ,  $\left(\frac{^{106}\text{Pd}}{^{108}\text{Pd}}\right)_{\text{spike}}$ , and  $\left(\frac{^{107}\text{Pd}}{^{108}\text{Pd}}\right)_{\text{sample}}$ .

Variables in Eq. 1	"reverse" isotope dilution mixtures ( $^{108}\text{Pd}$ -enriched spike – NIST 3138; $n = 7$ )	
	Standard deviation ( $k = 1$ )	% contribution
$[\text{Pd}]_{\text{NIST 3138}}$ ( $\mu\text{g/g}$ )	0.05	25.5 %
$\text{mass}_{\text{NIST 3138}}$ (g)	0.0005	0.4 %
$\text{mass}_{\text{spike}}$ (g)	0.0005	0.2 %
Atomic weight $_{\text{spike}}$	0.0003	0.00007 %
Atomic weight $_{\text{NIST 3138}}$	0.005	0.02 %
Atomic Ab. $_{^{108}\text{Pd}}$ (NIST 3138)	0.045	25.4 %
Atomic Ab. $_{^{108}\text{Pd}}$ (spike)	0.003	0.008 %
$\left(\frac{^{106}\text{Pd}}{^{108}\text{Pd}}\right)_{\text{NIST 3138}}$	0.002	47.9 %
$\left(\frac{^{106}\text{Pd}}{^{108}\text{Pd}}\right)_{\text{mixture}}$	0.00002	0.2 %
$\left(\frac{^{106}\text{Pd}}{^{108}\text{Pd}}\right)_{\text{spike}}$	0.00004	0.5 %
Variables in Eq. 2	isotope dilution mixtures ( $^{108}\text{Pd}$ -enriched spike – radioactive effluent; $n = 5$ )	
	Standard deviation ( $k = 1$ )	% contribution
$[\text{Pd}]_{\text{spike}}$ ( $\mu\text{g/g}$ )	0.1	94.7 %
$\text{mass}_{\text{spike}}$ (g)	0.0005	0.7 %
$\text{mass}_{\text{sample}}$ (g)	0.0005	1.4 %
Atomic weight $_{\text{sample}}$	0.00009	0.000005 %
Atomic weight $_{\text{spike}}$	0.0003	0.00006 %
Atomic Ab. $_{^{108}\text{Pd}}$ (spike)	0.003	0.007 %
Atomic Ab. $_{^{108}\text{Pd}}$ (sample)	0.0007	0.04 %
$\left(\frac{^{107}\text{Pd}}{^{108}\text{Pd}}\right)_{\text{sample}}$	0.0009	3.1 %
$\left(\frac{^{107}\text{Pd}}{^{108}\text{Pd}}\right)_{\text{mixture}}$	0.000007	0.05 %

incorporating the covariance of intensities between the isotopes following Eq. (4).

$$R_{\frac{x_{\text{Pd}}}{y_{\text{Pd}}}} = \frac{I_{x_{\text{Pd}}\text{sample}} - I_{x_{\text{Pd}}\text{blank}}}{I_{y_{\text{Pd}}\text{sample}} - I_{y_{\text{Pd}}\text{blank}}} \times \left( \frac{M_{x_{\text{Pd}}}}{M_{y_{\text{Pd}}}} \right) \left( \frac{\ln \left( \frac{R_{\text{IUPAC}}}{\left( \frac{I_{x_{\text{Pd}}\text{standard}} - I_{x_{\text{Pd}}\text{blank}}}{I_{y_{\text{Pd}}\text{standard}} - I_{y_{\text{Pd}}\text{blank}}} \right)} \right)}{\ln \left( \frac{M_{x_{\text{Pd}}}}{M_{y_{\text{Pd}}}} \right)} \right) \quad (4)$$

With,  $R_{\frac{x_{\text{Pd}}}{y_{\text{Pd}}}}$  is the isotope ratio corrected for mass bias and blank contribution,  $x_{\text{Pd}}$  and  $y_{\text{Pd}}$  are the Pd isotopes, and  $I$  is the recorded intensity ( $V$ ) in the sample ( $^{108}\text{Pd}$ -enriched spike or radioactive effluent), standard (NIST 3138), and blank. Furthermore,  $M$  is the atomic mass unit, and  $R_{\text{IUPAC}}$  is the natural Pd isotope ratio used for mass bias correction and calculated from the IUPAC representative isotopic abundances.

The uncertainty evaluation demonstrate that the majority of the uncertainty (73.9 %) arises from the standard deviation of the IUPAC representative isotopic abundances used for the NIST 3138. Indeed, these standard deviations could be significantly lower if an isotopic reference material existed for Pd. Consequently, the uncertainty of the isotope ratios would be also lower, and an even high accuracy can be

attained in isotope dilution methods such as in this study. Accurately characterizing a Pd isotopic reference material would require a comparative study among metrological laboratories, taking advantage of the range of available MC-ICP-MS instruments. Previous studies used such strategy to characterize widely used USGS (United States Geological Survey) reference materials [e.g., 32,33]. Moreover, the application of double or even triple isotope dilution techniques with additional isotope systems can be beneficial to accurately characterize a reference material by minimizing weighing errors. Such methodology is described in more detail by Quemet et al. [17] for the quantification of U in environmental samples.

The last major uncertainty (25.5 %) from the standard deviation of the total Pd content in the NIST 3138 working solutions, arises from the gravimetric dilution of the NIST 3138 vials. A more accurate weight determination can be achieved using the "substitution method", which is commonly used for the preparation or characterization of certified reference materials [17]. However, this method is time consuming and more restricted to metrological laboratories.

#### 3.4.2. Radioactive effluent

The relative contribution of the standard deviations of variables in Eq. 2 on the total Pd content in the radioactive effluent ( $27.3 \pm 0.2 \mu\text{g/g}$ , 0.7 %,  $k = 2$ ) are shown in Table 6 and Supplementary Fig. 2. The expanded uncertainty (0.7 %,  $k = 2$ ) originates in: (1) 94.7 % from the standard deviation of the total Pd content in the  $^{108}\text{Pd}$ -enriched spike ( $\pm 0.1 \mu\text{g/g}$ ,  $k = 1$ ); (2) 3.1 % from the standard deviation of the  $\left(\frac{^{107}\text{Pd}}{^{108}\text{Pd}}\right)_{\text{sample}}$  ( $\pm 0.0009$ ,  $k = 1$ ); and (3) 1.4 % from the standard deviation of the weighed volume of the radioactive effluent used to prepare the isotope dilution mixtures ( $\pm 0.0005 \text{ g}$ ,  $k = 1$ ). The remaining 0.8 % comes from the other variables in Eq. 2 (Table 6). The standard deviation on the  $\left(\frac{^{107}\text{Pd}}{^{108}\text{Pd}}\right)_{\text{sample}}$  was independently calculated by incorporating the covariance of intensities between the isotopes (Eq. 4).

The contribution of the uncertainties demonstrates the advantage of the isotope dilution technique such that standard deviations related to the laboratory preparation of isotopic mixtures or to the analytical measurement of isotope ratios do not have a significant contribution (< 5 %) on the expanded uncertainty of the total Pd content. Indeed, the uncertainties of both,  $\left(\frac{^{107}\text{Pd}}{^{108}\text{Pd}}\right)_{\text{sample}}$  and weighed volume of the radioactive effluent, could have been reduced by increasing the added volume of the radioactive effluent to the isotope mixtures. However, and in complement to the discussion on the analytical strategy (section 2.3), due to the limited available volume of the radioactive effluent we were restricted with sampling little volumes.

## 4. Conclusion

In this study, a radioactive effluent containing a high content of the radionuclide  $^{107}\text{Pd}$  was characterized with high analytical accuracy for its isotopic composition and total Pd content. Notably, the atomic abundance of the radionuclide  $^{107}\text{Pd}$  is quantified at  $14.971 \pm 0.003 \%$  (0.02 % expanded uncertainty,  $k = 2$ ), and the total Pd content is quantified at  $27.3 \pm 0.2 \mu\text{g/g}$  (0.7 % expanded uncertainty,  $k = 2$ ). The repeatability of the total Pd content, as obtained from the isotope dilution mixtures ( $n = 5$ ), is lower by a factor of 10 (at per-mil level) corresponding to a value of  $27.34 \pm 0.02 \mu\text{g/g}$  ( $k = 2$ , 1.0 ‰). The aforementioned low uncertainties were obtained by applying the isotope dilution technique after calibrating an isotopically-enriched ( $^{108}\text{Pd}$ ) spike and by measuring all Pd isotope ratios using a multi-collector ICP-MS. The developed methodology can be applied to characterize accurately future radioactive samples containing  $^{107}\text{Pd}$ . In addition, this methodology is potentially applicable to measure accurately other long-lived radionuclides, such as  $^{93}\text{Zr}$  and  $^{79}\text{Se}$ , particularly in the context of



radioactive waste generated by dismantling and decommissioning activities.

The studied radioactive effluent, fully characterized for its isotopic composition and total Pd content, can be employed as a  $^{107}\text{Pd}$  concentration standard by other nuclear analysis laboratories to validate quantification measurements and methods. This is of prime interest since a commercial reference material certified for  $^{107}\text{Pd}$  content is not currently available, and  $^{107}\text{Pd}$ -concentrated materials are scarce. However, sharing the  $^{107}\text{Pd}$  standard of this study with other laboratories should be considered sparingly due to the limited stock available. Moreover, the half-life of  $^{107}\text{Pd}$  has only been characterized twice up to now [4,34]. Coupled with accurate activity measurements (e.g., liquid scintillation counting), the  $^{107}\text{Pd}$  content quantified in this study can be used to determine more precisely the half-life of  $^{107}\text{Pd}$  and achieve a better knowledge of this long-lived radionuclide.

### CRedit authorship contribution statement

**Majd Shmeit:** Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Marina Faure:** Writing – review & editing, Validation, Methodology, Investigation, Conceptualization. **Celine Gautier:** Writing – review & editing, Validation, Supervision, Resources, Methodology, Funding acquisition, Conceptualization. **Hélène Isnard:** Writing – review & editing, Validation, Supervision, Resources, Methodology, Conceptualization.

### Declaration of competing interest

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

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### Appendix A. Supplementary data

Supplementary material 1 corresponds to an Excel document containing supplementary data distributed among seven separate spreadsheets: (1) IUPAC values used in this study for the representative Pd atomic abundances and atomic mass units along with the respective isotope ratios (Supplementary table 1); (2) average intensities (V) and blank contributions in the analyzed solutions (Supplementary table 2); (3) to (7) contain the isotopic data, those measured and corrected for mass-bias, for all analyzed solutions (Supplementary tables 3–7); and (8) contains the total Pd contents ( $\mu\text{g/g}$ ) as obtained from the isotope dilution mixtures (Supplementary table 8). Supplementary material 2 contains the Supplementary Fig. 1 and Supplementary Fig. 2. Supplementary data to this article can be found online at [<https://doi.org/10.1016/j.sab.2025.107119>].

### Data availability

Data used for this research is provided in the Supplementary material 1

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