Supporting Information

Detection of the Fission Product Palladium-107 in a Pond Sediment Sample from Chernobyl

Anica Weller¹, Tim Ramaker¹, Felix Stäger¹, Tobias Blenke¹, Manuel Raiwa¹, Ihor Chyzhevskyi², Serhii Kirieiev², Sergiy Dubchak³, and Georg Steinhauser¹*

¹ Leibniz Universität Hannover, Institute of Radioecology and Radiation Protection, 30419 Hannover, Germany

² State Specialized Enterprise "Ecocentre" (SSE "Ecocentre"), Chernobyl 07270, Ukraine

³ State Specialized Enterprise "Radon Association", Kyiv 03083, Ukraine

* Corresponding author. Email: steinhauser@irs.uni-hannover.de

Table of Contents

Materials and Methods	2
Table S1. Types of interference of Pd during ICP-MS measurements	4
Table S2. Operating parameters for ICP-QQQ-MS Agilent 8900	4
Table S3. Detection limits according to DIN 32645 for Pd isotopes in different MS modes.	4
Table S4. Isotopic ratios of Pd in spent nuclear fuel, literature values for natural Pd and measured natural Pd standard.	5
Figure S1. Recovery of zirconium (90 Zr), palladium (105 Pd), and yttrium (89 Y) from a strongly acidic cation exchange resin with elution in 0.01 mol·L ⁻¹ and 1 mol·L ⁻¹ HCl in 2 mL steps	6
Figure S2: Relative recovery of ¹⁰⁵ Pd from a Ni Resin [©] after injection of a) 10 μ g Pd and b) 10 ng Pd followed up by washing with 30 mL 0.01 mol·L ⁻¹ HCl and subsequent elution (right of the blue line) with 40 mL 8 mol·L ⁻¹ HNO ₃ . The uncertainty is calculated from the standard deviation (SD) of 3 replicates.	7
Figure S3. Recovery of several cations (Li, V, Ga, Rb, Sr, Y, Zr, Mo, Ag, In, Cs, Ba, Tl, Pb) from the Ni Resin. 10-100 ng of the respective cation were loaded at elution volume 0 mL, thereafter the resin was washed with 28 mL of 0.01 mol·L ⁻¹ HCl and then changed to 40 mL 8 mol·L ⁻¹ HNO ₃ . Please note that not all cations present in the multi-element standard are displayed because of their strong background and interferences in ICP-MS measurements	8
Figure S4. Introduction of He flux (0-5 mL·min ⁻¹) to a 1 mL·min ⁻¹ propane flux in the collision cell for a suppression of interferences on the C ₂ H ₄ mass shift 107 \rightarrow 135. a) Counts for a 10 µg·kg ⁻¹ Pd standard solution in a 1 mL·min ⁻¹ propane flux with additional He flux for unshifted ¹⁰⁶ Pd, C ₂ H ₄ -shifted ^{106\rightarrow134} Pd and C ₃ H ₆ -shifted ^{106\rightarrow148} Pd. b) Intensity loss of the C ₂ H ₄ -shifted ^{106\rightarrow134} Pd associated with an increasing He flux. c) Background on the C ₂ H ₄ -shift ^{107\rightarrow135} Pd by 10 µg·kg ⁻¹ Pd, blank, 10 µg·kg ⁻¹ Zr and 1 µg·kg ⁻¹ Ag	9
Figure S5. Content of various elements in the CEZ sediment sample (980 mg) after clean-up with a cation exchange and Ni Resin extraction. The mass concentration refers to the solution volume of 2 mL CEZ extract. Please note the logarithmic scale and that only the elements marked in red were fully quantified in the ICP-MS system. All other elements were determined by a quick scan of the MS system and are prone to variable influences from interferences. The quick scan element mass concentration should be treated with caution and only be used an estimation of the concentration range	10
Figure S6. Calibration curves of different stable Pd isotopes on the C ₂ H ₄ shift mode of the ICP-QQQ-MS with propane gas reaction	11
References	12

MATERIALS AND METHODS

All chemicals were used in analytical grade or purer. HNO₃ and HCl were purchased from the Institute of Geology, University of Hannover, in subboiled quality (purified from Suprapur acids from Merck[®]). The centrifuge tubes from VWR[®] were cleaned prior to use with three times suprapur 2 % HNO₃ and three times Milli-Q water (18.2 MΩ·cm) overnight in an oval shaker. For the Pd extraction, only PFA lab equipment were used. Extraction chromatographic resin in the form of 2 mL Ni Resin[®] cartridges were purchased from Eichrom technologies Inc. The cation exchange resin 50W-X8 was purchased from Bio-Rad Laboratories, Inc. Various ICP element standard were purchased from Sigma-Aldrich[®]: multi-element (Ca, Fe, K, Na: 100 mg·L⁻¹; Ag, Al, Ba, Be, Bi, Cd, Co, Cr, Cs, Ga, In, K, Li, Mg, Mo, Ni, Pb, Rb, Sr, Tl, V, Zn: 10 mg·L⁻¹), Ag (1000 mg·L⁻¹), Zr (1000 mg·L⁻¹), Y (1000 mg·L⁻¹), and Pd (1000 mg·L⁻¹). The quality of the MS argon gas (Linde[®]) was N4.8 (99.9975 %) and the collision gas propane (Messer Industriegase GmbH) was N3.5 (99.97 %), respectively.

Sample material

Sediment samples were taken in October 2018 from the cooling pond of the Chernobyl nuclear power plant (ChNPP) (51.369722 N, 30.144167 E ± 18 m), which is located inside the Chernobyl Exclusion Zone (CEZ). The sediment was first cleared of larger objects such as mussel shells and then wet-sieved into fractions >200 μ m, 63 μ m <x<200 μ m, and <63 μ m using sieves from VWR[®]. Previous studies showed that fuel particles from the Chernobyl NPP accident were in the range of 0.5 – 150 μ m,¹ most of which were in the 5-30 μ m range.² For this reason, we used the smallest fraction of <63 μ m for the palladium recovery. After the initial gamma-ray measurement for estimation of the ¹³⁷Cs and ²⁴¹Am activities, the sediment fraction <63 μ m was weighed and transferred into a PFA beaker. The ultra-trace level Pd recovery was based on the works of Pouyan *et al.*³ and Chwastowska *et al.*⁴ on road dust and soil samples. The available amount of the sediment fraction <63 μ m (220 – 980 mg) was digested slowly with 20 mL *aqua regia* (3:1 HCl: HNO₃) at 85 °C and evaporated to dryness. The digestion step was repeated once with 20 mL *aqua regia*, followed by evaporation to dryness. The residue was taken up in 10 mL 1 mol·L⁻¹ HCl and passed through a round filter. The filter was washed with three times each 10 mL 1 mol·L⁻¹ HCl. The filtrate was evaporated to 5 mL and both the filtrate and the filter were measured via gamma-ray spectrometry.

Pd isolation on cation exchange resin and Ni Resin[©]

For the separation of concomitant zirconium present in environmental samples (isobaric interference from $({}^{91}\text{Zr}{}^{16}\text{O})^+$), we firstly performed a separation on a cation exchange resin 50W-X8. Previous studies indicated a high affinity of Zr^{1V} towards the strongly acidic exchange resin in dilute hydrochloric acid, in contrast to Pd^{II, 5,6} 1 g of Bio-Rad 50W-X8 was filled into a column and preconditioned and cleaned with 20 mL 1 mol·L⁻¹ HCl. Afterwards, the column was loaded with the sample solution in 1 mol·L⁻¹ HCl and washed again with 15 mL 1 mol·L⁻¹ HCl. All fractions except the preconditioning solution were combined and then evaporated to dryness and taken up in 10 mL 0.01 mol·L⁻¹ HCl. We adapted the Ni Resin[®] method by Dulanská *et al.*⁷ and modified it according to the method by Fenker & DiPrete.⁸ Dulanská *et al.*⁷ used stable Pd as a carrier, however, in MS measurements, the elution of ultra-traces of Pd without additional carrier is preferred to avoid the too strong formation of interfering PdH⁺ species. The active extractant of Ni Resin[®] is dimethyl glyoxime (DMG), which forms stable Pd(DMG)₂ complexes in slightly hydrochloric acidic media. The Ni Resin[®] was preconditioned with

30 mL 0.01 mol·L⁻¹ HCl to eliminate impurities of Ag and Pd. Then, the 10 mL sample was carefully loaded onto the Ni Resin[©] and the PFA beaker was washed 6 times with 5 mL 0.01 mol·L⁻¹ HCl. The Pd(DMG)₂ complex is degraded in strong nitric acid solution. Consequently, Pd was eluted from the column when 40 mL 8 mol·L⁻¹ HNO₃ were applied to the resin. The eluate was evaporated to dryness and taken up in 2 mL 2% HNO₃ for MS measurement.

¹⁰⁷Pd measurement by ICP-QQQ-MS

The analysis of ultra-traces of ¹⁰⁷Pd in environmental samples requires enhanced chemical and instrumental separation for accurate MS measurements. MS methods face interferences from isobars with (almost) identical m/z values, as shown in Table S1. In the case of ¹⁰⁷Pd, its daughter nuclide and respective stable isotope ¹⁰⁷Ag as well as (¹⁰⁶Pd¹H)⁺ are the main isobaric and polyatomic interferences. Stable Ag occurs in the environment in soils in the range <10-5,000 μ g·kg^{-1.9} Both Ag and ¹⁰⁷Pd are found in spent UO₂ fuel.^{10,11} Another interference comes from oxide species, in particular the (⁹¹Zr¹⁶O)⁺ rates are not to be underestimated even in a stable plasma source with oxide rates CeO⁺/Ce <1. In any case, several possible MS interferences for ¹⁰⁷Pd analysis resulting from stable Ag as well as polyatomic interferences have not yet been published. An additional, instrumental separation step was performed by ICP-QQQ-MS with its collision/reaction cell (CRC). Several authors reported the enhanced performance of ICP-QQQ-MS instruments in regards to single quadrupole MS in special regards to nuclear waste characterization^{12,13} and noble metal analysis.^{14,15} The suppression of isobars enables lower backgrounds and detection limits of the analyte. Previous studies proposed the bimolecular reaction of Pd with propane for the separation of Ag and Pd in MS measurements.^{16,17} Palladium reacts with propane, forming the species Pd(C₂H₄)⁺ and Pd(C₃H₆)⁺, whereas Ag does not.

Herein, we analyzed ¹⁰⁷Pd using an Agilent 8900 ICP-QQQ-MS equipped the autosampler SPS 4 and the software MassHunter 4.4. The operating parameters for the ICP-QQQ-MS are specified in Table S2. Palladium was measured on the C_2H_4 shift m/z + 28 and C_3H_6 shift on m/z +42.

SUPPORTING TABLES

Pd isotope (nat. abundance)	Interference (nat. abundance)
¹⁰² Pd (1.02 %)	$^{102}Ru^{+}\ (31.55\ \%),\ ^{51}V^{51}V^{+},\ ^{204}Hg^{2+},\ ^{62}Ni^{40}Ar^{+},\ ^{65}Cu^{37}Cl^{+},\ ^{67}Zn^{35}Cl^{+},\ ^{101}RuH^{+},\ ^{86}Kr^{16}O^{+},\ ^{86}Sr^{16}O^{+}$
¹⁰⁴ Pd (11.14 %)	$^{104}Ru^{+}$ (18.62 %), $^{52}Cr^{52}Cr^{+}$, $^{208}Pb^{2+}$, $^{64}Zn^{40}Ar^{+}$, $^{103}RhH^{+}$, $^{88}Sr^{16}O^{+}$
¹⁰⁵ Pd (22.33 %)	⁵² Cr ⁵³ Cr ⁺ , ⁷⁰ Zn ³⁵ Cl ⁺ , ¹⁰⁴ RuH ⁺ , ¹⁰⁴ PdH ⁺ , ⁸⁹ Y ¹⁶ O ⁺
¹⁰⁶ Pd (27.33 %)	${}^{106}Cd^+, {}^{66}Zn^{40}Ar^+, {}^{105}PdH^+, {}^{90}Zr^{16}O^+, {}^{89}Y^{16}OH^+, {}^{88}Sr^{16}OH_2{}^+$
¹⁰⁷ Pd (0 %)	$^{107}Ag^{+} (51.84 \%), ^{106}PdH^{+}, ^{105}PdH_{2}^{+}, ^{91}Zr^{16}O^{+}, ^{67}Zn^{40}Ar^{+}, ^{90}Zr^{16}OH^{+}, ^{89}Y^{16}OH_{2}^{+}$
¹⁰⁸ Pd (26.46 %)	${}^{108}Cd^+, {}^{68}Zn^{40}Ar^+, {}^{107}AgH^+, {}^{92}Mo^{16}O^+, {}^{92}Zr^{16}O^+$
¹¹⁰ Pd (11.72 %)	${}^{110}Cd^+,{}^{55}Mn^{55}Mn^+,{}^{54}Fe^{56}Fe^+,{}^{70}Ge^{40}Ar^+,{}^{109}AgH^+,{}^{94}Mo^{16}O^+,{}^{94}Zr^{16}O^+$

Table S1. Types of interference of Pd during ICP-MS measurements.

Table S2: Operating parameters for ICP-QQQ-MS Agilent 8900.

	No gas mode	Propane/He mode
RF power	1550 W	1550 W
Sampling depth	10 mm	10 mm
Carrier gas	1.07 L·min ⁻¹ Ar	1.07 L·min ⁻¹ Ar
Sample uptake rate	0.10 rps	0.10 rps
Spray chamber temperature	2 °C	2 °C
Acquired mass number	90, 91,	90, 91,
	102,	102, 102→130, 102→144,
	104,	104, 104→132, 104→146,
	105,	105, 105→133, 105→147,
	106,	106, 106→134, 106→148,
	107,	107, 107→135, 107→149,
	108,	108, 108→136, 108→150,
	109,	109, 109→137, 109→151,
	110	110, 110→138, 110→152
Integration time	0.1 s	1 s
Replicates	5	5
Sweeps/Replicate	100	100
Cell gas	No gas	Propane N3.5 (99.95 %), He N4.6 (99.996 %)

 Table S3. Detection limits according to DIN 32645 for Pd isotopes in different MS modes.

	¹⁰² Pd (ng·kg ⁻¹)	¹⁰⁴ Pd (ng·kg ⁻¹)	¹⁰⁵ Pd (ng·kg ⁻¹)	¹⁰⁶ Pd (ng·kg ⁻¹)	^{108}Pd (ng·kg ⁻¹)	¹¹⁰ Pd (ng·kg ⁻¹)
No gas	0.43	1.40	2.29	1.90	1.52	1.01
C ₂ H ₄ shift	0.40	1.82	1.93	2.85	1.39	1.57
C ₃ H ₆ shift	1.02	2.96	3.57	3.36	3.82	3.18

Table S4. Isotopic ratios of Pd in spent nuclear fuel, literature values for natural Pd and measured natural Pd standard.

	¹⁰² Pd/ ¹⁰⁵ Pd	¹⁰⁴ / ¹⁰⁵ Pd	¹⁰⁶ Pd/ ¹⁰⁵ Pd	¹⁰⁷ Pd/ ¹⁰⁵ Pd	¹⁰⁸ Pd/ ¹⁰⁵ Pd	¹¹⁰ Pd/ ¹⁰⁵ Pd
Spent UO ₂ fuel of BWR reactor ^a	0	0.44	0.49	0.51	0.34	0.11
Natural isotopic ratio ^b	0.046	0.499	1.224	0	1.185	0.525
Measured isotopic ratio of 1	0.043	0.486	1.211	0	1.230	0.562
µg∙kg ⁻¹ Pd standard						
	1.052	1.007	1.011	0.007	0.062	0.022
Mass bias correction factor	1.053	1.027	1.011	0.987	0.963	0.933
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a Data taken from: Pfeiffer, F.; McStocker, B.; Gründler, D.; Ewig, F.; Thomauske, B.; Havenith, A.; Kettler, J. Abfallspezifikation und Mengengerüst, GRS-278 (in German). https://www.grs.de/en/node/1749 (accessed March 2019)

b Data taken from: Brookhaven National Laboratory, NNDC National Nuclear Data Center. http://www.nndc.bnl.gov/ (accessed May 2021).

SUPPORTING FIGURES



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Figure S5. Content of various elements in the CEZ sediment sample (980 mg) after clean-up with a cation exchange and Ni Resin extraction. The mass concentration refers to the solution volume of 2 mL CEZ extract. Please note the logarithmic scale and that only the elements marked in red were fully quantified in the ICP-MS system. All other elements were determined by a quick scan of the MS system and are prone to variable influences from interferences. The quick scan element mass concentration should be treated with caution and only be used an estimation of the concentration range.



Figure S6. Calibration curves of different stable Pd isotopes on the C_2H_4 shift mode of the ICP-QQQ-MS with propane gas reaction.

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