Determination of Pd-107 in radioactive waste

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JOINT WORKSHOP OF TRISKEM AND RADDEC

$^{107}_{46}Pd$ β-

61 neutrons

$T_{1/2}$ ~ 6 x 10^6 years
E_{max} ~ 40 keV
[📖 LNHB, nuclide site]

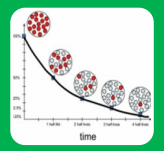
Context

Context: Pd-107 in nuclear waste

ANDRA
Agence nationale pour la gestion des déchets radioactifs

Classification of nuclear waste

Radioactivity level + Period

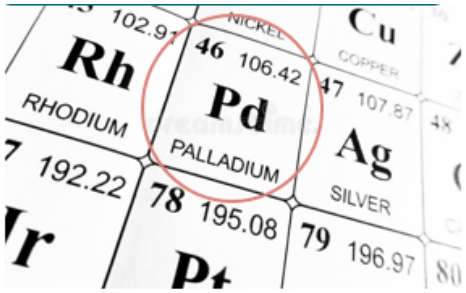


Many characterizations

For low- and intermediate-level waste in France: **143 radionuclides** to be quantified

Pd-107

Palladium



- Transition metal and platinoid
- 6 stable and 30 radioactive isotopes

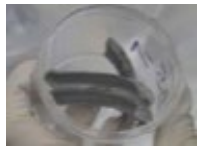
Isotope	Natural abundance of stable Pd (molar %)
^{102}Pd	1.02 %
^{104}Pd	11.14 %
^{105}Pd	22.33 %
^{106}Pd	27.33 %
^{108}Pd	26.46 %
^{110}Pd	11.72 %

Pd-107

- Anthropogenic radionuclide
- Fission product with a long period: impact for long-term management of nuclear waste
  $T_{1/2}$ ~ 6 x 10^6 years
- Pure β^- emitter with a low energy (~ 40 keV): **difficult-to-measure radionuclide**

Necessity to determine Pd-107 activities in nuclear waste?

concretes



metals

resins

effluents and sludges

graphites

Context: challenges to analyze Pd-107 in nuclear sludges

- Sludge composition
  - pH ~ 2, high salt content with $NaNO_3$ ~ 2 mol/L, high concentration of suspended matters, high concentrations of metals (Fe, Ni, Pb…)
  - Relatively high level of radioactivity (α ~ 5000 Bq/g, βγ ~ 50000 Bq/g)

1. **Preparation with tracer addition**
   - ➢ Tracer: Pd enriched in one isotope
2. **Digestion**
   - ➢ Micro-wave oven
   - ➢ Alkali fusion
3. **Purification**
   - ➢ Precipitation
   - ➢ Liquid-liquid extraction
   - ➢ Ion exchange chromatography
   - ➢ Extraction chromatography
4. **Measurements**
   - ➢ Tracer: ICP-AES, ICP-MS
   - ➢ Pd-107: liquid scintillation counting, ICP-MS

Context: challenges to analyze Pd-107 in nuclear sludges

- Sludge composition
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  - Relatively high level of radioactivity (α ~ 5000 Bq/g, βγ ~ 50000 Bq/g)

1. **Preparation with tracer addition**
   - Tracer: Pd enriched in one stable isotope

   → Tracer enriched in Pd-105

2. **Digestion**
   - Micro-wave oven
   - Alkali fusion

   → Micro-wave oven

3. **Purification**
   - Precipitation
   - Liquid-liquid extraction
   - Ion exchange chromatography
   - Extraction chromatography

   → Liquid-liquid extraction + anion exchange chromatography

4. **Measurements**
   - Tracer: ICP-AES, ICP-MS
   - Pd-107: liquid scintillation counting, ICP-MS

   → Q ICP-MS

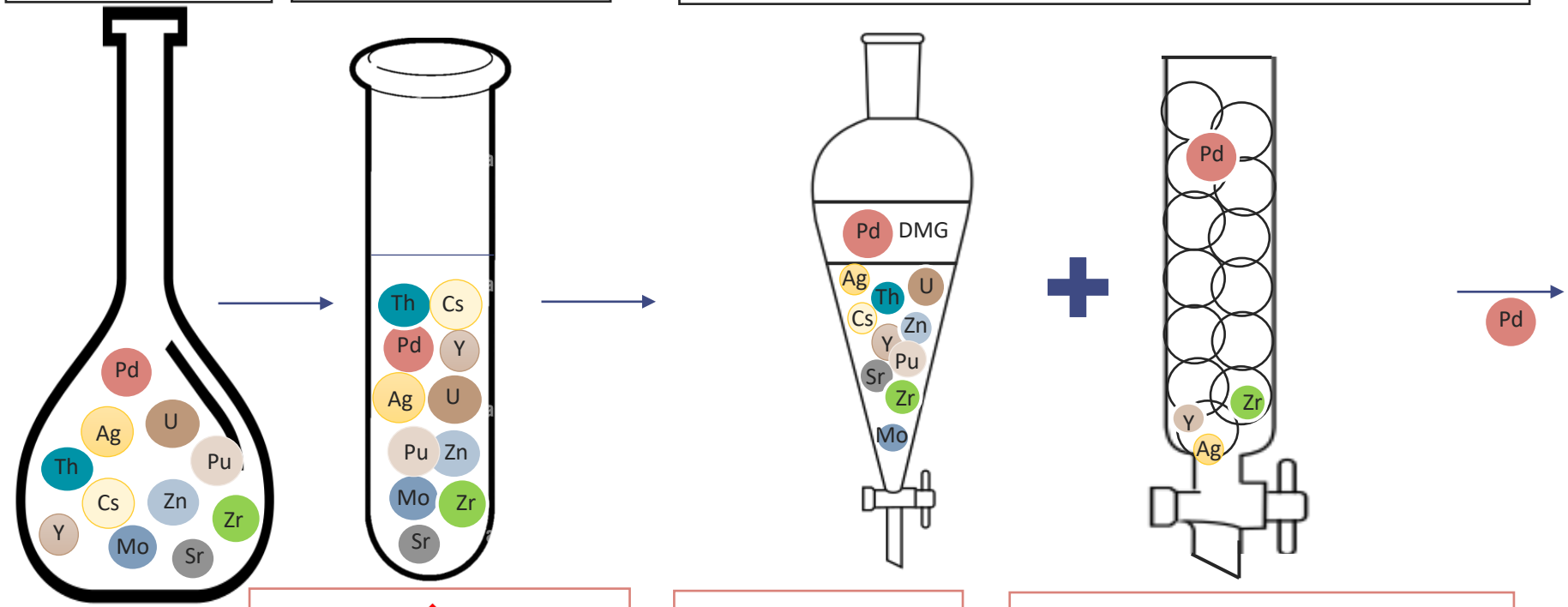
Context: challenges to analyze Pd-107 in nuclear waste

1- Sludge reception at CEA

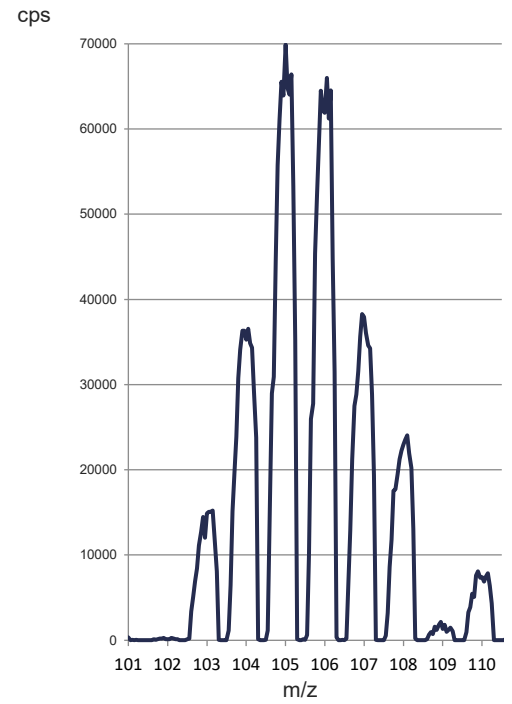
2- Acid digestion in microwave oven with HNO_3/**HF**

3- Purification of Pd
- Liquid-liquid extractions with Dimethyglyoxime (DMG) and **chloroform**
- Anion exchange resin

4- Measurement of Pd-107

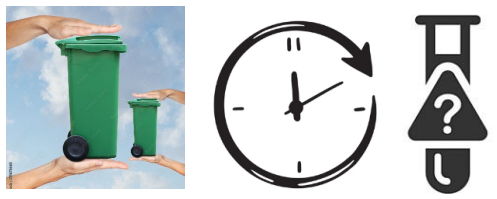


Q ICP-MS spectrum

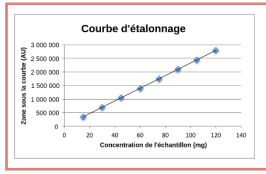


Toxic: Use appropriate protective equipment + handling restricted to permanent staff in France

CMR + non compliant with REACH + radiation exposure of staff

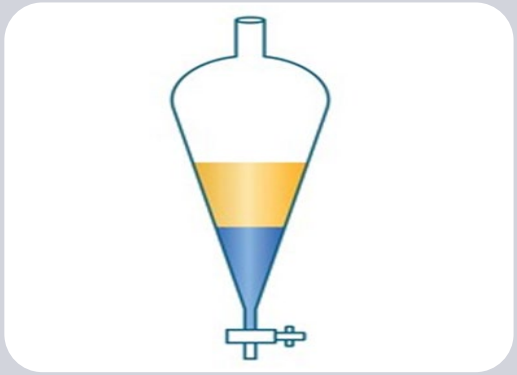


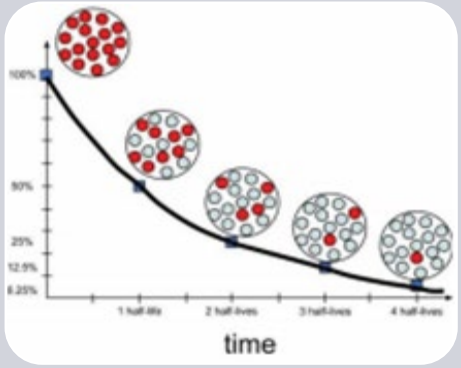
Large effluent volumes + time-consuming + instability of Pd in nitric acid

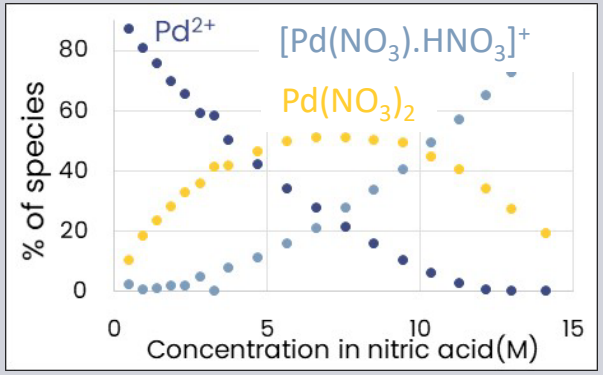


No Pd-107 standard available and outdated half-life

Context: challenges to analyze Pd-107 in nuclear sludges







Challenge 1:

Develop a new purification method of Pd in nuclear sludges

Challenge 2:

Improve measurement and nuclear data for Pd-107

⇨ Pd-107 standard, new value of half-life

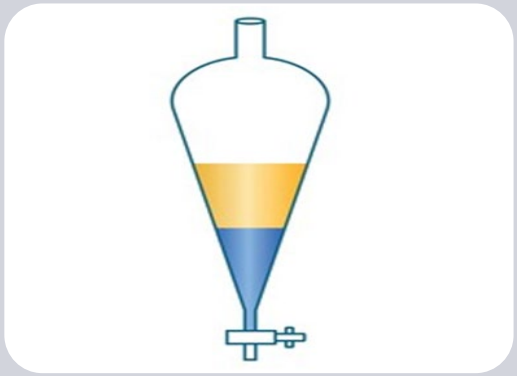
Collaboration with two laboratories: LANIE (CEA) and PTB (Germany)

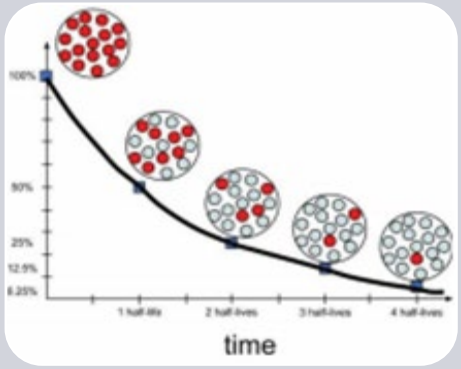
Challenge 3:

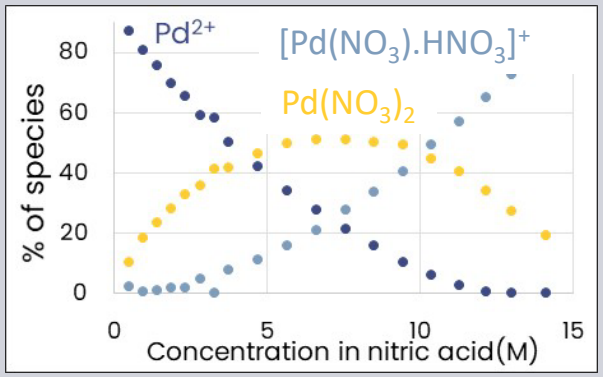
Understand the behaviour of Pd in nitric acid by a speciation study

Collaboration with two laboratories: L3MR (CEA) and LEPMI (CNRS)

Context: challenges to analyze Pd-107 in nuclear sludges







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New purification method of Pd in nuclear sludges

📖 Faure M., Gautier C., Fichet P. *et al.* Methods of separation and quantification by ICP-MS for Pd-107 in radioactive waste. *J Radioanal Nucl Chem* **334**, 4687-4707 (2025)

Constraints for the new purification method

Current method

New method

- Still efficient and selective
  - Keeps Pd and eliminates interfering elements
- Removes toxic and CMR reagents to be REACH compliant
  - No more HF & chloroform
- Decreases effluent volumes
- Less time-consuming

Interfering elements affecting Pd measurement by Q ICP-MS

m/z used for ICP-MS:

- 107: isotope of interest
- 105: isotope of the tracer used for recovery yield
- 108: isotope for the correction of initial Pd present in the sample

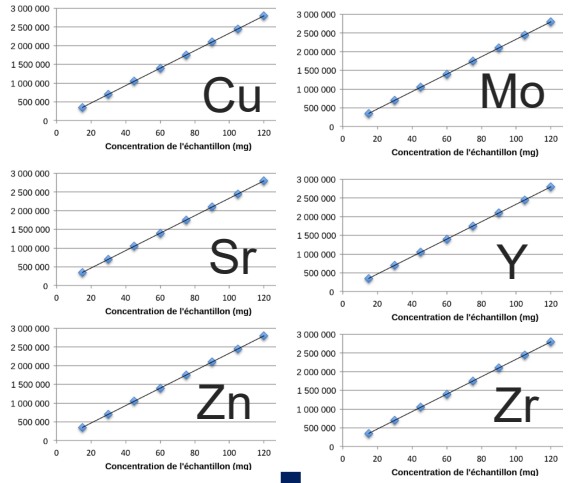
Potential elements that can interfere

Ag
Cu
Cd
Mo
Sr
Y
Zn
Zr

Direct interferents

Ag-107 Cd-108

Other types of interferences



Potential contribution for m/z 105, 107 and 108

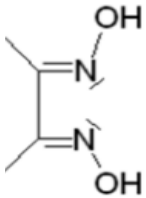
Element	Threshold concentration (µg/L) from which interference occurs at m/z 105, 107 and/or 108
Ag	As soon as they are detected (i.e. > DL)
Cd	
Y	As soon as their concentrations exceed 0.1 µg/L
Zr	
Sr	When their concentrations exceed 1 to 10 µg/L
Mo	
Cu	No interference was observed up to 100 µg/L
Zn	

Necessity to eliminate in priority: Ag, Cd, Y and Zr

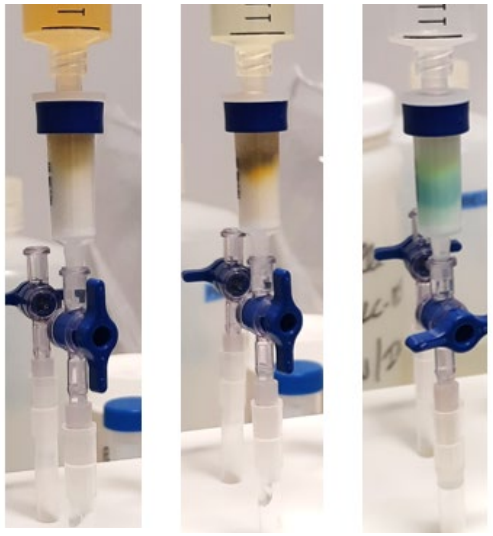
Development of the new purification method

Method based on Dulanska et al. (2016): implementation of Ni® resin bearing DMG

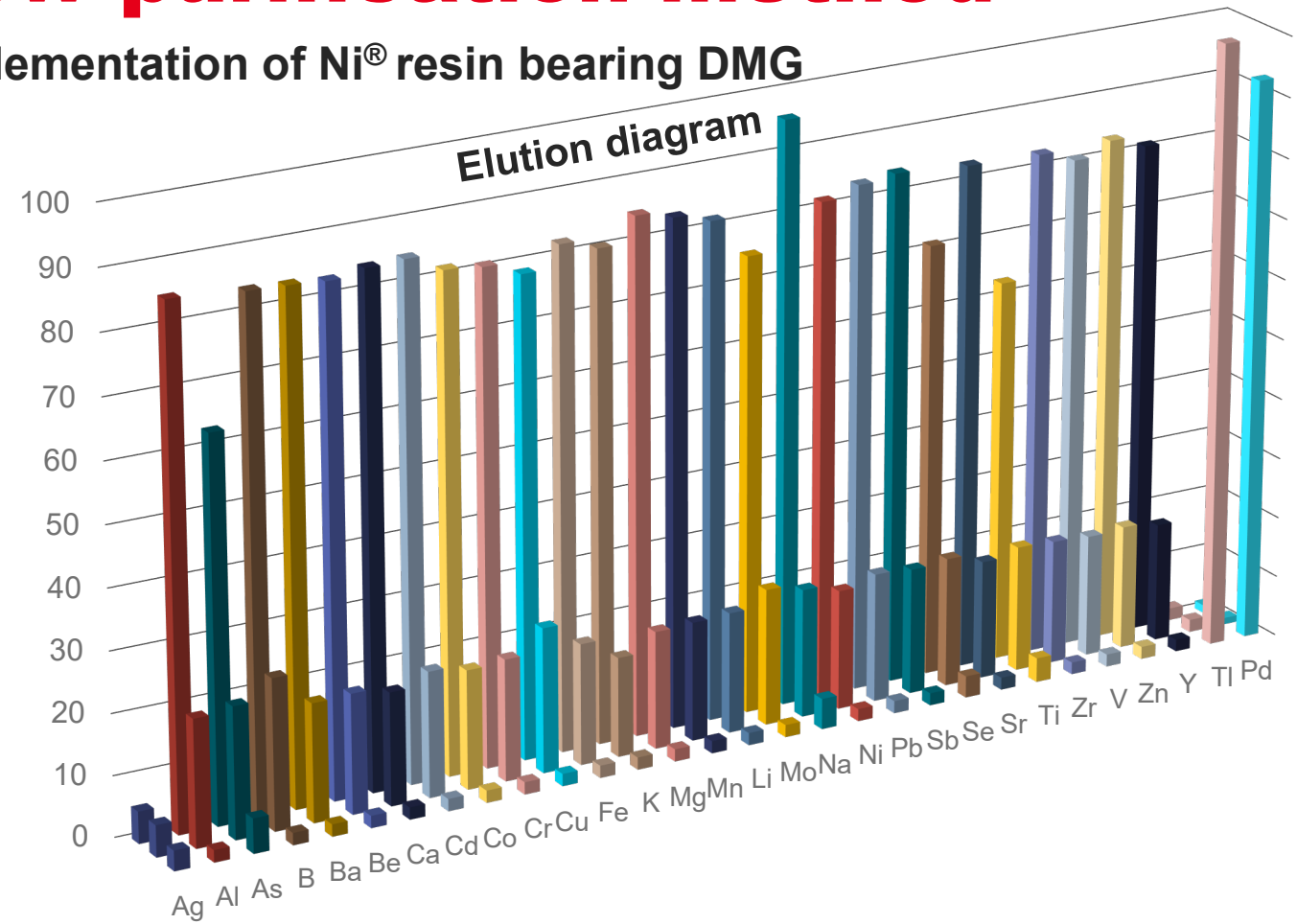
- Conditioning of Ni® resin with 0.5M HCl
- Sample loading and rinsing with 0.5M HCl
- Elution with 5mL of 15M HNO_3
- Quantification by ICP-AES & ICP-MS



DMG



Loading Elution Post elution



Loading: 5µg Pd + 0.5mg of 30 other elements	**Pd**	**Tl**	**Zr**	**Ag**	**Other elements**
% eluted elements in HNO_3 fraction	95%	95%	0.3%	7.0%	<LQ

📖 Dulanská, S., Horváthová, B., Remenec, B. et al. Determination of ^{107}Pd in radwaste using Ni® Resin. J Radioanal Nucl Chem 310, 645-650 (2016)

Development of the new purification method

Remaining challenges:

- Conditioning of Ni® resin with 0.5M HCl
- Sample loading and rinsing with 0.5M HCl
- Elution with 5mL of 15M HNO_3
- Quantification by ICP-AES & ICP-MS

Ag precipitates: the precipitate settles on top of the Ni® resin and is partially re-dissolved during the subsequent stages ⇨ How to remove Ag?

Development of the new purification method

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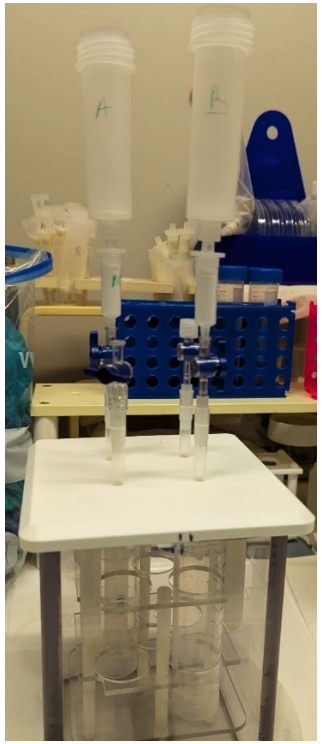
Addition of a filtration step



Development of the new purification method

Remaining challenges:

Conditioning of Ni® resin with 0.5M HCl

Sample loading and rinsing with 0.5M HCl

Elution with 5mL of 15M HNO_3

Quantification by ICP-AES & ICP-MS

Tl is co-eluted with Pd: possibility to change HNO_3 concentration without increasing elution volume and eluting Tl ⇨ How to remove Tl?

+ **traces of Ag and Zr** ⇨ How to remove them?

Optimisation of elution steps

Development of the new purification method

Optimisation of elution steps:

→ **Remove Ag, Zr and traces of other elements, and possibly Tl**

Design Of Experiment (DOE)
Screening design: Hadamard matrix

Preliminary tests to select factors:

Elution with 15mL 6M HNO_3 +
0.025M oxalic acid ⇨ high Pd recovery

Development of the new purification method

Optimisation of elution steps:

→ **Remove Ag, Zr and traces of other elements, and possibly Tl**

Design Of Experiment (DOE)
Screening design: Hadamard matrix

Preliminary tests to select **7 factors**:

HNO_3 elution, HCl elution, oxalic acid elution, rinsing with HNO_3, rinsing with oxalic acid (OA), rinsing with ascorbic acid (AA) and rinsing with citric acid (CA)

Exp. No.	Replicate	[HNO3] elution	HCl elution	Oxalic acid elution	Rinsing with HNO3	Rinsing with oxalic acid	Rinsing with ascorbic acid	Rinsing with citric acid
1		12M	with HCl 1M	with OA 0.025M	without HNO3	with OA 0.025M	without AA	without CA
2		8M	with HCl 1M	with OA 0.025M	with HNO3 1M	without OA	with AA 0.025M	without CA
3		8M	without HCl	with OA 0.025M	with HNO3 1M	with OA 0.025M	without AA	with CA 0.025M
4		12M	without HCl	without OA	with HNO3 1M	with OA 0.025M	with AA 0.025M	without CA
5		8M	with HCl 1M	without OA	without HNO3	with OA 0.025M	with AA 0.025M	with CA 0.025M
6		12M	without HCl	with OA 0.025M	without HNO3	without OA	with AA 0.025M	with CA 0.025M
7		12M	with HCl 1M	without OA	with HNO3 1M	without OA	without AA	with CA 0.025M
8		8M	without HCl	without OA	without HNO3	without OA	without AA	without CA

only 8 experiments to perform !

Development of the new purification method

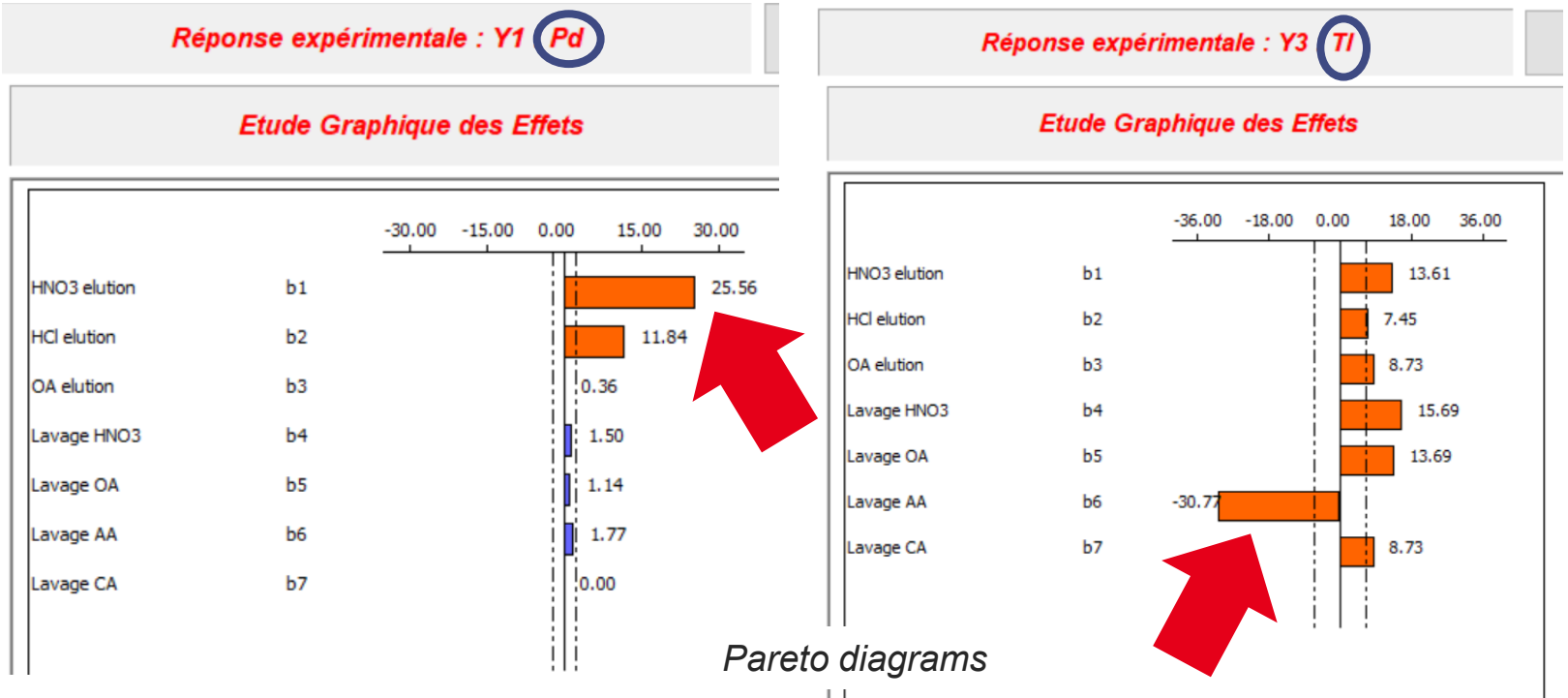
Optimisation of elution steps:

→ **Remove Ag, Zr and traces of other elements, and possibly Tl**

Design Of Experiment (DOE)
Screening design: Hadamard matrix

Preliminary tests to select **7 factors**:

HNO_3 for elution, HCl elution, oxalic acid elution, rinsing with HNO_3, rinsing with oxalic acid (OA), rinsing with ascorbic acid (AA) and rinsing with citric acid (CA)



Pareto diagrams

Use of Nemrod software to determine the main influencing factors:

- Pd: HNO_3 elution and HCl elution
- Tl: rinsing with ascorbic acid

Development of the new purification method

Conditioning of Ni® resin with 0.5M HCl

↓

Sample loading in 0.5M HCl and filtration

↓

Rinsing 1 with 0.5M HCl

Most of interfering elements are eliminated

↓

Rinsing 2 with 0.025M ascorbic acid

Tl is eliminated

↓

Elution 1 with 15mL 6M HNO_3 + 0.025M oxalic acid

↓

Elution 2 with 5mL 15M HNO_3

↓

Quantification by ICP-AES & ICP-MS

% Pd	Preliminary test	Test after optimization
Medium used before elution	0.5M HCl	0.025M ascorbic acid
Elution 1 with 15mL 6M HNO_3 + 0.025M oxalic acid	89%	32%
Elution 2 with 5mL 15M HNO_3	8%	47%
Total recovery	97%	79%

Results not in agreement

Development of the new purification method

Conditioning of Ni® resin with 0.5M HCl

↓

Sample loading in 0.5M HCl and filtration

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↓

Elution 2 with 5mL 15M HNO_3

↓

Quantification by ICP-AES & ICP-MS

% Pd	Preliminary test	Test after optimization	Comple-mentary test	Comple-mentary test
Medium used before elution	0.5M HCl	0.025M ascorbic acid	0.025M ascorbic acid then 0.5M HCl	0.025M ascorbic acid then 3M HCl
Elution 1 with 15mL 6M HNO_3 + 0.025M oxalic acid	89%	32%	96%	not done
Elution 2 with 5mL 15M HNO_3	8%	47%	4%	99%
Total recovery	97%	79%	100%	99%

Need to have a re-equilibration step with HCl before Pd elution

Development of the new purification method

Optimisation of elution steps:

Design Of Experiment (DOE)

Conditioning of Ni® resin with 0.5M HCl

Sample loading, filtration and rinsing with 0.5M HCl

Majority of elements are eliminated

Rinsing with 0.025M ascorbic acid

Tl is eliminated

Two options are available

Re-equilibration step with 3M HCl

Preparation of Pd elution

Elution with 5mL 15M HNO_3

Elution of Pd with good recovery

Option chosen

Re-equilibration step with 0.5M HCl

Preparation of Pd elution

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Development of the new purification method

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Elution of Pd with good recovery

Loading: 5µg Pd + 0.5mg of 30 other elements	**Pd**	**Other elements**
% eluted elements	>91%	traces

LOQ = 20µg/L

Development of the new purification method

Optimisation of elution steps:

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Elution of Pd with good recovery

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% eluted elements	>91%	traces

LOQ = 20µg/L

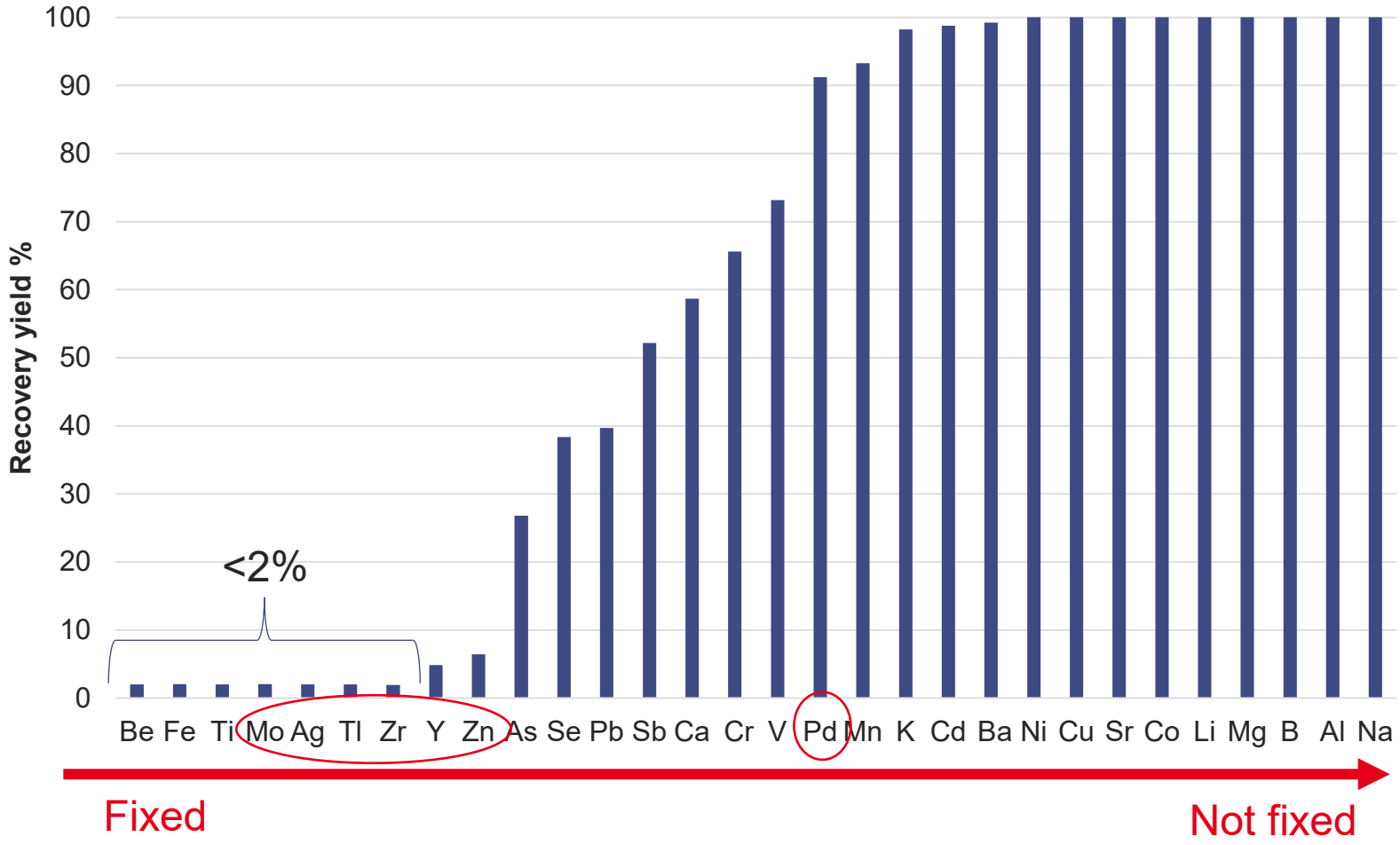
Addition of a purification step to achieve a higher selectivity

Development of the new purification method

Additional purification after Ni® resin → Addition of a second Ni® resin: long and still Zr

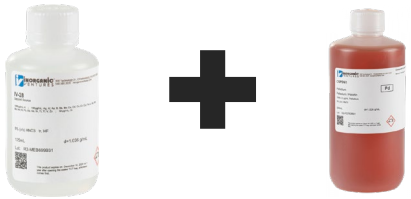
Method based on Tosato et al. (2023): implementation of LN® resin

- Conditioning of LN® resin with 0.005M HCl
- Sample loading in 0.005M HCl
- Rinsing with 0.005M HCl
- Concentration measurement by ICP-AES



Tosato, M., Gandini, A., Happel, S. et al. Chromatographic separation of silver-111 from neutron-irradiated palladium target: toward direct labeling of radiotracers. EJNMMI Radiopharm. Chem. 8, 43 (2023)

Development of the new purification method



Simulated samples

Sample digestion
in micro-wave oven with HNO_3

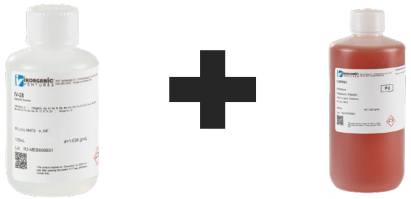
Filtration

Ni® resin

LN® resin

Concentration measurement
by ICP-MS Q

Development of the new purification method



Simulated samples

Sample digestion in micro-wave oven with HNO_3

Filtration

Ni® resin

LN® resin

Concentration measurement by ICP-MS Q

% eluted elements	Pd	Zn	Cu	Mo	Zr	Cd, Y, Sr	Ag
Ni® resin LOQ=20µg/L	>97%	0.3%	0.06%	0.7% [175µg/L]	0.5% [125µg/L]	<0.03%	0.05%
Ni® resin + LN® resin LOQ=4µg/L	>85%	0.3%	0.06%	<0.02%	<0.02%	<0.02%	0.05%

≃ 77 µg/L

≃ 16 µg/L

≃ 10 µg/L

On average, 50 times less Ag in the real sludges than in the simulated samples

Purification method of Pd



Non radioactive simulated sample spiked with stable Pd

Low-level radioactive effluent spiked with Pd-107 standard

Real sludge containing Pd-107

Current method


Sample digestion in micro-wave oven with HNO_3/**HF**

4 liquid-liquid extractions with DMG and chloroform

Anion exchange resin

Concentration measurement by Q ICP-MS

New method

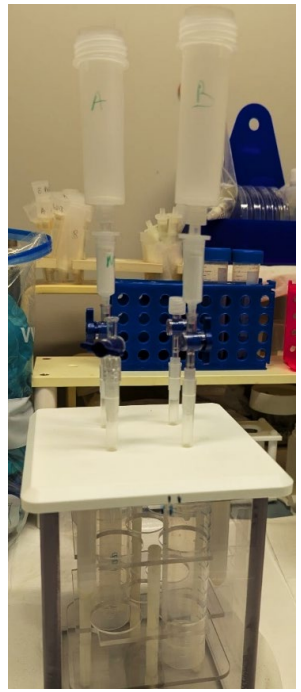
Sample digestion in micro-wave oven with HNO_3

Filtration

Ni-Resin®

LN-Resin®

Concentration measurement by Q ICP-MS



Comparison of purification methods

Sample type	Pd recovery yields after separation	
	Current separation	New separation
Non radioactive simulated sample with stable Pd (5µg)	45 %	85 %
Radioactive effluent spiked with Pd-107 standard (0.3µg)	37 %	67 %
Real sludge already containing Pd-107	47 %	43 %

Values given for one separation

Duration	5 days	4 days
Consumed reagents	500 mL	150 mL

⇨ **Improved Pd yields with the new method for simple matrices or matrices with low Pd quantity**
⇨ **No significant difference of Pd yield for real sludges**
⇨ **Less time-consuming and less effluent volumes**

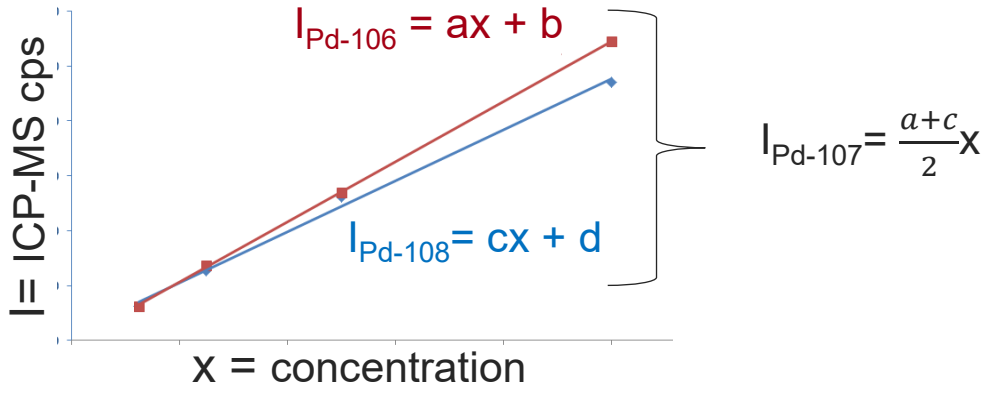
Measurement of Pd-107 in nuclear sludges

Quantification of Pd-107 by ICP-MS

No Pd-107 standard available before 2025

Current quantification method

Natural Pd standard



$I_{Pd-107} = \frac{a+c}{2}x$

Average of Pd-106 & Pd-108 slopes to obtain Pd-107 calibration curve

Conversion of concentration (µg/L) to activity (Bq/g)

$$A = \frac{\mathbf{m} \times \ln 2 \times Na}{M \times T_{1/2}}$$

A: Activity (Bq)
M: Molar mass (g/mol)
$T_{1/2}$: Half-life (s)
Na: Avogadro's number (mol^{-1})
m: mass (g)

Need of an accurate half-life $T_{1/2}$

*$T_{1/2}$ = (5.94 ± 0.13) x 10^6 years
Uncertainty: 2.1% at k = 2

📖 *Kossert K, Faure M, Deptuck D (2025) On the spectrum and maximum energy of the first forbidden unique beta decay of ^{107}Pd. *Applied Radiation and Isotopes* **222** 111863

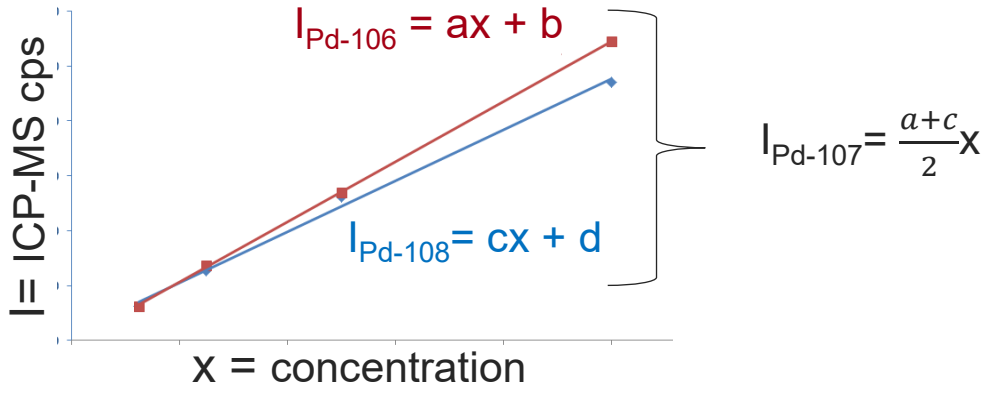
Measurement of Pd-107 in nuclear sludges

Quantification of Pd-107 by ICP-MS

No Pd-107 standard available before 2025

Current quantification method

Natural Pd standard



Average of Pd-106 & Pd-108 slopes to obtain Pd-107 calibration curve

Application to a real radioactive sludge

→ Current purification method: 3.24 ng/g (30% at k=2)

→ New purification method: 3.62 ng/g (30% at k=2)

⇨ **No significant difference (<15%): validation of the new purification method**

5. Conclusions and prospects

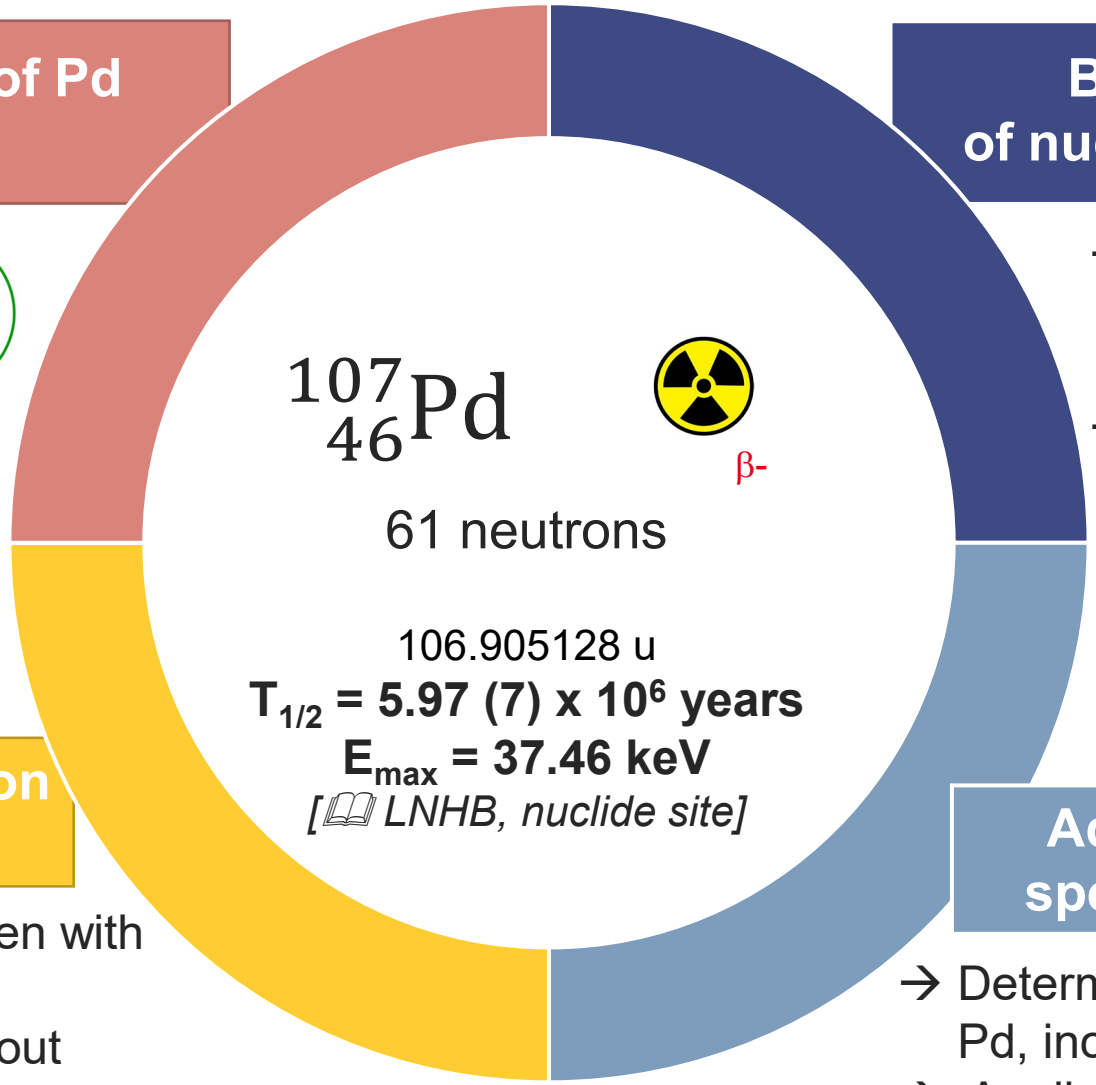
Conclusions and perspectives

New purification method of Pd in nuclear sludges

- → No CMR or HF: REACH compliant
- → Less effluent generated
- → Faster and still selective
- → Applicable to other valorization projects concerning Pd ?

Validation of two quantification methods for Pd-107

- → Possibility to quantify Pd-107 even with a natural Pd standard
- → Application to radionuclides without commercially available standard (Zr-93)



Better knowledge of nuclear data for Pd-107

- → New value of half-life for Pd-107, new maximum β energy value
- → Improved quantification
- → Optimization of waste management in particular, at long term

Additional data on Pd speciation in nitric acid

- → Determination of three species of Pd, including Pd adducts
- → Application to other chemical elements

Acknowlegments

Thanks to:

- my co-authors: Marina Faure (phD student), Christèle Colin, Lucie Hélot, Elodie Laporte

- Majd Shmeit, Hélène Isnard and Karsten Kossert for the collaboration on Pd-107 measurements

- Romain Dagnélie, Emilie Thory and Isabelle Billard for their support on speciation study

- Pascal Fichet for his technical support

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France

celine.gautier@cea.fr

References related to our work

- 🕮 Faure M., Gautier C., Fichet P. *et al.* Methods of separation and quantification by ICP-MS for Pd-107 in radioactive waste. *J Radioanal Nucl Chem* **334**, 4687-4707 (2025)
- 🕮 Shmeit M, Faure M, Gautier C, Isnard H (2025) Quantifying the accurate content of ^{107}Pd in a radioactive effluent using the isotope dilution technique and multi-collector ICP-MS. *Spectrochimica Acta Part B: Atomic Spectroscopy* **225** 107119.
- 🕮 Kossert K, Faure M, Deptuck D (2025) On the spectrum and maximum energy of the first forbidden unique beta decay of ^{107}Pd. *Applied Radiation and Isotopes* **222** 111863
- 🕮 Faure M., Billard I., Gautier C., Spectrophotometric determination of Pd (II) aqueous speciation in nitric acid, *in review process*

Thank you for listening

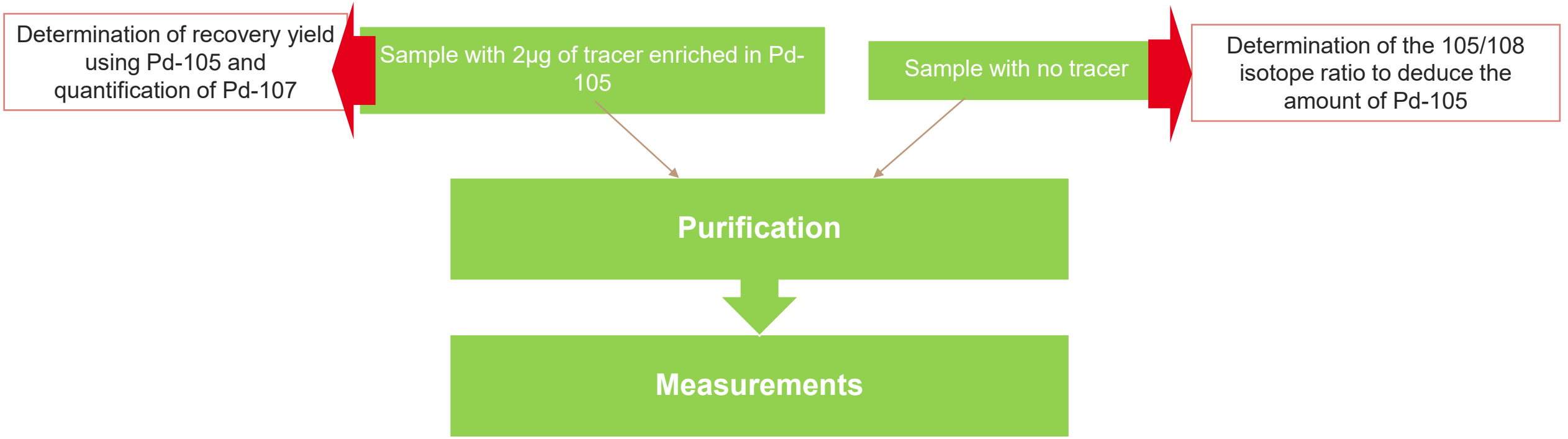
Interfering elements affecting Pd measurement by ICP-MS

Isotopes	Interferences in ICP-MS for Pd
^{102}Pd	$^{204}Pb^{2+}$; $^{86}Sr^{16}O^{+}$
^{104}Pd	$^{40}Ar^{64}Zn^{+}$; $^{208}Pb^{2+}$; $^{88}Sr^{16}O^{+}$
^{105}Pd	$^{40}Ar^{65}Cu^{+}$; $^{88}Sr^{16}O^{1}H^{+}$; $^{88}Sr^{17}O^{+}$; $^{87}Sr^{18}O^{+}$; $^{89}Y^{16}O^{+}$; $^{68}Zn^{37}Cl^{+}$; $^{70}Zn^{35}Cl^{+}$
^{106}Pd	$^{40}Ar^{66}Zn^{+}$; $^{106}Cd^{+}$; $^{88}Sr^{18}O^{+}$; $^{90}Sr^{16}O^{+}$; $^{89}Y^{16}O^{1}H^{+}$; $^{89}Y^{17}O^{+}$; $^{90}Zr^{16}O^{+}$
^{107}Pd	$^{107}Ag^{+}$; $^{40}Ar^{67}Zn^{+}$; $^{91}Y^{16}O^{+}$; $^{90}Zr^{16}O^{1}H^{+}$; $^{90}Zr^{17}O^{+}$; $^{91}Zr^{16}O^{+}$
^{108}Pd	$^{40}Ar^{68}Zn^{+}$; $^{108}Cd^{+}$; $^{92}Mo^{16}O^{+}$; $^{92}Zr^{16}O^{+}$
^{110}Pd	$^{40}Ar^{70}Zn^{+}$; $^{110}Cd^{+}$; $^{94}Mo^{16}O^{+}$; $^{94}Zr^{16}O^{+}$

Direct measurement

Use of these masses for yield determination

Measurement of Pd-107 in nuclear waste



Comparison of purification methods

5µg Pd + 500µg of other elements	Simulated samples	
	Pd recovery (%)	Remaining other elements (%)
Current method	45%	Zn = 0.01% Cu = 0.04% Ag, Cd, Mo, Pb, Sr, Y, Zr <= LQ (0.02%)
New method	>85%	Ag = 0.05% Zn = 0.3% Cu = 0.06% Cd, Mo, Pb, Sr, Y, Zr <= LQ (0.02%)

Pd recovery is higher with the new method but traces of Ag remains

→ Combinaison of Ni-resin & Anion exchange resin AG1-X8

Measurement and nuclear data of Pd-107

Current value determined in 1969 by Flynn et al.:
$T_{1/2}$ = (6.5 ± 0.3) × 10^6 years
Uncertainty: 4.6%

LASE

Purification and characterization of a sample rich in Pd-107

$$T_{1/2} = \frac{m \times \ln 2 \times Na}{M \times A}$$

A: Activity (Bq)
M: Molar mass (g/mol)
$T_{1/2}$: Period (s)
Na: Avogadro's number (mol^{-1})
m: mass (g)

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Na: Avogadro's number (mol^{-1})
m: mass (g)

Need of specific measuring instruments with high precision

Precise measurements of the mass (m)

Precise measurements of activity (A)

Collaboration with specialised laboratories

Measurement and nuclear data of Pd-107

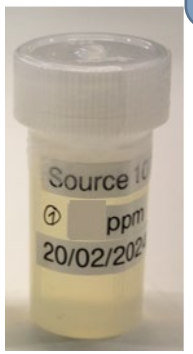
Separations, Characterization, Preparation

LASE

- Dissolution of a radioactive precipitate and separations
- α, β, γ, and ICP-MS Q characterizations: pure Pd
- Change of medium for analyses outside LASE
- Fractionation and weighing prior to transport
- Confirmation of Ag absence → second separation on a purified aliquot

Isotopic and concentration measurements by MC ICP-MS (m)

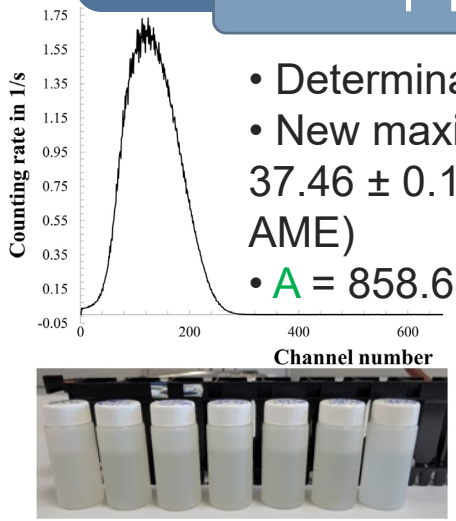
LANIE at CEA



- Verification of Ag absence
- 27.3 ± 0.2 µg/g, with Pd-107 abundance = 14.971 ± 0.003 %
  ⇨ m = 4.09 µg/g of Pd-107

Liquid scintillation measurements (A)

PTB



- Determination of the β spectrum
- New maximum β energy: 37.46 ± 0.19 keV (34.0 ± 2.3 keV AME)
- A = 858.6 ± 8.3 Bq/g of Pd-107

Physikalisch-Technische Bundesanstalt
Nationales Metrologieinstitut

$$T_{1/2} = \frac{\mathbf{m} \times \ln 2 \times Na}{M \times A}$$

$T_{1/2}$ = (5.94 ± 0.13) x 10^6 years
Uncertainty: 2.1% at k = 2

Precision improvement of a factor 2 / Flynn et al.

Difference ~ 9%

Measurement and nuclear data of Pd-107

Separations, Characterization, Preparation

LASE

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- α, β, γ, and ICP-MS Q characterizations: pure Pd
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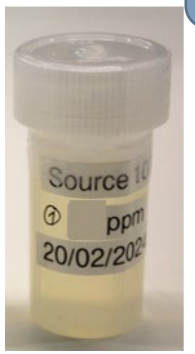
Isotopic and concentration measurements by MC ICP-MS (m)

LANIE at CEA



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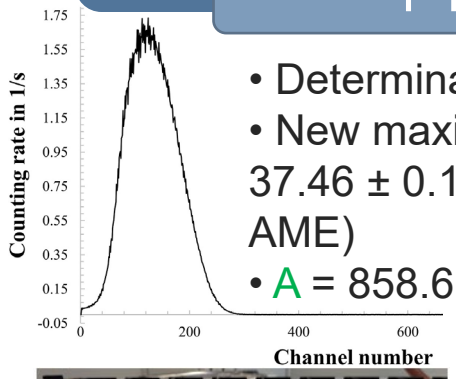

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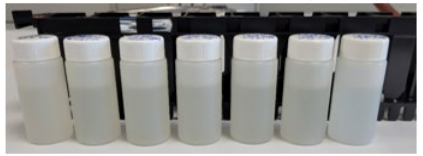

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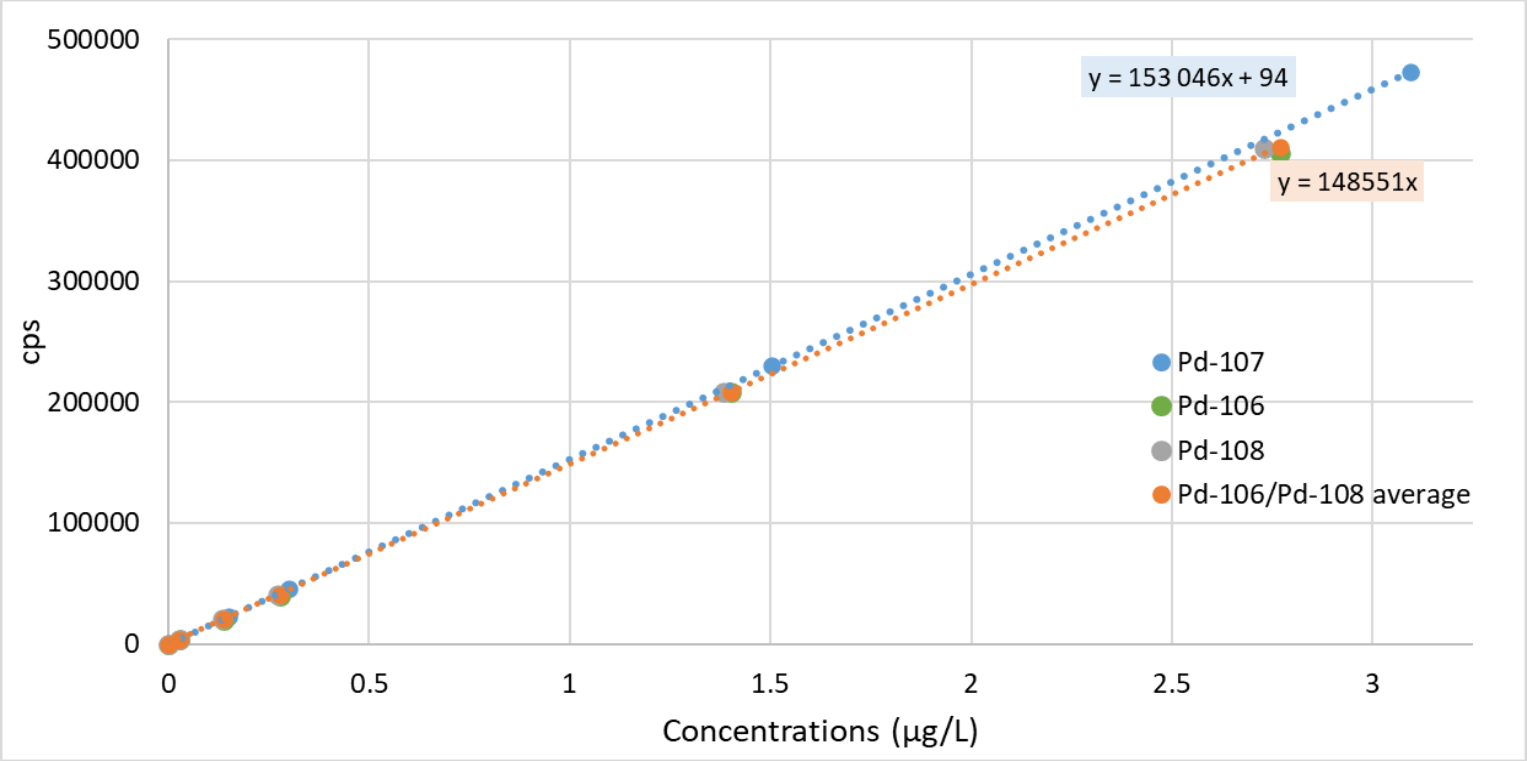
→ Standard of Pd-107

Measurement of Pd-107 in nuclear waste

Comparison of calibration curves obtained with natural Pd standard and Pd-107 source**



⇨ No significant difference for Pd-107 quantification when using Pd-107 standard or natural Pd standard (< 3%)
⇨ Both quantification methods are validated

📖 **Shmeit M, Faure M, Gautier C, Isnard H (2025) Quantifying the accurate content of ^{107}Pd in a radioactive effluent using the isotope dilution technique and multi-collector ICP-MS. *Spectrochimica Acta Part B: Atomic Spectroscopy* **225** 107119.

Speciation of palladium in nitric acid

Nitric acid is widely used for radioactive waste analysis and spent nuclear fuel dissolution

Instability of Pd concentration in nitric acid solutions

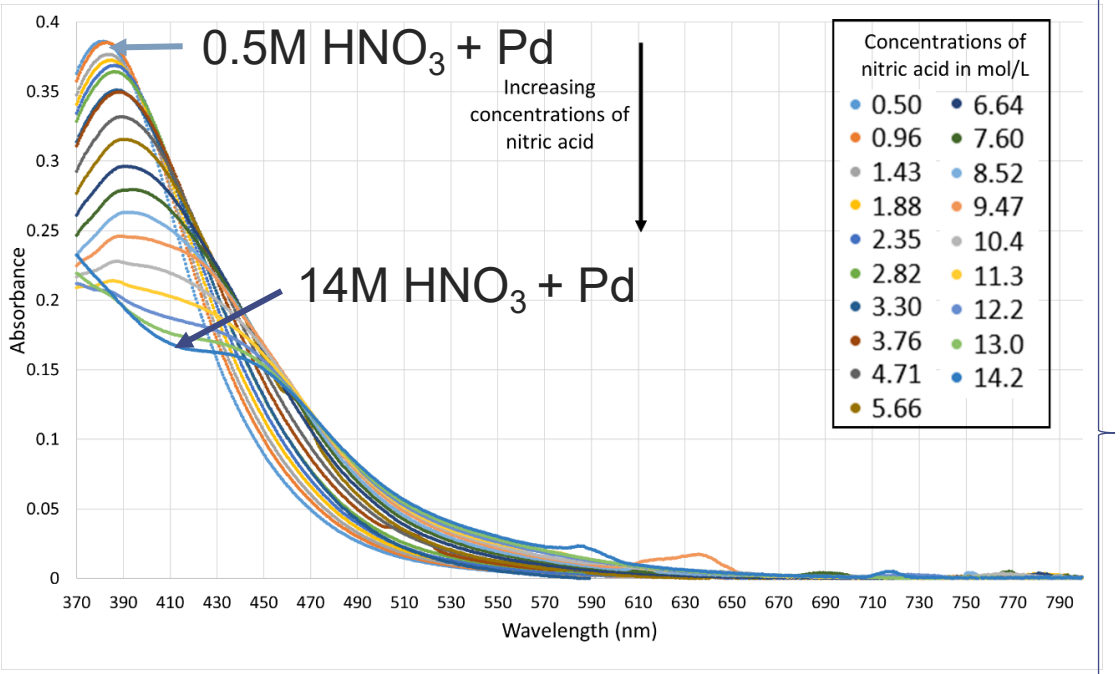
Limited literature data on Pd speciation in nitric acid solutions

Need to improve knowledge on Pd speciation in nitric acid

Speciation study by UV-visible spectrophotometry with **L3MR** laboratory at CEA Saclay

Speciation of palladium in nitric acid

Mixing **stable Pd** with **nitric acid**
from 0.5M to 14M



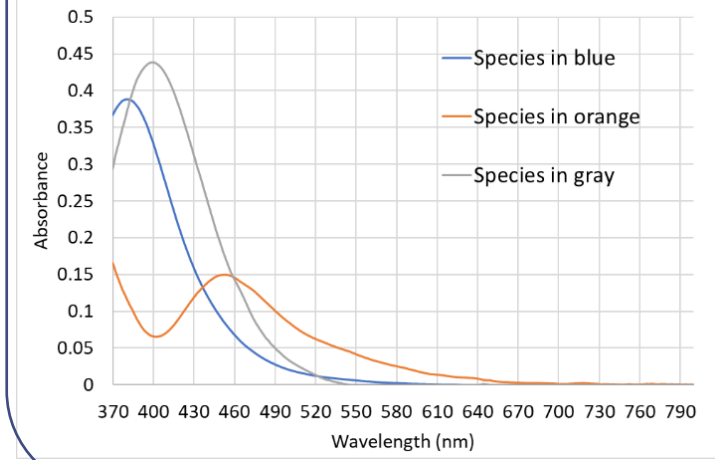
UV-visible spectra of 19 Pd solutions at 100 mg/L in various concentrations of nitric acid, 2 hours after preparation

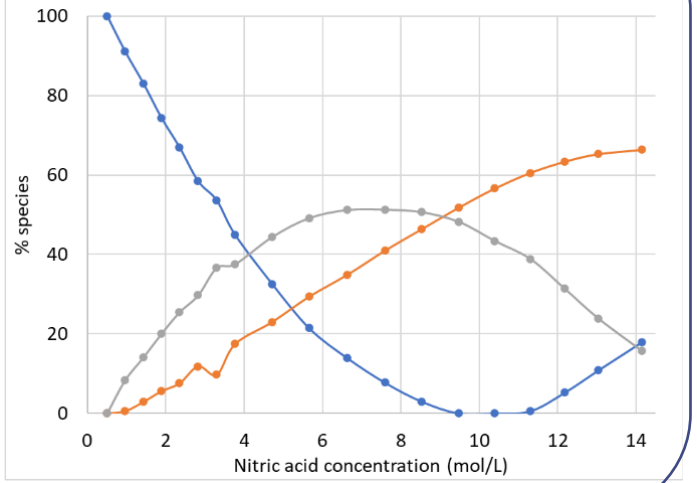
Data analysis with **LEMPI** at CNRS Grenoble

Principal Component Analysis (PCA) & Multivariate Curve Resolution (MCR)

Number of chemical species → 3 ✓ / 4 X

Pure spectra of Pd species + Speciation diagram of Pd





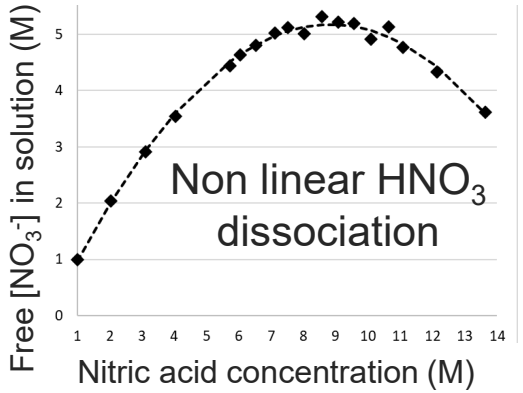
Need to identify the nature of the species
⇨ Chemical model assumptions

Speciation of palladium in nitric acid

120 possibilities of models

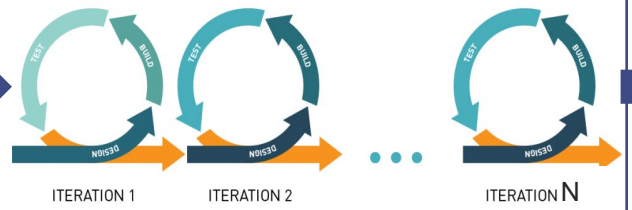
The concentrations of the three Pd species are expressed as a function of:

- Equilibrium constants (K)
- Activity coefficients (γ) using the B-dot model
- Initial concentrations of Pd and NO_3^- with the data from Ruas et al. and Baudat et al.



Fitting step (with MINUIT software)

Find the best equilibrium constants to deduce the chemical model



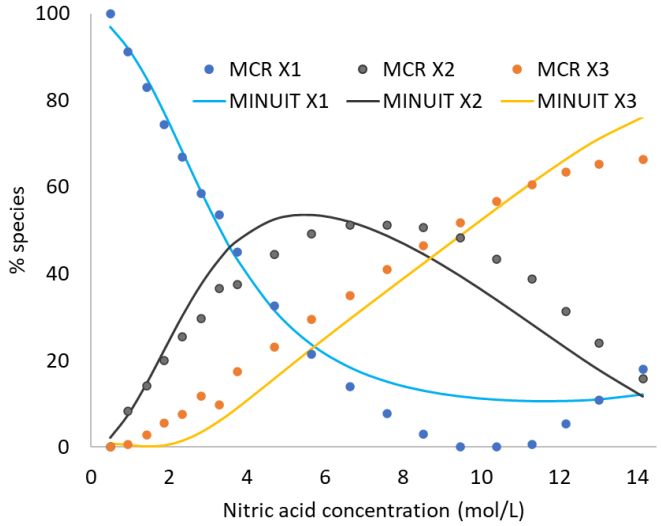
$\chi_1^2 > \chi_2^2 > \chi_n^2$

Evaluate fit quality (χ^2)

Chemical model for Pd speciation

$Pd^{2+} + 2NO_3^- \rightleftarrows Pd(NO_3)_2$

$Pd^{2+} + NO_3^- + HNO_3 \rightleftarrows [Pd(NO_3).HNO_3]^+$



$\chi^2 = 2.59$

K1 = 1.17 ± 0.03 ; K2 = 1.10 ± 0.04

⇨ Pd adducts with HNO_3

⇨ K_1 and K_2 consistent with literature values ⇔ validity of the model