Speciation of plutonium in phosphate medium and solubility in aqueous solution

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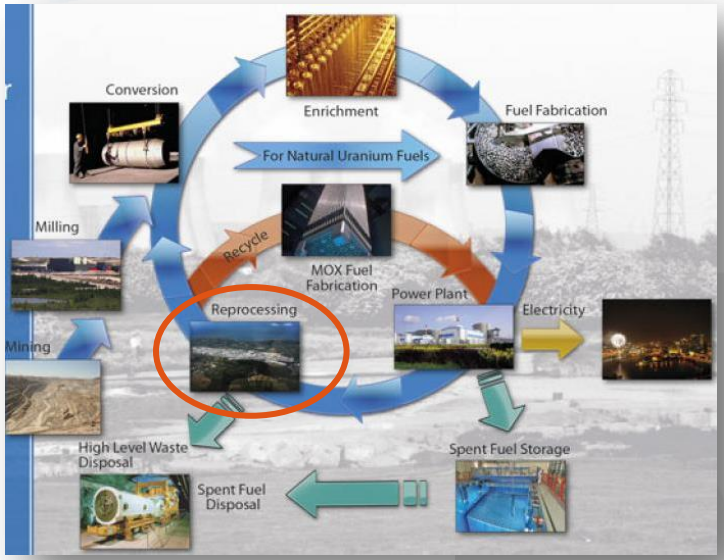
Context

Nuclear Fuel Cycle



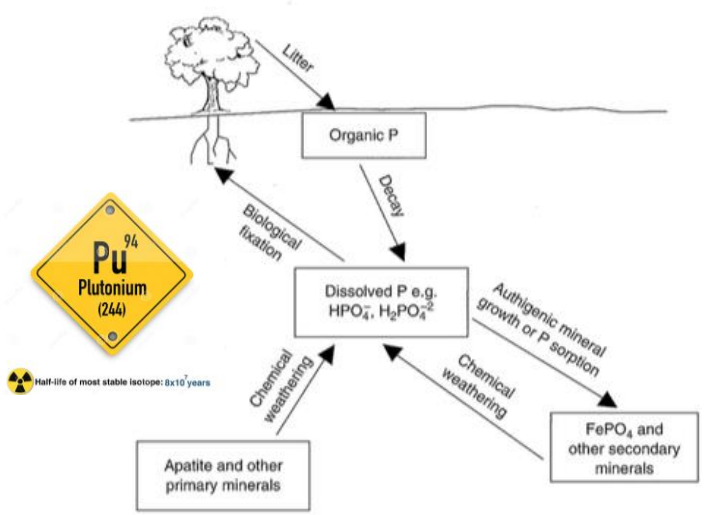
- ✓ PUREX / separation with TBP
- ✓ H_3PO_4 is the last degradation product of TBP

Plutonium ions

Strong interaction

Phosphate species

Environment



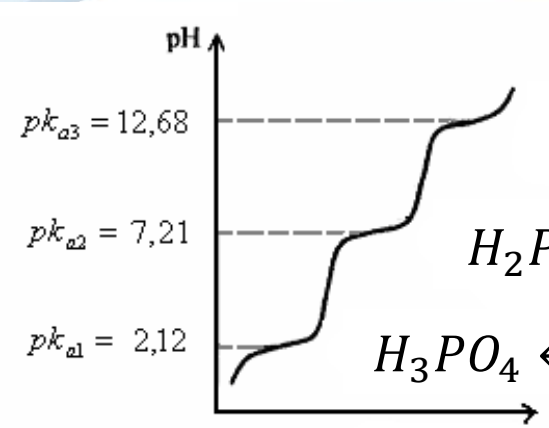
- ✓ High amount of phosphates (degradation of rocks minerals, fertilizer…)
- ✓ Fall out of nuclear testing
- ✓ Nuclear power plants accidents

Modeling of Pu behavior in presence of phosphate species requires fundamental data on Pu-phosphate interaction

IAEA., *Introduction to the Nuclear Fuel Cycle* (2010)

Phosphoric Acid (H_3PO_4)

Range pH



Dissociation of H_3PO_4

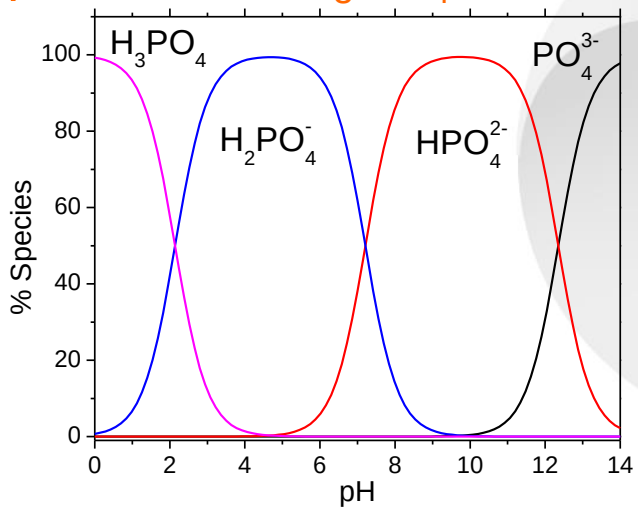
$$HPO_4^{2-} \leftrightarrow PO_4^{3-} + H^+$$

$$H_2PO_4^{-} \leftrightarrow HPO_4^{2-} + H^+$$

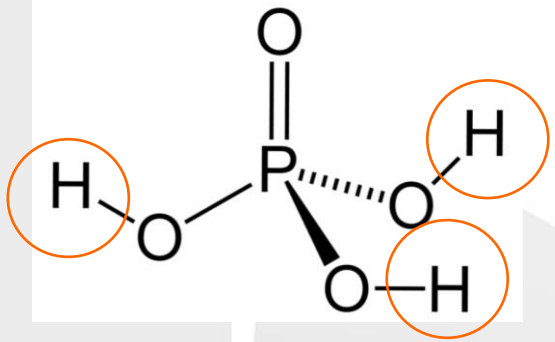
$$H_3PO_4 \leftrightarrow H_2PO_4^{-} + H^+$$

- ✓ Three principal species
- ✓ Well known chemistry

Speciation of H_3PO_4 in solution



Gouveia D. S., Materials Science Forum (2006), **530**, 593-598



Strong interactions with M^{n+}

Protons can be removed leading to the formation anionic species

Plutonium (Pu)

89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac	**Th**	**Pa**	**U**	**Np**	**Pu**	**Am**	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lr**
Actinium (227)	Thorium 232.0377	Protactinium 231.03588	Uranium 238.02891	Neptunium (237)	Plutonium (244)	Americium (243)	Curium (247)	Berkelium (247)	Californium (251)	Einsteinium (252)	Fermium (257)	Mendelevium (258)	Nobelium (259)	Lawrencium (266)

Plutonium
Rich and complex chemistry

Plutonium can exist in several oxidation states leading to different behavior and a large variety of chemical form

Oxidation state	**+III**	**+IV**	**+V**	**+VI**
Chemical form	Pu^{3+}	Pu^{4+}	PuO_2^{+}	PuO_2^{2+}
Effective charge on An	+3	+4	+2.3	+3.2

Reactivity : Pu^{4+} >> PuO_2^{2+} ≈ Pu^{3+} >> PuO_2^{+}

Clark D. L., *Los Alamos Science* (2000), **26**, 364-381
Moskaleva L. V. *et. al.*, *Physical Chemistry Chemical Physics* (2006), **8**, 3767-3773

Aim of the study

Development of protocols for Pu ions to study the interaction with phosphates

BUT

- The chemistry of plutonium is complex (several oxidation states SIMULTANEOUSLY)
- Limited amount available in academic laboratory (2 mg ^{239}Pu in glove box)

Use of **ANALOGUES** for each Pu oxidation state

✓ Cations with similar chemical behaviour
✓ No interference due to redox properties

Plutonium	**Pu^{3+}**	**Pu^{4+}**	**PuO_2^{+}**	**PuO_2^{2+}**
Analogue	Eu^{3+} Nd^{3+}	Th^{4+}	NpO_2^{+}	UO_2^{2+}

Choppin G.R., *et. al.*, *Radiochimica acta* (1999), **85**, 89-95

Methodology

Determination thermodynamic data

Aqueous solution

- **Ultra-trace scale(C_{An} ~ 10^{-10}M)**

Analogues of Pu(III) and Pu(IV)

Liquid-liquid extraction for ^{152}Eu(III) and ^{227}Th(IV)

- **Macro-concentration (~10^{-3}M)**

Analogues of Pu(V) and Pu(VI)

UV-Vis spectrophotometry for $NpO_2^+$and UO_2^{2+}

Solid

- **Synthesis and characterization of rhabdophane**

Analogue of Pu(III)

$NdPO_4$
$Eu_{0.01}Nd_{0.99}PO_4$
$(^{152}Eu/Eu)_{0.01}Nd_{0.99}PO_4$
} XRD and TGA

- **Solubility as a function of time**

Monitored by γ spectrometry for ^{152}Eu(III)

Stability constants

$$M + nL \overset{\beta_n}{\leftrightarrow} ML_n \qquad \beta_n = \frac{[ML_n]}{[M][L]^n}$$

Solubility products

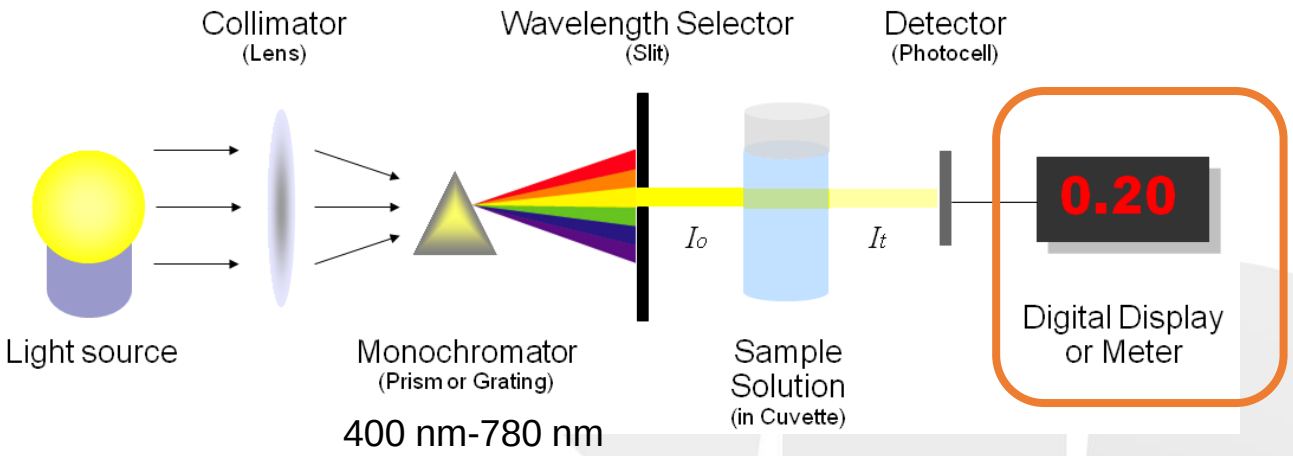
$$M_yX_z(s) \leftrightarrow yM^{z+}(aq) + zX^{y-}(aq)$$

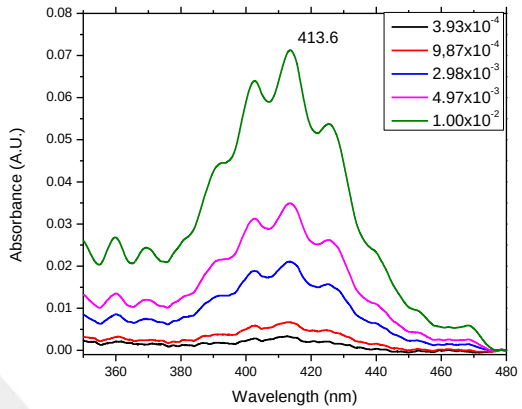
$$K_{sp} = [M^{z+}]^y[X^{y-}]^z$$

Interaction of Pu (VI)-H_3PO_4

UV-Vis spectrophotometry

Principle:
UV-Vis spectrocopy works on the basis of the absorption phenomenon of light and the amount of absorbed light is directly proportional to the amount of the analyte present in a sample solution.





Uranium UV-Vis absorption spectra

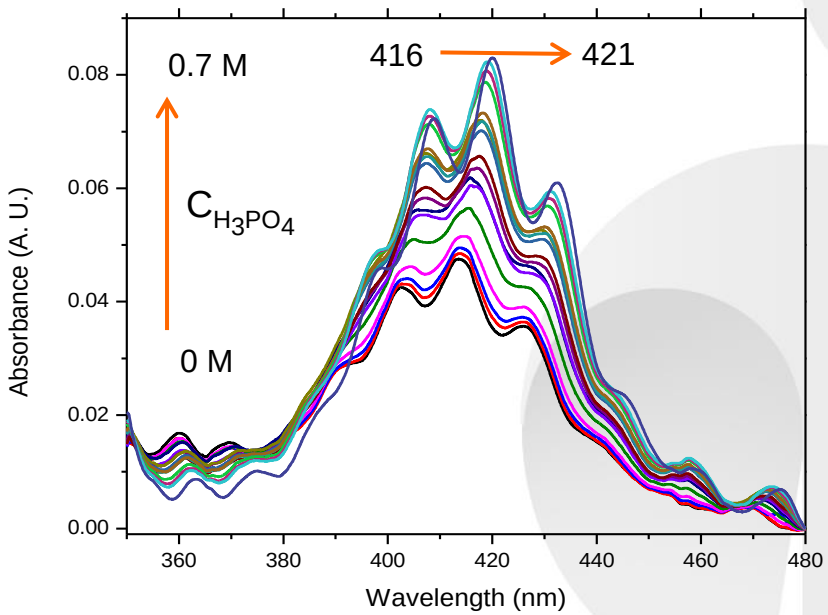
To determine the stability constants, the ligand concentration is increased in actinide solutions

Akash M. S. H., *et. al*., (2020) *Essentials of Pharmaceutical Analysis* , pp 29-56

Interaction of Pu (VI)-H_3PO_4

Use of U(VI) as analogue of Pu(VI)

UV-Vis spectrophotometry



U(VI)-H_3PO_4 absorption spectra

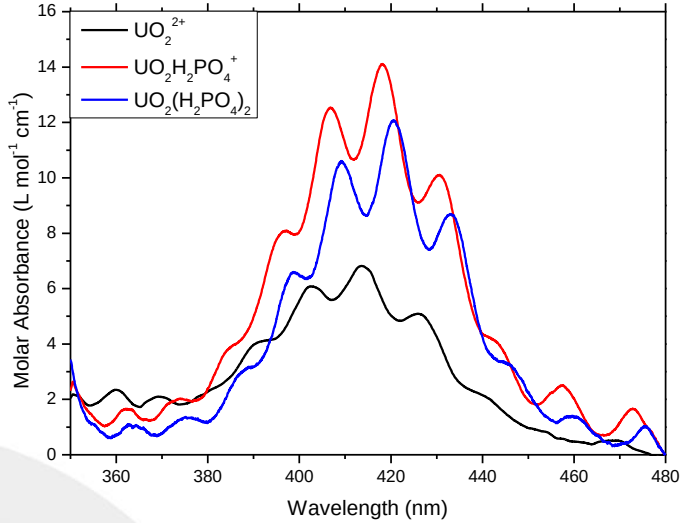
[U]=7x10^{-3} mol L^{-1}

I= 1 mol L^{-1} in $HClO_4$

T= 20, 30, 40 and 50°C

Determination of stability constants at different temperatures and thermodynamic parameters

Stability constant determinated by HypSpec software



Formation of complexes 1:1 and 1:2

$$UO_2^{2+} + PO_4^{3-} + 2H^+ \overset{\beta_1}{\leftrightarrow} UO_2H_2PO_4^+$$

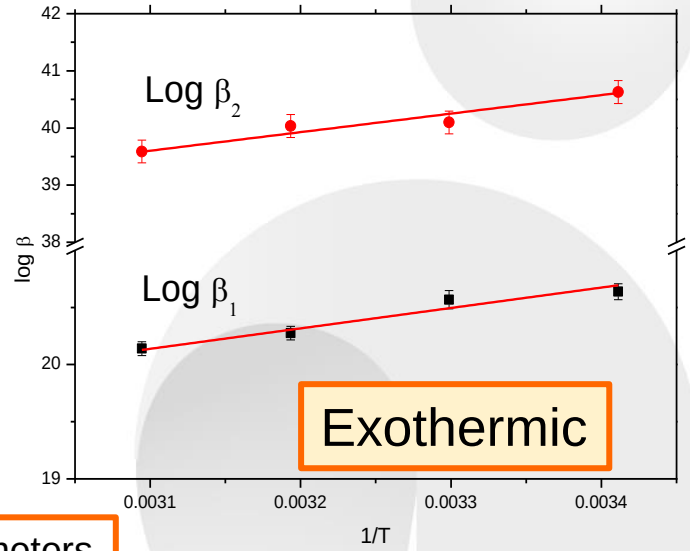
$$UO_2^{2+} + 2PO_4^{3-} + 4H^+ \overset{\beta_2}{\leftrightarrow} UO_2(H_2PO_4)_2$$

Interaction of Pu (VI)-H_3PO_4

Use of U(VI) as analogue of Pu(VI)

Influence of the temperature

Stability constants of U(VI)-H_3PO_4 at 1 M $HClO_4$ = OECD/NEA-Thermodynamic data base



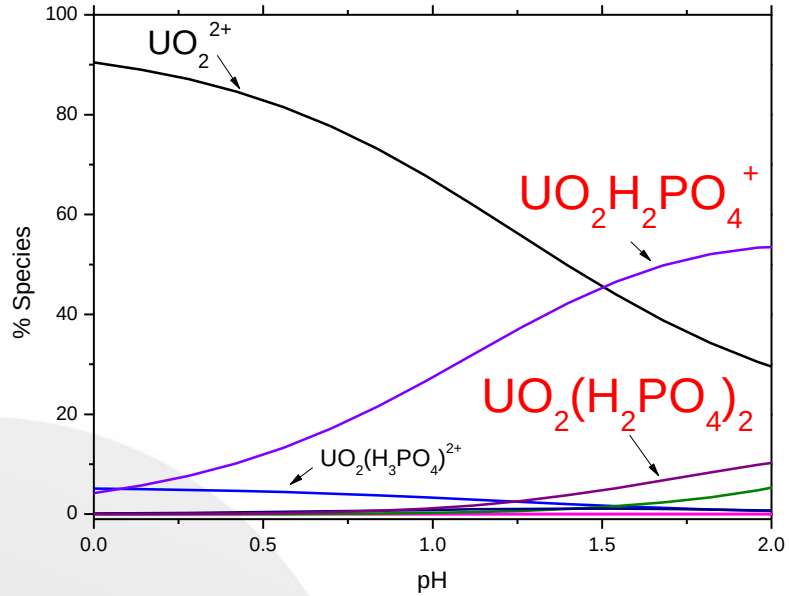
Thermodynamic parameters

	$UO_2H_2PO_4^+$	$UO_2(H_2PO_4)_2$
ΔH (kJ mol^{-1})	-32±5	-58±11
ΔS (J mol^{-1} K^{-1})	285±20	579±37

Sandino A., *et. al., Geochimica et cosmochimica* Acta (1992), **56**, 4135-4145
Mathur J. N., *Polyhedron* (1991), **10**, 47-53

No data selected in TDB

Distribution diagram for the aqueous species in the system U(VI)-H_3PO_4-H_2O

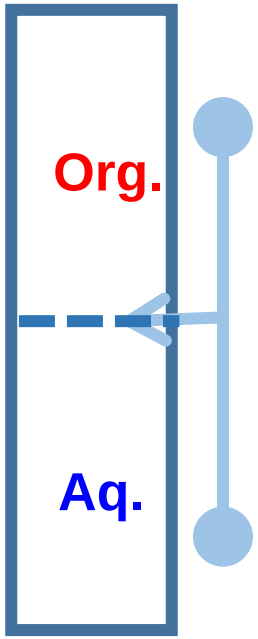


First results were presented in 50th JDA-2021, March 22-25
Writting paper in progress

Interaction of Pu(III)-H_3PO_4

Liquid-liquid extraction at ultra trace scale

Organic phase



Aqueous phase

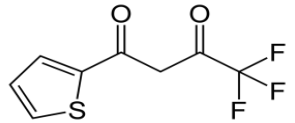
M^{n+}

Metal + Extractant

COMPETITION

Metal + Ligand

Thenoyltrifluoroacetone (HA) in toluene



^{152}Eu, ^{227}Th

$$D = \frac{A_{org}}{A_{aq}}$$

Gamma spectrometry

Ligand in $(Na,H)ClO_4$

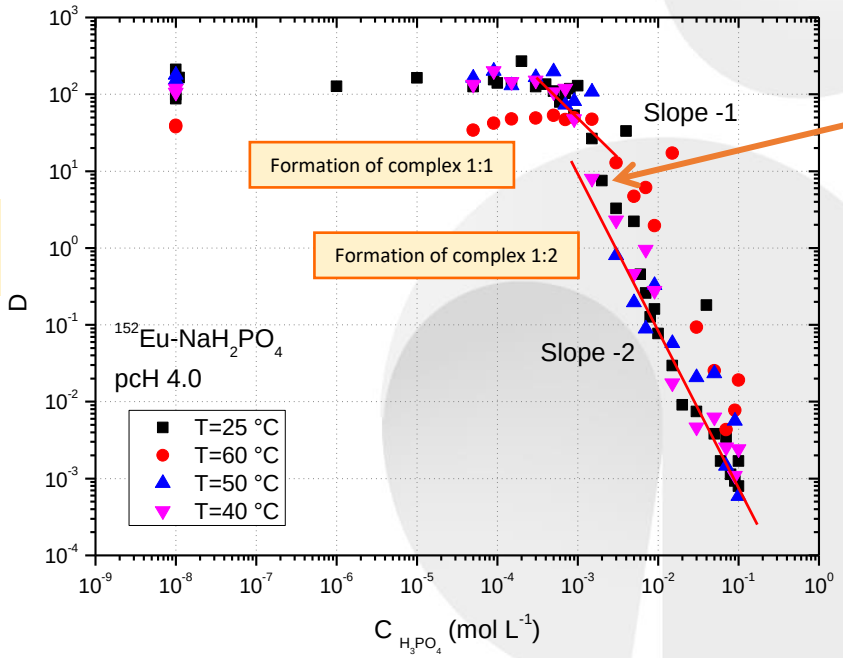
H_3PO_4

Interaction Pu(III)-H_3PO_4

Use of Eu(III) as analogue of Pu (III)

Variations of D as a function of H_3PO_4 concentration at different temperature (pcH=4, I=0.5 mol L^{-1} (Na,H)ClO_4, T=25, 40, 50, 60°C, C_{TTA}=2.5x10^{-2} mol L^{-1})

$$D = \frac{A_{org}}{A_{aq}}$$



Experimental issues:

- Systematic deviation in mass balance

Possible solutions tested

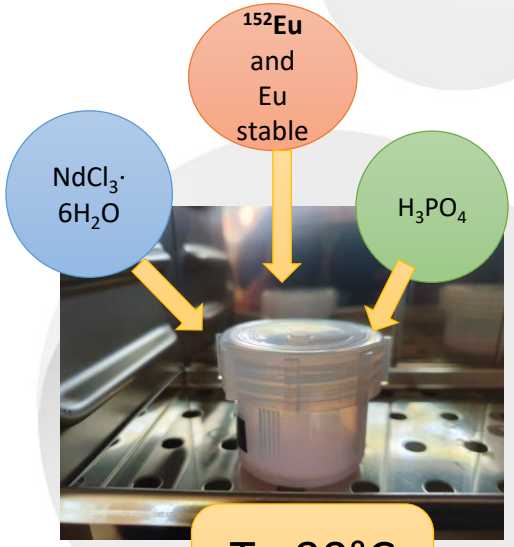
- Change of the electrolyte (NaCl/HCl or (Na,H)ClO_4/Acetate buffer)
- Vials for sample´s preparation (glass and parylene)
- Change the extractant (TTA / toluene to HDEHP / cyclohexane) in progress

The protocol requires more experiments to understand the deviation in the mass balance and obtain more reliable data

Interaction Pu(III)-H_3PO_4

Synthesis of rhabdophane type samples

$$Nd^{3+} + {PO_4}^{3-} + nH_2O = NdPO_4 \cdot nH_2O$$



T= 90°C
14 days

Washing

Centrifugation

$NdPO_4 \cdot nH_2O$
$Eu_{0.01}Nd_{0.99}PO_4 \cdot nH_2O$
$(^{152}Eu/Eu)_{0.01}Nd_{0.99}PO_4 \cdot nH_2O$

Air drying
overnight

Activity
6.78kBq of ^{152}Eu
per mg of solid

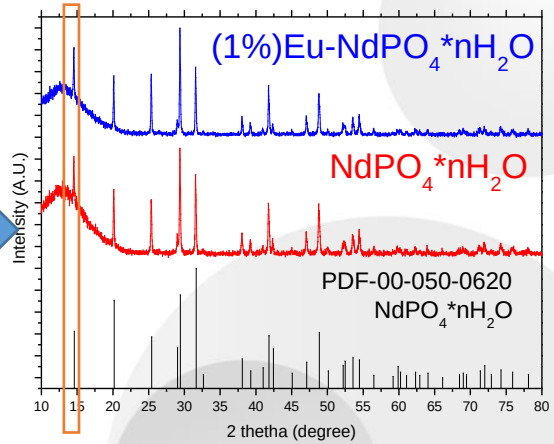
Roncal-Herrero T. *et. al.*, Journal of Nanoparticle Research (2011), **13**, 4049-4062.
Mesbah A., *et. al.*, Journal of Solid State Chemistry (2017), **249**, 221-227.
Clavier N., *et al.*, Spectrochimia Acta Part A: Moleculat and Biomolecular Spectroscopy (2018), **205**, 85-94
Gausse C., *et. al.*, European Journak of Inorganic Chemistry (2016), **28**, 4615-4630

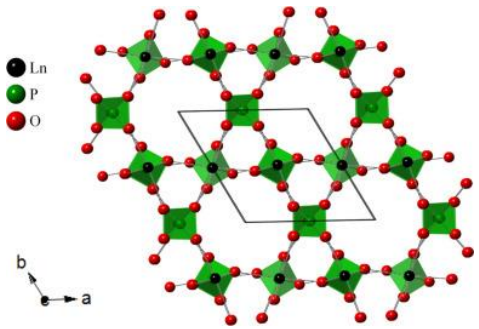
Interaction Pu(III)-H_3PO_4

Characterization of rhabdophane type powders

XRD patterns of $NdPO_4{\cdot}nH_2O$ and $Eu_{0.01}Nd_{0.99}PO_4{\cdot}nH_2O$

A good agreement with structures reported for $NdPO_4{\cdot}nH_2O$



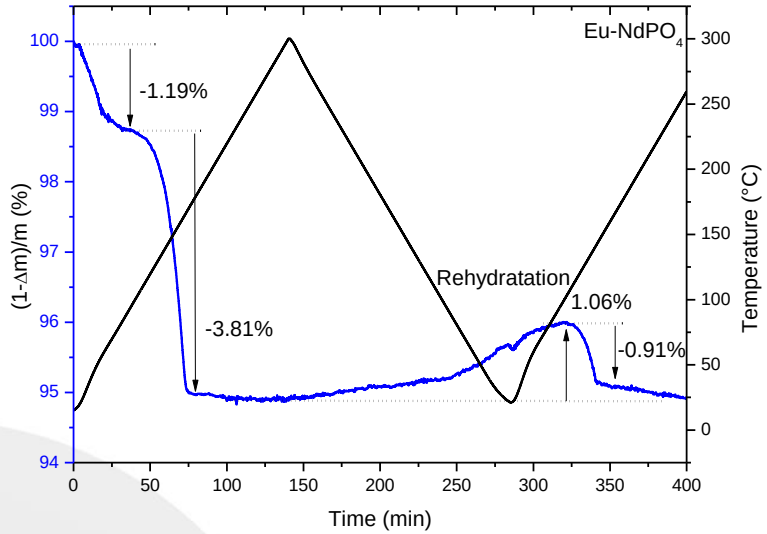


Monoclinic crystal structure

Unit cell parameters

	$Eu_{0.01}Nd_{0.99}PO_4{\cdot}nH_2O$
a (Å)	28.3452
b (Å)	6.3878
c (Å)	12.0395
β°	108.228

TGA weight loss curve showing the hydration reversibility in $Eu_{0.01}Nd_{0.99}PO_4{\cdot}nH_2O$



The rate of water elimination in two steps are in a good agreement with structures reported as **$LnPO_4{\cdot}0.667H_2O$**

Mesbah A., *et. al.*, *Journal of Solid State Chemistry* (2017), **249**, 221-227.
Gausse C., *et. al.*, *European Journak of Inorganic Chemistry* (2016), **28**, 4615-4630

Interaction Pu(III)-H_3PO_4

Solubility experiments on $(^{152}Eu/Eu)_{0.01}Nd_{0.99}PO_4 \cdot nH_2O)$

Aim: Validation with low amount of solid for further experiments with Pu

Preparation of samples

- Weighing in glove box

50.1 mg/ 50.1 mL
11.3 mg/ 11.3 mL
6.9 mg/ 6.9 mL
5.5 mg/ 5.5 mL
2.2 mg/ 2.2 mL
1.8 mg/ 1.8 mL

Solubility experiments

- **Conditions**

Medium: HCl 0.1 M
Temperature: 25°C

$$\frac{mg\ of\ habdophane}{mL\ of\ 0.1\ M\ HCl} = 1$$

- **Sampling**: 1% of total volume replaced by the same volume of fresh HCl

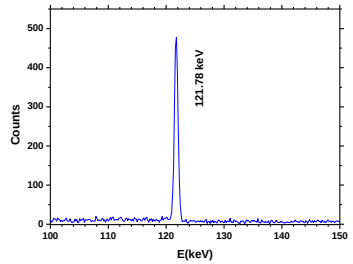
Sampling frequency :
each hour during 5 days
3 per day during 1 weeks
1 per day during 2 months

- **Conditioning of each sample for Gamma counting** (centrifugation, weighing)

Analysis

- **Gamma counting**

Peak at 121.8 keV (^{152}Eu)



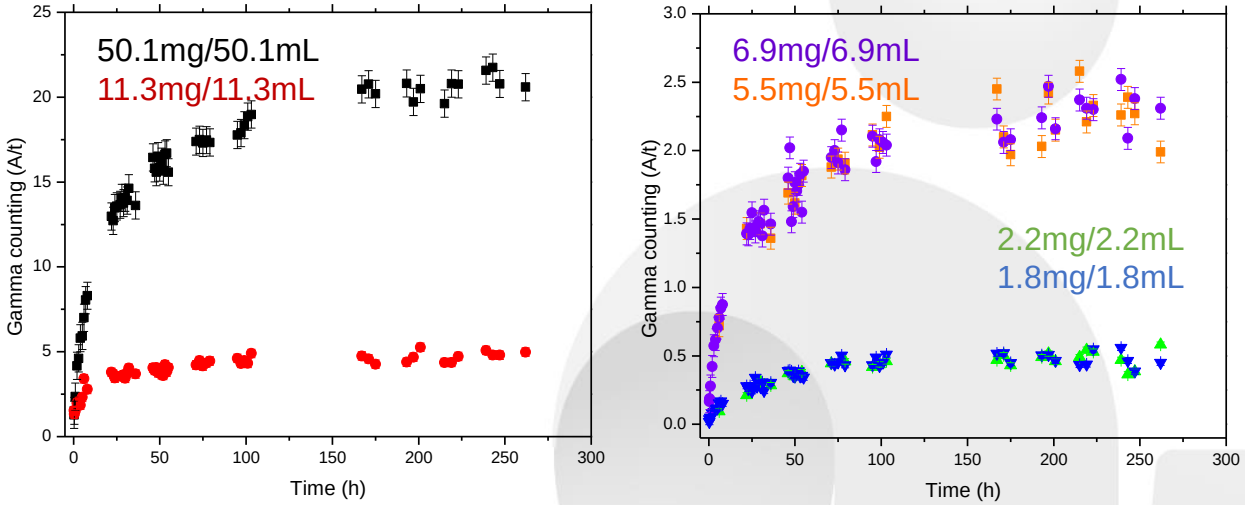
Monitoring ^{152}Eu
(500s≤time≤50000s)

UV Vis spectrophotometry (Nd)
Phosphate analysis to be developped

Interaction Pu(III)-H_3PO_4

Solubility experiments on $(^{152}Eu/Eu)_{0.01}Nd_{0.99}PO_4 \cdot nH_2O$)

Evolution of ^{152}Eu and Nd during the dissolution of $Eu_{0.01}Nd_{0.99}PO_4 \cdot nH_2O$ in 0.1 M HCl solution at 25°C



Same trend and time to reach the equilibrium

Experiment in process

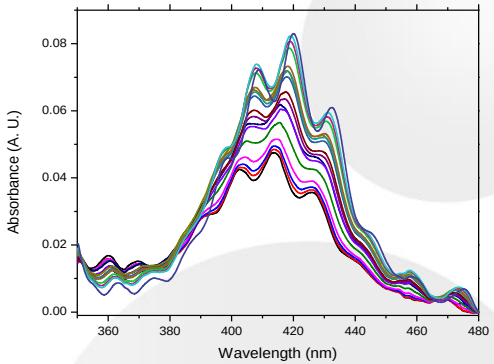
- Calibration of γ counting according with specific geometry in order to convert activity in concentration
- Determination of Nd and PO_4 to check the dissolution is congruent.

Conclusion

Aqueous solution

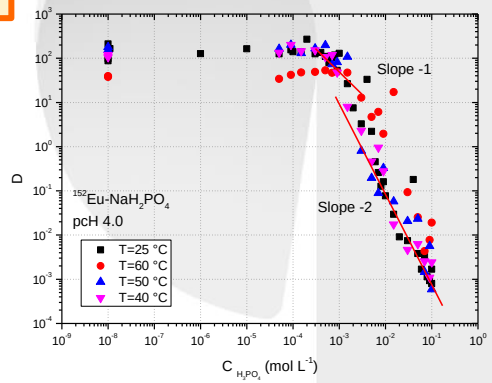
Analogue for Pu (VI)

- Determination of stability constants and thermodynamic parameters (entropy and enthalpy) for **U(VI)-H_3PO_4** complex in a good agreement with reported literature data.



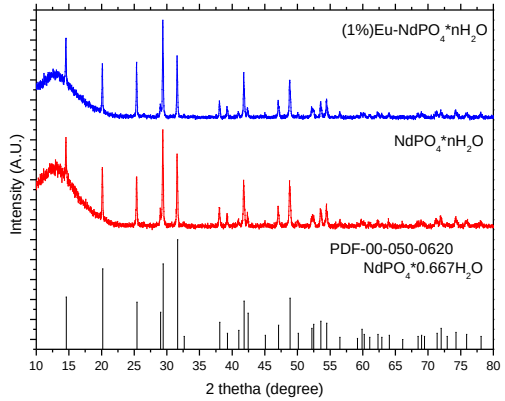
Analogue for Pu (III)

- The protocol for liquid-liquid extraction involving ^{152}Eu must be improved



Solid State

Analogue for Pu(III)



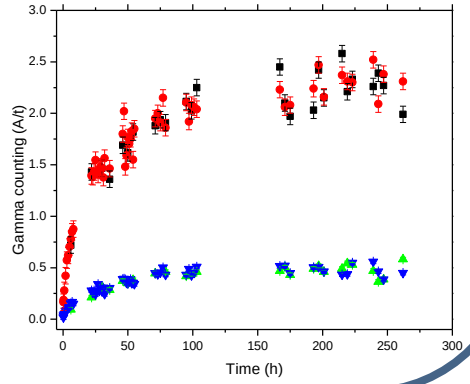
- According with XRD and TGA analysis, the solids synthetized were found to be **rhabdophane** type .

$NdPO_4 \cdot nH_2O$

$Eu_{0.01}Nd_{0.99}PO_4 \cdot nH_2O$

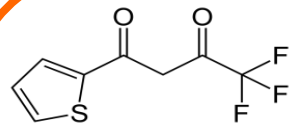
$(^{152}Eu/Eu)_{0.01}Nd_{0.99}PO_4 \cdot nH_2O$

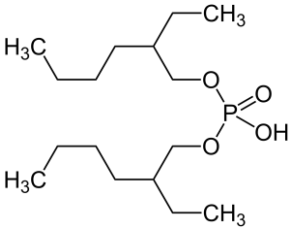
- The solubility measurements seem to indicate that the experimental conditions proposed (reduce amount of solid) could be applied for Pu.



Future work

Analogue of Pu(III)





Aqueous solution

- The protocol for complexation Eu(III)-H_3PO_4 using liquid-liquid extraction will be tested with other extractants (HDEHP, TBP).

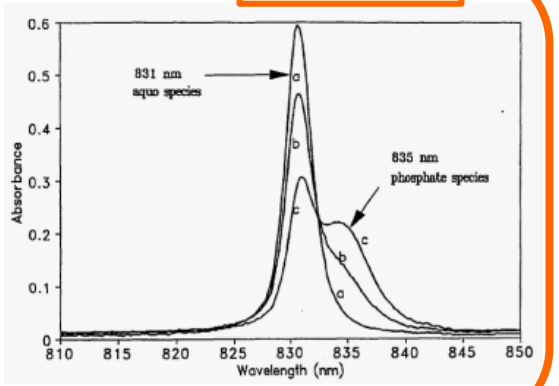
Solid state

- Determination of solubility products
  - ✓ Calibration of gamma-spectrometer for conversion into concentration
  - ✓ Verify the congruence of the dissolution

Pu(VI)

Aqueous solution

- The protocol elaborated with U(VI will be applied to Pu (VI)-H_3PO_4 using the absorption band at 835 nm.



Pu(III)

Solid State

- Determination of the solubility product of $PuPO_4 \cdot nH_2O$ (prepared at CEA Marcoule)

Acknowledgment

Thank you for your attention

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Philippe MOISY
Thomas DUMAS