

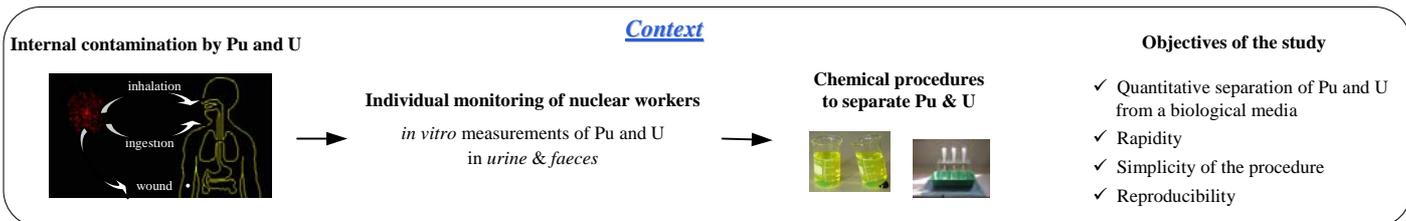
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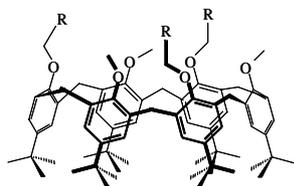
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**Abstract:** Individual monitoring of workers exposed to a risk of internal contamination with actinides is achieved through *in vivo* measurements (anthroporadiometry) and *in vitro* measurements (urine and faeces). The procedures currently used for actinides analysis in urine are well established and validated but are time-consuming, which limits the frequency and the flexibility of individual monitoring. The aim of this work is to propose an alternative radiochemical procedure for plutonium and possibly in the presence of uranium. Indeed when Pu and U are both analyzed, it is necessary to separate them prior to alpha spectrometry measurement. The extractant molecule used is a calix[6]arene bearing hydroxamic functions. The affinity of this molecule towards Pu and U is studied and the possibility to separate both elements is shown.



### Calix[6]arene



1,3,5-OCH<sub>3</sub>-2,4,6-OCH<sub>3</sub>-R-*p*-terbutylcalix[6]arene  
R = CONHOH (LH<sub>3</sub>) or R = COOH (L'H<sub>3</sub>)

#### Properties of LH<sub>3</sub>

- Hydroxamic chelating functions (CONHOH) of LH<sub>3</sub> are supposed to present a very **high affinity** towards Pu(IV) [1]
- LH<sub>3</sub> has a very good **affinity** towards **uranyl ion** thanks to the geometry of the cavity and the chelating groups nature [2]

⇒ LH<sub>3</sub> is supposed to be a promising molecule to extract Pu and U

### Pu(IV) affinity for a calix[6]arene bearing hydroxamic functions

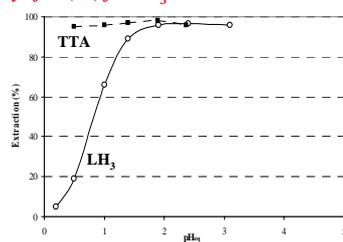
#### Obtaining of Pu(IV)

Checked by liquid-liquid extractions with TTA (selective agent of Pu(IV))

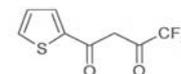
Extraction (%) of Pu(IV) by TTA as a function of pH

pH	0.5	1.0	1.4	1.8	1.9	2.4
Pu extraction by TTA (%)	95	96	97	96	98	96

#### Affinity of Pu(IV) for LH<sub>3</sub>



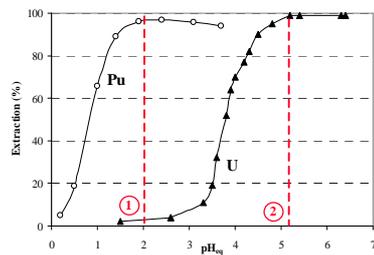
Extraction (%) of Pu by LH<sub>3</sub> and TTA versus pH



Thenoyl trifluoroacetone (TTA)

- Procedure used allows to obtain Pu(IV) in solution
- Very good affinity of Pu(IV) for the calix[6]arene bearing hydroxamic functions (LH<sub>3</sub>) from pH 1.5 to 3

### Pu / U separation



Extraction (%) of Pu and U by LH<sub>3</sub> versus pH

Successive extractions of Pu and U

	pH	Pu extraction (%)	U extraction (%)
1 <sup>st</sup> step	2.0	93	0
2 <sup>nd</sup> step	5.0	8	99

1<sup>st</sup> step Aqueous phase: pH=2.0, 0.36 M NaNO<sub>2</sub>, 2.8×10<sup>-9</sup> M <sup>242</sup>Pu, 4.2×10<sup>-9</sup> M <sup>238</sup>U, 10<sup>-2</sup> M (CH<sub>3</sub>COOH + CH<sub>3</sub>COO)  
Organic phase: [LH<sub>3</sub>]<sub>0</sub>=10<sup>-3</sup> M in THN

2<sup>nd</sup> step Aqueous phase: aqueous phase after the first step  
Organic phase: [LH<sub>3</sub>]<sub>0</sub>=10<sup>-3</sup> M in THN

Possibility to separate Pu from U at the extraction step by choosing the adequate pH value

### Conclusion

The affinity of a calix[6]arene bearing hydroxamic groups towards plutonium and uranium has been studied.

The results show (1) the very good affinity of this molecule for Pu(IV)

(2) the possibility to separate Pu from U at the extraction step by choosing the adequate pH value

- Pu could be extracted at pH 2 by LH<sub>3</sub> whereas U is not extracted
- the increase of the pH of the previous aqueous phase at pH 5 could then allow to extract quantitatively U

These results are very promising. Some improvements remain to be done to separate completely both actinides in the urinary media and by using a chromatographic support.

### Experimentals

#### Obtaining of Pu(IV)

- Hot solution containing 0.36 M NaNO<sub>2</sub>, 0.5 M HNO<sub>3</sub>, 2.8×10<sup>-9</sup> M <sup>242</sup>Pu
- addition of 10<sup>-2</sup> M CH<sub>3</sub>COOH and stir 1 h (to complex Pu(IV) and to limit hydrolysis phenomena)

To check the presence of Pu(IV): liquid-liquid extractions with 0.5 M TTA (thenoyltrifluoroacetone) in xylene. TTA is a specific complexant of Pu at the +4 oxidation state [3].

#### Extraction procedure with the calix[6]arene LH<sub>3</sub>

**Aqueous phases:** 2.8×10<sup>-9</sup> M <sup>242</sup>Pu or/and 4.2×10<sup>-9</sup> M <sup>238</sup>U, 0.36 M NaNO<sub>2</sub>, 10<sup>-2</sup> M [CH<sub>3</sub>COOH + CH<sub>3</sub>COO], pH from 0.2 to 3.

**Organic phases:** LH<sub>3</sub> 10<sup>-3</sup> M in 1,2,3,4-tetrahydronaphtalene (THN).

**Extractions:** mixing equal volumes of the two phases for 2 hours at 298±1 K, followed by 10 minutes centrifugation (3000 rpm).

#### Measurements of Pu and U

<sup>242</sup>Pu and <sup>238</sup>U in aqueous phases were measured by ICP-MS (Inductively Coupled Plasma Mass Spectrometry) with a quadrupole mass spectrometer "PlasmaQuad PQ2+" (Thermo Electron), after appropriate dilution in 0.4 M HNO<sub>3</sub>.

### References

- [1] R.J. Taylor, I. May, A.L. Wallwork, I.S. Dennis, N.J. Hill, B.Ya. Galkin, B.Ya. Zilberman, Yu.S. Fedorov, J. Alloys and Comps 271 (1998) 534.
- [2] B. Boulet, C. Bouvier-Capely, C. Cossonnet, G. Cote, to be published to: Solvent extraction and Ion exchange.
- [3] CETAMA (Commission d'ETablissement des Methodes d'Analyse du CEa), Note 340 (1972)

### Acknowledgments

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