

Selective extraction of Pu(IV) by a calix[6]arene bearing hydroxamic groups Application to bioassays

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Abstract

This work falls within the context of the general pattern of individual monitoring of workers exposed to a risk of internal contamination with actinides. The aim is to propose a new procedure for analyzing Pu traces from urine media and in the presence of uranium. The extractant molecule used is a calix[6]arene bearing hydroxamic acid functions. The affinity of this molecule towards Pu(IV) and U(VI) has been studied and the possibility to separate both elements has been shown.

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1. Introduction

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). *In vivo* measurements are fast and easy to implement but not adapted for the measurement of α emitters such as the actinides at low level activity. In this case, the incorporated activity is estimated from the determination of the activity eliminated in the excreta. The procedures currently used for actinides analysis in excreta consist of lengthy chemical purification (mineralisation of the sample and numerous steps on chromatographic columns to selectively separate the actinides [1]) associated with long counting times due to low activity levels. To reach detection limits low enough to respect the regulation, at least 5 days are commonly necessary. These procedures 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 a faster radiochemical procedure for quantitative analysis of actinides in urine. In this paper, we focused on plutonium analysis, possibly in the presence of uranium.

It is well known that calixarene molecules can have a very good affinity for actinides [2–6]. In our previous work, a calixarene-based uranophilic extractant, the 1,3,5-OCH₃-2,4,6-OCH₂CONHOH-*p*-*tert*butylcalix[6]arene (LH₃) (see Fig. 1), has been selected and has been found to have a very good affinity towards uranyl ion [7]. Furthermore, the hydroxamic acid chelating functions (CONHOH) of LH₃ are expected to have a very high affinity towards Pu(IV) [8]. Thus, the affinity of the calix[6]arene LH₃ towards plutonium is studied by solvent extraction in this paper and the experimental conditions allowing the separation of plutonium from uranium are defined.

2. Experimental

2.1. Reagents and apparatus

Calixarene molecule (LH₃) was synthesized by Chelator S.A. (France) [9]. Stock solutions of plutonium and uranium were prepared by dilution of a 1.7×10^{-7} M ²⁴²Pu solution in 4 M HNO₃ and by dilution of 10^{-6} M depleted U at the +6 oxidation state in 0.5 M HNO₃, respectively.

All the other chemicals used including 1,2,3,4-tetrahydronaphthalene, acetic acid, HNO₃, NaNO₃, NaNO₂, etc., from Aldrich or VWR were of analytical grade.

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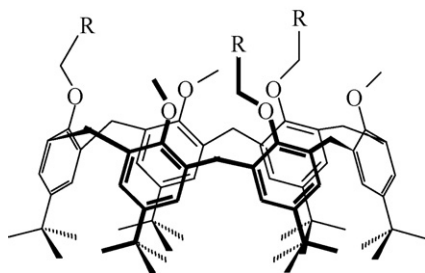


Fig. 1. Structure of LH₃: 1,3,5-OCH₃-2,4,6-OCH₂R-*p*-*tert*butylcalix[6]arene; R = CONHOH.

To be representative of the concentrations currently measured in routine monitoring, Pu and U concentrations were in the order of 10⁻⁹ M. All the measurements of ²⁴²Pu and ²³⁸U in aqueous phases were performed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with a quadrupole mass spectrometer "PlasmaQuad PQ2+" (Thermo Electron).

2.2. Extraction procedure

Extractions of Pu and U by LH₃ were studied at 298 ± 1 K. Unless otherwise stated, the Pu aqueous phases contained 2.8 × 10⁻⁹ M ²⁴²Pu, 0.36 M NaNO₂, and an acetate buffer (10⁻² M). The U aqueous phases contained 4.2 × 10⁻⁹ M ²³⁸U, 4 × 10⁻² M NaNO₃, and an acetate buffer (10⁻² M). The organic phases contained 10⁻³ M LH₃ dissolved in 1,2,3,4-tetrahydronaphthalene (THN). The liquid–liquid extractions were performed by gently mixing equal volumes of the aqueous and the organic phases for 2 h, which was enough to reach the equilibrium, followed by 10 min centrifugation (3000 rpm). The equilibrium pH of aqueous phases was measured after separation of the two phases.

Samples for ICP-MS measurements were prepared by appropriate dilution of the aqueous phases in 0.4 M HNO₃. The extraction results and distribution ratios were calculated by comparison of the aqueous phases before and after the extraction step. The precision of these results were estimated at about 5%, including ICP-MS measurements, mass and volume uncertainties, and repeatability in duplicate of the experiments.

3. Results and discussion

3.1. Affinity of LH₃ towards Pu

From literature data, hydroxamic acid functions have a high affinity towards Pu⁴⁺ [8,10–12]. Thus, first experiments were performed to define experimental conditions to obtain Pu at the +4 oxidation state, as follows. NaNO₂ was introduced in a warm solution containing 1 M HNO₃ and Pu. After mixing 30 min, 10⁻² M CH₃COOH was introduced with the aim to form Pu(IV) complex and to limit hydrolysis phenomena. Liquid–liquid extractions were performed with a specific complexant of Pu at the +4 oxidation state, the thenoyltrifluoroacetone (TTA), in order to check the presence of Pu(IV) in the aqueous phases [13]. From pH 0.5 to pH 2.4 the percentage of plutonium extracted by 0.5 M TTA in xylene was found to be higher than 95% (Table 1). This result indicates that the majority of plutonium was at the +4 oxidation state in this range of pH. Thus this preparation of

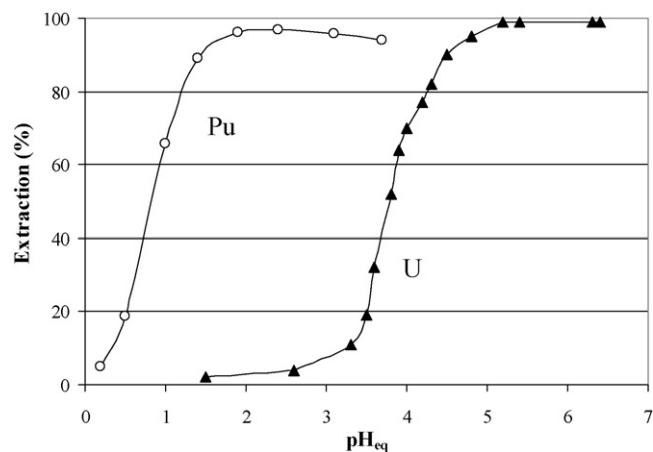


Fig. 2. Extraction (%) of Pu and U by LH₃ vs. pH.

the Pu aqueous phase can be used to obtain Pu(IV) before the extraction step with the calixarene LH₃.

The affinity of LH₃ towards Pu(IV) was also studied as a function of pH. The results show that LH₃ extracts quantitatively Pu above pH 2 (see Fig. 2). Another experiment was performed at pH 2 with a calix[6]arene bearing carboxylic acid functions (R = COOH, see Fig. 1), instead of hydroxamic acid functions like in the case of the calix[6]arene LH₃. In these conditions Pu was not extracted. This result confirms the very good affinity of hydroxamic acid functions for Pu(IV).

3.2. Selectivity

In order to determine experimental conditions to isolate Pu from U, we have superimposed the extraction curves of Pu(IV) and of U(VI) by the calix[6]arene LH₃ as a function of pH (see Fig. 2). The extraction curves show that both elements can be selectively extracted depending of the aqueous phase pH. Indeed, a first step allows the quantitative extraction of plutonium at pH 2. Then, increasing the pH of the aqueous phase up to pH 5 allows the quantitative extraction of uranium.

3.3. Successive extractions of Pu and U

Having found the optimal conditions to extract Pu and U individually, experiments were then performed to extract successively both elements from the same solution. One molar NaNO₂ and CH₃COOH were successively added in a solution containing 2.8 × 10⁻⁹ M Pu and 4.2 × 10⁻⁹ M U in 1 M HNO₃. After heating and stirring the solution, the pH of the aqueous phase was adjusted at pH 2 with NaOH. Thereafter, the organic phase containing 10⁻³ M LH₃ in THN was mixed with the aqueous phase. After centrifuging, 500 μL aliquot of the aqueous phase was taken for Pu analysis by ICP-MS. The pH of the remaining aqueous solution was later increased to pH 5 with NaOH. This solution was then mixed with 10⁻³ M LH₃ in THN. After this second extraction, 500 μL aliquot of the aqueous phase was sampled for U analysis by ICP-MS. The percentages of Pu and U extractions at each step are presented in Table 2.

Table 1
Extraction (%) of Pu by TTA as a function of pH

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

Table 2
Successive extractions of Pu and U (extraction (%) at each step)

	pH	Pu extraction (%)	U extraction (%)
First step	2.0	93	0
Second step	5.0	8	99

First step: aqueous phase: pH 2.0, $[\text{NaNO}_2]=0.36\text{ M}$, $[\text{CH}_3\text{COOH} + \text{CH}_3\text{COO}^-]=10^{-2}\text{ M}$, $^{242}\text{Pu}_0=2.8 \times 10^{-9}\text{ M}$, $^{238}\text{U}_0=4.2 \times 10^{-9}\text{ M}$; organic phase: $[\text{LH}_3]_0=10^{-3}\text{ M}$ in THN. Second step: aqueous phase: aqueous phase after the first step; organic phase: $[\text{LH}_3]_0=10^{-3}\text{ M}$ in THN.

Under these conditions, 93% of Pu was extracted at pH 2 by LH_3 without extraction of U. Again, increasing the pH of the previous aqueous phase to pH 5, after the first extraction, allows the quantitative extraction of uranium by LH_3 . However, it can be noticed that at this pH, more than 8% of the remaining 7% plutonium was also extracted. Some improvements are still necessary to optimize the Pu extraction at the first step (pH 2).

4. Conclusion

In this work we have studied the affinity of a calix[6]arene bearing hydroxamic acid groups towards plutonium and uranium. The results showed the very good affinity of this molecule for Pu(IV) and the possibility to separate Pu from U at the extraction step by choosing the appropriate pH value. These first results are very promising and show that in the context of monitoring of nuclear workers it will be possible to separate Pu from U by LH_3 . Further works are in progress to validate these results on mineralised urine samples.

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