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An alternative procedure for uranium analysis in drinking water using AQUALIX columns: Application to varied French bottled waters

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ABSTRACT

The general population is chronically exposed to uranium (^{234}U, ^{235}U, and ^{238}U) and polonium (^{210}Po) mainly through day-to-day food and beverage intake. The measurement of these naturally-occurring radionuclides in drinking water is important to assess their health impact. In this work the applicability of calix[6]arene-derivatives columns for uranium analysis in drinking water was investigated. A simple and effective method was proposed on a specific column called AQUALIX, for the separation and preconcentration of U from drinking water. This procedure is suitable for routine analysis and the analysis time is considerably shortened (around 4 h) by combining the separation on AQUALIX with fast ICP-MS measurement. This new method was tested on different French bottled waters (still mineral water, sparkling mineral water, and spring water). Then, the case of simultaneous presence of uranium and polonium in water was considered due to interferences in alpha spectrometry measurement. A protocol was proposed using a first usual step of spontaneous deposition of polonium on silver disc in order to separate Po, followed by the uranium extraction on AQUALIX column before alpha spectrometry counting.

1. Introduction

The naturally-occurring radionuclides ^{234,235,238}U and ^{210}Po are important for their contribution to the natural radiation exposure in the environment. ^{210}Po belongs to ^{238}U radioactive family series. In areas where uranium is mined and extracted, ^{210}Po may accumulate in tailings. It is distributed through local waterways and is subsequently incorporated into foodstuffs [1]. Thus, the measurement of uranium and polonium in drinking water is important to assess their health impact [2].

The methods currently used for these analyses are based on the measurement by alpha spectrometry of both radioelements and are sometimes performed on separated aliquots of drinking water, to avoid alpha spectrometry interferences, between ^{232}U (E_α=5320 keV) and ^{210}Po (E_α=5304 keV). The methods for uranium determination require tedious sample preparation techniques (evaporation, precipitation, column separation…) before counting by alpha spectrometry [3]. The procedures for ^{210}Po measurement in water usually involve sample pre-concentration (evaporation and precipitation) and/or Po separation and auto-deposition followed by alpha spectrometry measurement [4,5]. For both radioelements, the alpha spectrometry counting times are often long (several days) due to low activity levels. The recent events – Litvinenko's poisoning in 2006 or the important amount of radionuclides released in the environment after the nuclear accident in Fukushima in 2011 – remind that there is an increasing need to develop faster analytical methods of environmental samples for emergency response.

In order to develop a new procedure, the use of macrocyclic molecules like calixarenes is of great interest to extract radioelements. Our laboratory developed tricarboxylic or trishydroxamic calix[6]arene molecules (Fig. 1) able to entrap the actinides U, Pu and Am from complex matrix like urine [6–8].

To propose methods suitable for routine sample analysis, these calix[6]arene molecules have been immobilized on an inert solid support, for implementation into a chromatographic column. These original molecules and their use have been patented [9]. A radiochemical procedure based on the use of a chromatographic column containing these calix[6]arene molecules has been already proposed for U, Pu, Am analysis in urine, which is faster and easier than the current procedures [10]. Preliminary results on one natural spring water (with low content of mineral species) have shown that some of these calix[6]arene-derivatives columns, called AQUALIX, could be used for U analysis in water [10]. These first results were promising but it was essential to validate this use for waters of a different nature, especially for waters with high content of mineral species and carbonate species. Indeed, it appeared that the content of carbonate species in water was an

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important parameter on the extraction efficiency of U by the AQUALIX column [10]. In this paper, the applicability of AQUALIX column for uranium analysis was extensively investigated on different French bottled waters (still mineral water, sparkling mineral water, and spring water). Then, the separation of uranium and polonium was considered, since the simultaneous presence of these radioelements is possible in some waters and interferences occur in alpha spectrometry. In addition, special attention was given to the sample preparation of waters containing polonium due to problems of solubility of this radioelement in solution.

2. Experimental

2.1. Reagents and instrumentation

^{208}Po and ^{209}Po were obtained from National Physical Laboratory, UK. ^{233}U was from CERCA/LEA (AREVA) and depleted U was from SPEX Certiprep, Ind., USA. All the other chemicals used including ascorbic acid, HNO_3, HCl, $NaNO_3$, etc. from Aldrich or VWR were of analytical grade. Calixarene molecules were synthesized as described in the patent [9].

All the measurements of ^{238}U and ^{233}U in aqueous phases were performed in this study by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using a quadrupole mass spectrometer 7700x (Agilent). All the measurements of Po were performed by α spectrometry using an OCTETE Plus alpha spectrometer (ORTEC) equipped with Passivated Implanted Planar Silicon detectors.

2.2. Water samples

The French bottled waters (still mineral water, sparkling mineral water, and spring water) tested in this study and their compositions are described in Table 1. For each experiment, 500 mL of water was used and spiked with 0.01 μg of ^{233}U (3.6 Bq) to determine the extraction yield of uranium on the AQUALIX column. A first acidification step was performed at $pH = 2 \pm 0.2$ or 0.5 ± 0.1, in order to eliminate the carbonate species that may prevent the U extraction by calixarene molecules, as suggested in our previous works [10]. This acidification step may be combined with a gas extraction step, especially for sparkling water, to improve the elimination of carbon dioxide. The gas extraction step was performed under magnetic stirring while removing gas under vacuum. Finally, the pH of water was adjusted to 5 by addition of ammonium hydroxide, before the loading on AQUALIX column.

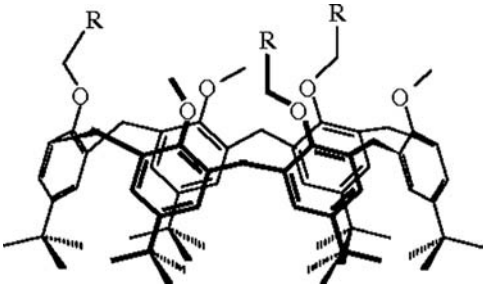

Fig. 1. 1,3,5-OCH_3-2,4,6-OCH_2R-*p*-*tert*-butylcalix[6]arene ($L_{Carb}H_3$: R=COOH; $L_{Hyd}H_3$: R=CONHOH).

2.3. Chromatographic separation procedure on AQUALIX

The immobilization of carboxylic calixarenes ($L_{Carb}H_3$) on polymer was performed as previously described [10]. The AQUALIX column was filled with 1 g of bed resin and the column height was 4.5 cm. The various solutions were passed through the AQUALIX column without applying any pressure. Thanks to the high grain size polymer, the flow rate on AQUALIX was around 3 mL/min. The AQUALIX columns were conditioned with a 0.3 M acetate buffer at pH=5 until the eluate pH was around pH=5. The loading solution (500 mL of water) was introduced on the top of the AQUALIX column. The AQUALIX column was then rinsed with 10 mL of 0.04 M $NaNO_3$, adjusted at pH=5. U was finally eluted with 30 mL of 1 M HNO_3 before ICP-MS measurement or 30 mL of 0.1 M hydroxylammonium chloride in 1 M HCl before alpha spectrometry measurement. After appropriate dilution in 0.44 M nitric acid, each solution recovered at the bottom of the AQUALIX column was analyzed by ICP-MS to determine the U concentration. The U retention percentage and U elution percentage can then be estimated for each experiment.

2.4. Study on Po stability in water

Preliminary tests were performed to determine the optimal acid concentration to avoid Po loss due to hydrolysis. Spring water was spiked with ^{209}Po and stored up to 3 weeks in polyethylene bottles, with or without HCl stabilization. The quantities of Po remaining in solution were determined as a function of time, by alpha spectrometry after Po auto-deposition with ^{208}Po tracer.

Other experiments were then performed to attempt to recover Po in water sample that was not initially stored with HCl. Spring water was spiked with ^{209}Po then stored in a polyethylene bottle without any acidification. After 2 years, HCl was added to reach a concentration of 0.5 M in the polyethylene bottle and Po recovered

Table 1
Water composition (mg L^{-1}), pH and total dissolved solid (TDS) content (mg L^{-1}) after evaporation to dryness at 180 °C, according to the data indicated on the bottle.

Species (mg L^{-1})	Spring water	Mineral water			Sparkling water		
	Water A	Water B	Water C	Water D	Water E	Water F	Water G
Mg^{2+}	7	119	26	43.1	85	6.8	11
Ca^{2+}	68	549	80	203.8	190	155	90
Na^{+}	11	14	6.5	5	165	11.8	1708
K^{+}	4	4.1	1	2	10	1.3	132
SO_4^{2-}	5	1530	12.6	328.9	38	46.1	174
HCO_3^{-}	234	383.7	360	399	1300	445	4368
Cl^{-}	19	18.8	6.8	8	44	25	322
NO_3^{-}	< 1	4.3	3.7	4.3	–	4.8	–
F^{-}	< 0.3	0.4	–	0.28	1.2	1.2	1
U[a]	1.6×10^{-4}	1.57×10^{-3}	1.90×10^{-3}	8.3×10^{-4}	8.3×10^{-4}	3.15×10^{-3}	0.8×10^{-4}
pH	7.5	7.2	7.2	7.5	6	6	6.6
TDS	274	2513	309	844	1200	479	4774

[a] Determined in this study by ICP-MS measurement.

in solution has been regularly determined by alpha spectrometry after Po auto-deposition with ^{208}Po tracer.

2.5. Po auto-deposition

For water whose Po analysis was required, a first step of Po auto-deposition was performed before the U extraction on the AQUALIX column. Water samples (100 mL or 500 mL) were acidified with 1 M HCl and ascorbic acid was added to prevent iron to deposit. Then Po sources for α spectrometry measurements were prepared by spontaneous auto-deposition of polonium on stainless steel or silver discs, during 5 h at ambient temperature and under stirring. ^{208}Po or ^{209}Po radiotracers were added to determine the deposition yield. At the end of the Po auto-deposition, water was recovered and the gas extraction step was performed under magnetic stirring by removing gas under vacuum. Finally, the pH of water was adjusted to pH=5 by addition of ammonium hydroxide, before the loading on AQUALIX column.

All experiments were performed at 25 °C. Each experiment was repeated 2 or 3 times. All results correspond to the mean of these replicates and are presented with their standard deviation (1σ).

3. Results and discussion

3.1. Uranium analysis in bottled water

To investigate the applicability of AQUALIX columns on bottled water, various waters (spring water, mineral water and sparkling water) were tested (Table 1). The study focused first on uranium extraction from still mineral waters (waters B, C, and D).

In the preliminary experiments [10], it was observed that an acidification step was important before the uranium extraction on AQUALIX from spring water A, to eliminate carbonate ions. The U extraction on AQUALIX from still mineral waters (B, C, and D) was thus performed after a preliminary acidification step at pH=2 or 0.5 under magnetic stirring, for different acidification durations, with or without a gas extraction step. The results of uranium retention on AQUALIX are given in Table 2.

Among still mineral waters, water B was first tested because of its high content in mineral species, as showed by its high total dissolved solid (TDS) content (Table 1). According to this first set of experiments on water B, it seems that a first step of acidification at pH=2 is not sufficient, since the U retention is not quantitative, whatever the acidification time. Among anions present in water B (see Table 1), even if the concentration of sulfate ions (0.016 M) is twice the concentration of carbonate ions (0.007 M), the high stability constant between the carbonate ions and uranyl ions ($\log \beta_2{}^{\circ} = 16.94 \pm 0.12$ and $\log \beta_3{}^{\circ} = 21.6 \pm 0.05$) [11] leads to a high competition between carbonate ions and calixarenes molecules. An acidification step at pH=0.5 of water B was then considered with or without an additional gas extraction step to promote the formation of carbonic acid and then carbon dioxide gas. The results (Table 2) show that the acidification step at pH 0.5 is necessary before the uranium extraction by AQUALIX, to eliminate efficiently the carbonate species in water B. The additional step of gas extraction before the loading on the column gives also good results of U retention on AQUALIX, but the gas extraction is not essential for water B.

For other still mineral waters, the results show that after an acidification step at pH 0.5 with or without gas extraction time, U is quantitatively extracted on AQUALIX. In contrast, for the tested spring water (water A), the U retention on AQUALIX is slightly better without the gas extraction step, since (98 ± 2)% and (89 ± 4)% of uranium is extracted after an acidification step respectively at pH=0.5 and 2.

The elution step was also optimized. The extraction equilibrium between the 1,3,5-OCH$_3$-2,4,6-OCH$_2$COOH-*p*-*tert*-butylcalix[6]arene (noted $L_{Carb}H_3$) and the uranyl ion is based on the proton exchange of two carboxylic functions [12], according to the equation:

$$UO_2{}^{2+} + \overline{L_{Carb}H_3} \overset{K_{eq}}{\longleftrightarrow} \overline{(UO_2)(L_{Carb}H_3)} + 2H^+ \qquad (1)$$

where the overbars refer to the species in the stationary phase.

So, the elution should be achieved by increasing the acidic concentration. Various reagents (nitric acid, hydrochloric acid, ammonium oxalate ($(NH_4)_2C_2O_4$), and hydroxylammonium chloride (NH_4OCl)) were tested for the U elution from the AQUALIX column on water C (Table 3).

The results show that 0.1 M ammonium oxalate is not efficient to elute quantitatively uranium. Whereas the acidification with 1 M HNO_3 allows to elute U (83%) from the AQUALIX column, the same concentration of HCl elutes only 58% of U. With the addition

Table 2
Uranium retention (%) on AQUALIX for still mineral waters (B, C, and D) and spring water (A), after an acidification step at pH=0.5 or 2, with or without a gas extraction step.

	Acidification pH	No gas extraction step		With a gas extraction step	
		Acidification time (min)	U retention (%)	Gas extraction time (min)	U retention (%)
Water B	2.0 ± 0.2	15	77 ± 11	–	–
		60	65 ± 8		
		120	71 ± 9		
Water B	0.5 ± 0.1	45	100 ± 1	15	86 ± 3
				30	86 ± 3
Water C	0.5 ± 0.1	15	98 ± 2	30	91 ± 6
Water D	0.5 ± 0.1	15	86 ± 1	15	90 ± 1
				30	82 ± 3
Water A	0.5 ± 0.1	15	98 ± 2	30	67 ± 10
	2.0 ± 0.2	15	89 ± 4	–	–

Table 3
Elution yield (%) of uranium from the AQUALIX column for water C.

Reagent	HNO_3	HCl	HCl	HCl	HCl	$(NH_4)_2C_2O_4$	NH_4OCl	NH_4OCl
Conc. (M)	1	0.5	1	2	8	0.1 M in water	0.1 M in 0.2 M HCl	0.1 M in 1 M HCl
Elution yield (%)	83 ± 7	50 ± 6	58 ± 9	49 ± 7	55 ± 8	38 ± 10	28 ± 6	74 ± 8

Table 4
Uranium retention (%) on AQUALIX for sparkling waters, after an acidification step at pH=0.5 with a gas extraction step.

	Gas extraction time (min)	U retention (%)
Water G	No gas extraction/45 min of acidification	60 ± 6
	5	53 ± 6
	15	81 ± 4
	30	83 ± 5
Water E	5	80 ± 8
	15	75 ± 7
	30	93 ± 5
Water F	15	93 ± 3
	30	92 ± 6

Table 5
U extraction from mineral water on various sets of the manufactured AQUALIX columns.

Set of AQUALIX columns	U retention (%)
1	94 ± 3
2	97 ± 5
3	96 ± 3
4	95 ± 2

of 0.1 M of hydroxylammonium chloride in 1 M HCl, the elution yield of U is closed to those obtained with 1 M HNO_3 as eluent.

For all other tested still mineral and spring waters, after U extraction on AQUALIX more than 80% of U can be eluted with 1 M HNO_3 and about 70% of U is eluted with 0.1 M of hydroxylammonium chloride in 1 M HCl.

Then, the protocol was tested on various French sparkling waters. Among them, the water G was first selected because of its high content in mineral species (TDS content=4774 mg L^{-1}) and its high content in bicarbonate species (4368 mg L^{-1}), as compared with previous still mineral waters. Preliminary experiments on water G after an acidification step at pH=0.5 during 45 min, without a gas extraction step, showed that only 60% of U was extracted by AQUALIX. Thus a gas extraction step at pH=0.5 was thus performed before the U extraction for sparkling waters (E, F, and G). The results are given in Table 4.

At first, it is noteworthy that the U extraction on AQUALIX is always efficient, in spite of the high content in mineral species in water G (TDS=4774 mg L^{-1}) as compared with the natural U concentration in this water (around 0.08 μg L^{-1}). That demonstrates the very good affinity and selectivity of calixarene molecules for uranium, in presence of high content of alkaline earth cations.

For all tested sparkling waters, the best uranium extraction was obtained for a gas extraction time ≥ 15 min at pH=0.5. After the extraction on the AQUALIX column, uranium can be eluted quantitatively with 1 M HNO_3 or with 0.1 M of hydroxylammonium chloride in 1 M HCl.

3.2. Robustness and analytical performances of AQUALIX procedure

The repeatability of AQUALIX procedure was first investigated on 15 experiments of U extraction from mineral water with the AQUALIX column. The results showed on average that (91 ± 6)% of U is extracted on the AQUALIX column and (93 ± 11)% of U is then eluted by 1 M HNO_3.

The robustness of AQUALIX procedure was also studied on different sets of manufactured AQUALIX columns. For each set, 3 columns were tested. The results are summarized in Table 5.

These results demonstrate that the manufacturing of AQUALIX columns is well controlled, since the U retention percentages are very closed on different sets of the manufactured AQUALIX columns.

To sum up, it has been demonstrated that the AQUALIX column could be used to analyze uranium in various French waters (still mineral water, spring water and sparkling mineral water). The results showed that an acidification step at pH=0.5, before the loading of water (500 mL) on AQUALIX column, is essential to quantitatively extract U on the column. Moreover, an additional gas extraction may be necessary especially for sparkling waters, to eliminate carbon dioxide. Finally, a single protocol of gas extraction at pH=0.5 during 30 min before U extraction at pH=5 on the AQUALIX column can be recommended for all waters. Thanks to relatively high grain size polymer, the flow rate on AQUALIX is fast and the loading of 500 mL takes about 2 h. The analysis time is thus considerably shortened (about half a day) by combining the separation on AQUALIX with fast quadrupole ICP-MS measurement, as compared with current procedures which used a pre-concentration step by co-precipitation with MnO_2 or $Fe(OH)_3$. Indeed it is often recommended to let the precipitate settle several hours before decantation and centrifugation or filtration [3,13]. With this AQUALIX protocol, the detection limits in water are 0.03 ng L^{-1} (3.7 10^{-4} mBq L^{-1}) for ^{238}U, 0.002 ng L^{-1} (1.6 10^{-4} mBq L^{-1}) for ^{235}U, and 0.0006 ng L^{-1} (0.14 mBq L^{-1}) for ^{234}U. With the preconcentration step on AQUALIX, low detection limits have been achieved as compared with the direct measurement of water by ICP-MS, especially for ^{234}U. Thanks to its easiness and low detection limits, the AQUALIX protocol can be useful for both emergency and routine radiation exposure monitoring.

3.3. Uranium analysis in bottled waters in presence of polonium

3.3.1. Sample preparation of waters spiked with polonium

A key factor in the preparation and analysis of polonium is sample stabilization [4]. Indeed Po is present in natural water as hydrolyzed species that easily adsorbs onto colloidal minerals (silica and aluminosilicates) and organics (fulvo or humic acids) but also on sample vessel walls [14,15]. First experiments were performed to determine the optimal acid concentration to stabilize Po in water. The quantity of Po remaining in solution was determined as a function of time, on spring water stored with or without HCl addition up to 3 weeks in polyethylene bottles.

Results shown in Fig. 2 show that in absence of HCl, Po is quickly adsorbed on bottle walls and only about 20% of Po remains in solution after 3 weeks. Sample stabilization with HCl concentration higher than 0.5 M is thus crucial to keep water containing Po prior to analysis.

Other experiments were then performed to attempt to recover Po in a spring water sample that was stored in polyethylene bottles without any acidification. Two years later, 0.5 M HCl was

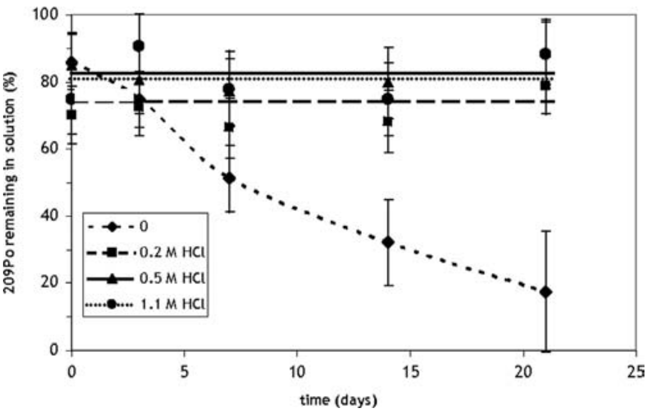

Fig. 2. Po remaining in solution (%) as a function of time, after hydrochloric acid addition at different concentrations.

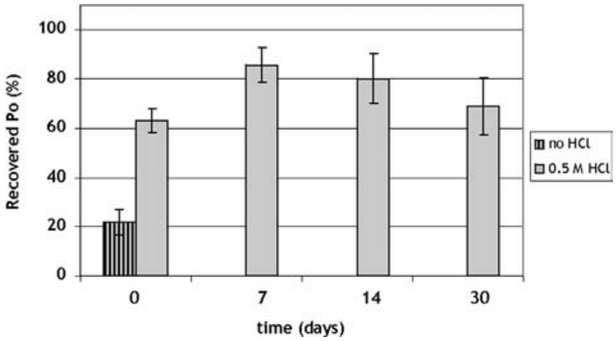

Fig. 3. Po recovered in solution (%) as a function of time, after 0.5 M HCl acidification of water sample previously stored 2 years without any acidification.

added in the polyethylene bottle and Po recovered in solution has been regularly determined.

The results illustrated in Fig. 3 demonstrate that 7 days after acidification more than 80% of Po can be recovered in solution, while only 20% of Po is still remaining in solution after 2 years of storing without any acidification. But a small fraction of polonium (15%) has never been recovered in solution. The subsequent acidification with HCl of samples containing polonium is thus essential before the polonium deposition, if water samples were not initially stored in hydrochloric acid medium.

3.3.2. Analysis of polonium and uranium in water samples

^{210}Po belongs to ^{238}U radioactive family series, and may thus be present simultaneously in water. The measurement of these naturally-occurring radionuclides is usually performed by alpha spectrometry and requires the chemical separation of both radioelements because of interferences between ^{232}U tracer and ^{210}Po. With the AQUALIX procedure we developed previously for uranium analysis in drinking water, there will be no concern of interferences if U and Po are respectively detected by ICP-MS and alpha spectrometry and if ^{233}U and ^{208}Po are used as tracers. Unfortunately for laboratories performing the measurements of uranium and polonium by alpha spectrometry, it is essential to separate both radioelements, since ^{232}U is in this case used as U tracer. If polonium and uranium are present in the water sample, preliminary experiments showed that polonium is partially co-extracted on AQUALIX (56% of Po is extracted together with U) and then partially co-eluted with uranium (65% of Po is recovered together with U). It is then necessary to separate both radioelements before U extraction on AQUALIX.

A crucial point in the sample treatment for Po analysis is the caution required to avoid loss due to high volatility of Po species, especially halide forms. Some methods to analyze Po are based on a preliminary evaporation step before the spontaneous deposition on metallic disc and alpha counting [5,16]. This evaporation step allows to analyze high volume of sample (1000 mL) and thus to reach low detection limits (0.6–8.5 mBq L^{-1}) [16]. But, its main drawback is that this step is time consuming because the evaporation must be carry out very carefully ($T \leq 80$ °C) in order to avoid Po volatilisation. In spite of these precautions, Po loss may still occur. A first set of experiments was thus conducted to compare the direct Po deposition with the Po deposition after sample evaporation. These experiments were performed on two types of water samples ($V = 100$ mL), non-acidified water and acidified water (HCl 1 M).

The results presented in Table 6 clearly show that there is no difference between the direct deposition and the deposition after evaporation. Furthermore, it is demonstrated that the evaporation step does not improve the Po recovery in water stored without any acidification, although the evaporation step was carried out after HCl addition (1 M). These results were not surprising because HCl was added after sampling. Thus Po adsorbed on storage bottle walls was not recovered, that explains the very low Po recovery for water stored without acidification.

Table 6
Comparison between direct Po deposition and Po deposition after sample evaporation, for non-acidified water and acidified water (HCl 1 M). The deposition steps were performed 1 month or 3 months after the ^{209}Po spike.

	Po recovery (%)			
	Non-acidified water		Water + 1 M HCl	
Elapsed time[a]	1 month	3 months	1 month	3 months
Direct deposition	33 ± 4	13 ± 5	92 ± 9	98 ± 3
Deposition after evaporation	31 ± 3	12 ± 7	82 ± 4	99 ± 4

[a] Elapsed time between the ^{209}Po spike in sample and the deposition step.

Table 7
Effect of the disc composition on direct Po deposition and on subsequent U extraction on the AQUALIX column.

	Stainless steel disc	Silver disc
Direct Po deposition yield (%)	80 ± 3	80 ± 5
U extraction yield (%) on AQUALIX	25 ± 11	89 ± 6

Before implementing this improved Po deposition method, last tests were performed on 500 mL water with deposition system especially designed for this larger sample volume (French plastics company DEDIENNE), and compared with 100 mL-system. The direct Po deposition yields were (89 ± 5)% and (80 ± 3)% respectively with 100 mL-system and 500 mL-system. These results demonstrate that the direct deposition of Po in 500 mL-sample is efficient.

Finally, the analysis of waters spiked with a mixture of Po and U was considered. In a first set of experiments, the direct Po deposition from 500 mL of mineral water was performed on stainless steel disc, then the gas extraction step at pH = 0.5 during 30 min was carried out and followed by the U extraction on AQUALIX at pH = 5.

The results presented in Table 7 show that the U extraction yield is lower after the auto-deposition of Po on stainless steel disc, as compared with percentage of extracted U on AQUALIX (91 ± 6)% when no preliminary Po deposition step is performed. In these experiments we observed that the water sample was slightly colored after the Po auto-deposition. A mass scan was performed with ICP-MS on each solution after Po deposition. The mass spectra (data not shown) show that the main components of stainless steel (Fe, Cr, Ni, Mo, Sn and W) are released in the water sample, probably due to the partial decomposition of stainless steel disc by hydrochloric acid during the Po deposition step. The presence of these species in the water sample may prevent the subsequent U extraction, due to competing extraction of these species by calixarene molecules. To avoid this interference on the AQUALIX column, the Po auto-deposition on silver disc was tested before the U extraction on AQUALIX. The mass spectrum of water measured by ICP-MS (data not shown), after Po auto-deposition on silver disc is similar to the mass spectrum of 1 M HCl blank, with two additional peaks of silver at m/z 107 and 109. The results (see Table 7) demonstrate that the use of silver disc for Po auto-deposition allows the separation of both radioelements. Thus 80% of Po is deposited on silver disc in a first step and then around 90% of U is extracted on the AQUALIX column in the second step. Po deposition yield on silver disc could be improved (typically over

80%) and the deposition time reduced by heating the water sample at 80 °C during the auto-deposition step [4].

4. Conclusion

The laboratory developed calixarene columns to extract and separate selectively the actinides from urines samples. The aim of this work was to investigate the applicability of calixarene columns for U and Po analysis in drinking water. A simple and effective method has been developed on a specific calixarene column called AQUALIX for the separation and preconcentration of uranium from drinking water. This new procedure was applied with success on different French bottled waters (still mineral water, sparkling mineral water, and spring water). In spite of the high content in mineral species in some waters (TDS up to 4774 mg L^{-1}), as compared with the natural U concentration level in French bottled waters (between 0.08 and 2.1 μg L^{-1}), it is noteworthy that the U extraction on AQUALIX is always efficient. That demonstrates the very good affinity and selectivity of the carboxylic calixarene ($L_{Carb}H_3$) for uranium, in presence of high content of alkaline earth cations. The average overall recovery for U is (82 ± 12)% and the total analysis time is considerably shortened (around half a day) by combining the separation on AQUALIX with ICP-MS measurement. For water containing both U and Po, these radioelements have to be separated before the water loading on AQUALIX, because of the partial co-extraction and co-elution of polonium with uranium on AQUALIX. Thus a protocol combining a first step of spontaneous deposition of polonium on silver disc followed by the uranium extraction on AQUALIX column has been proposed to separate both radioelements before alpha spectrometry measurement.

Thanks to its simplicity and low detection limits, the AQUALIX procedure is well suited for both emergency and routine radiation exposure monitoring.

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