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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 $pH=2\pm0.2$ 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.

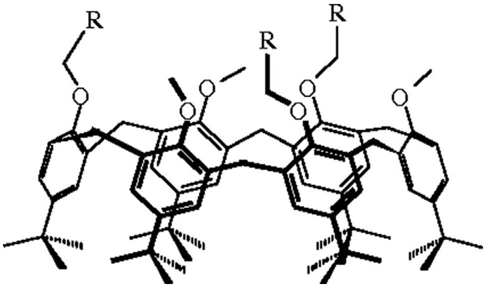

Fig. 1. 1,3,5-OCH_3-2,4,6-OCH_2R-*p*-*tert*-butylcalix[6]arene ($L_{Carb}H_3$: R=COOH; $L_{Hyd}H_3$: R=CONHOH).

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.