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PAPER

Fully automated lab-on-valve-multisyringe flow injection analysis-ICP-MS system: an effective tool for fast, sensitive and selective determination of thorium and uranium at environmental levels exploiting solid phase extraction

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An on-line solid-phase extraction method linked to inductively coupled mass spectrometry (ICP-MS) has been developed for the determination of low levels of uranium and thorium in environmental samples. The hyphenation of lab-on-valve (LOV) and multisyringe flow injection analysis (MSFIA), coupled to an ICP-MS, allows the simultaneous determination of thorium and uranium in different types of environmental sample matrices achieving high selectivity and sensitivity levels. On-line separation and preconcentration of thorium and uranium are carried out by means of UTEVA resin. The potential of the LOV-MSFIA makes possible the full automation of the system by the on-line regeneration of the column. The limits of detection reached are 0.4 ng L⁻¹ of uranium and 2.8 ng L⁻¹ of thorium. The reproducibility of the LOV-MSFIA-ICP-MS is 1.7% of RSD. Moreover, a high sensitivity, a wide working range (0–200 µg L⁻¹ for uranium and thorium) and an injection frequency up to 9 h⁻¹ (depending on the sample volume) should be highlighted. Different water sample matrices (seawater, well water, freshwater, tap water and mineral water), a phosphogypsum sample with natural uranium and thorium content and a channel sediment reference material were satisfactorily analyzed with the proposed method.

1. Introduction

Uranium and thorium are naturally occurring radioactive elements, which are present in soil, rocks, water and other samples at trace levels.¹ Determination of uranium and thorium in environmental and biological samples has considerable potential as a tool for assessing human exposure. Despite the relatively low specific activity of natural uranium and thorium isotopes, there exists an important health concern because uranium and thorium are known to cause acute toxicological effects for human and their compounds are potential occupational carcinogens. These elements and compounds are highly toxic which cause progressive or irreversible renal injury. Therefore, the WHO recommends that 15 µg L⁻¹ of U and 1 Bq L⁻¹ of ²³²Th (246 µg L⁻¹ of ²³²Th) should not be exceeded in drinking water.² These recommendations require a regular monitoring of uranium and thorium, and consequently, rapid and sensitive methods for their determination. Furthermore, determinations of uranium and thorium are important from the point of view of their technological applications, especially in metallurgy, ceramic and nuclear industries. Their determinations

in geological materials are also helpful in mineral exploration programs.

ICP-MS has become an increasingly important tool for the determination of longer-lived radionuclides. Principal advantages of ICP-MS are rapidity and sensitivity, with the capability of determining all the actinide elements within a minute, at low concentrations. In addition, there is no need to separate the elements one from another, as there is in spectrophotometry, because this is achieved by the mass spectrometer. Besides, there are less interference problems than in alpha-spectrometry, hence the number of sample pre-treatment stages and the time per analysis can be greatly reduced. However, one of the main limitations of this technique is the need for sample preparation prior to analysis, as high levels of matrix can produce interferences in the plasma which result in a suppression of analyte ionization, or block the nebulizer or torch due to the deposition of dissolved solids coming out of solution. Sample dilution will decrease the matrix effects but will also decrease the U and Th concentrations.

Solid-phase extraction (SPE) separates the analytes of interest from the matrix without reducing its concentration, and has the advantage, when coupled on-line, of requiring only a small sample volume. Horwitz *et al.*^{3,4} have developed several types of extraction chromatographic resins that can be used for enrichment and separation of uranium and thorium. So it is well known that uranium tetravalent actinide specific resin (UTEVA)^{5–8} is

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very applicable for separation of U and Th from various types of samples. Moreover, preconcentration improves the detection limits, increases the sensitivity and enhances the accuracy of the results.

Flow techniques represent a versatile fluid handling methodology that can be used for automating radiochemical separations.⁹ Some separation/preconcentration flow systems with ICP-MS have been described for analysis of U and Th in environmental matrices.^{5,10} However, none of those systems is fully automated. Actually, there are few systems using solid phase extraction which are able to automate the resin replacement.⁹ Furthermore, these methods are based on the use of the FIA technique, which although widely utilized, has several disadvantages in front of the use of multicommutated techniques.¹¹ Automation based on multicommutated techniques of the analytical method allows precise control of sample and reagent volumes and flow rates, which lead to improvement in reproducibility. Lab-on-valve (LOV)^{12–14} significantly facilitates integration of various analytical units in the valve and provides great potential for miniaturization of the entire instrumentation. Precise fluid manipulation by the LOV system and the channel configuration also make it a powerful platform for bead injection (BI). This provides proven robustness and reliability of operation, and makes the microfluidic system compatible with real life samples and peripheral instruments. Multisyringe flow injection analysis (MSFIA)^{11,15} allows multi-channel operation with a high injection throughput in order to complete the required steps of the analytical protocol.

The main aim of this work is the development of a selective, sensitive and environmental-friendly method for the determination of uranium and thorium at low concentrations, reaching environmental levels. Thus in this paper a fully automated method for separation, preconcentration, and determination of thorium and uranium in environmental samples exploiting extraction chromatographic materials in the LOV-MSFIA system coupled to ICP-MS is presented.

2. Experimental

2.1 Reagents and standard solutions

All solutions were prepared from analytical grade reagents and Millipore quality water. All uranium and thorium solutions were obtained by appropriate dilution of standards with 3 mol L⁻¹ HNO₃. Analytical reagents were: nitric acid (HNO₃), oxalic acid (H₂C₂O₄) and aluminium nitrate (Al(NO₃)₃·9H₂O). Uranium atomic absorption standard solution (1004 mg L⁻¹ in 1.2 wt% HNO₃), thorium atomic absorption standard solution (1012 mg L⁻¹ in 5.1 wt% HNO₃) and bismuth atomic absorption standard solution (1000 mg L⁻¹ in 5 wt% HNO₃), used as internal standard solution to allow correction for instrumental drift, were purchased from Sigma-Aldrich (Spain). Plutonium standard (203 ng L⁻¹ in 1 mol L⁻¹ HCl) was prepared and certified by Ciemat (Spain). UTEVA (Uranium and TEtraValent Actinides) resin 50–100 μm was purchased from Triskem Industries (Triskem International, France). This resin is an extraction chromatographic material in which the extractant system is diamyl amylphosphonate (DAAP) and it shows affinity for nitrate complexes of the actinide elements. Glass fibre prefilters (Millipore) were used to retain the resin into the column.

2.2 Samples

Water samples were prepared in a final solution of 3 mol L⁻¹ HNO₃.

A closed-vessel microwave digestion device (MLS-47100 StartD) was utilized to dissolve solid samples. A channel sediment standard reference material (BCR-320R) from the Institute for Reference Materials and Measurements (IRMM) was analyzed for validation of both analytes determination. A microwave-assisted acid digestion was carried out. Hence, a weighed dried sample (*viz.*, 200 mg) was transferred to PTFE vessels to which an acid mixture containing 9 mL of concentrated HNO₃ (65%, Merck, Germany) and 2 mL of concentrated HF (40%, Merck, Germany) was added.

The microwave digestion program consists of the following five steps: 6 min at 250 W, 6 min at 400 W, 6 min at 650 W, 6 min at 250 W and 10 min without power supply. The clear digests were heated again to near dryness and diluted to 100 mL in a final solution containing 3 mol L⁻¹ HNO₃ and 0.5 mol L⁻¹ Al(NO₃)₃. A phosphogypsum sample with natural uranium and thorium content was also analyzed. The acid digestion of this sample was carried out with the same microwave digestion program but with 500 mg of the dried sample mixed with 10 mL of concentrated HNO₃ (65%, Merck, Germany). The digests were filtered and diluted to 250 mL in a final solution containing 3 mol L⁻¹ HNO₃.

2.3 Manifold and software

The hyphenated LOV-MSFIA-ICP-MS system used is shown in Fig. 1.

The LOV microconduit (Sciware, Spain), fabricated from methacrylate encompassing six integrated microchannels

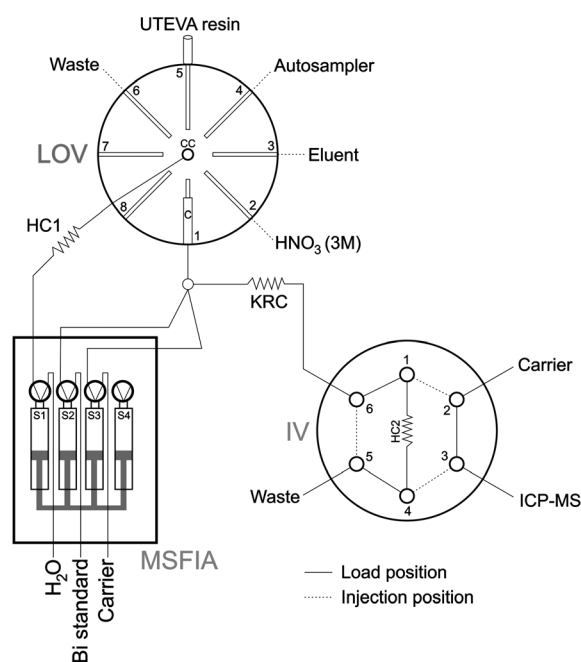


Fig. 1 Miniaturized LOV-MSFIA-ICP-MS system for thorium and uranium isolation, preconcentration and detection. S: syringe, LOV: lab-on-valve, ICP-MS: inductively coupled plasma mass spectrometer, HC: holding coil, KRC: knotted reaction coil, IV: injection valve, C: column and CC: central conduit.

(1.5 mm i.d./16.0 mm length, excepting the bead column channel made of 3.2 mm i.d.), was mounted atop of a six-port multi-position selection valve (SV) (Multiburette 4S; Crison Instruments, Spain). The central port of the integrated LOV sample processing unit, connected to S1, *via* a holding coil, is made to address the peripheral ports of the unit (1–6), for sequential aspiration of the various constituents for the bead injection (BI) process, *via* the central communication channel (CC) in the selection valve. One of the LOV channels (port 1) serves as microcolumn position for the renewable beads. This column is filled in with an appropriate amount of UTEVA resin (0.03 g) to avoid compaction and, thus, possible overpressures. To contain the sorbent within the cavity of the LOV microbore module and prevent them from escaping, the outlet of the column was furnished with a glass fibre prefilter (Millipore) retaining the beads while allowing the solution to flow freely. The suspension of extraction chromatographic resin was contained in a 3.0 mL plastic syringe, which was mounted vertically on port 5 of the integrated microsystem. Eluent and solutions' reservoirs were attached to peripheral ports, 2 (3 mol L⁻¹ HNO₃) and 3 (0.05 mol L⁻¹ H₂C₂O₄ to 0.01 mol L⁻¹ HNO₃), respectively, whereas ports 4 and 6 were employed for sample aspiration and waste, respectively.

MSFIA comprises basically a multisyringe burette (BU4S; Crison Instruments, Spain) with programmable flow rates. This burette is equipped with two 10 mL glass syringes (S1 and S3) and one of 1 mL (S2) (Hamilton, Switzerland) which are used as liquid drivers. Each syringe has a three-way solenoid valve (N-Research, USA) at the head, which facilitates the application of multicommutation schemes (on: in-line flow; off: to reservoirs). There is also a six-port injection valve (IV) (MultiBurette 4S; Crison Instruments, Spain) which helps to drive the flow in the desired way (load: connecting the HC₂ to the waste; inject: in-line flow connecting the HC₂ to the detector).

The flow network is constructed with 0.8 mm internal diameter poly(tetrafluoroethylene) (PTFE) tubing, including a 1.25 m holding coil (HC₂), corresponding to a volume of 0.625 mL and a 1.5 m knotted reaction coil (KRC). The holding coil connected with the LOV (HC₁) is constructed with 1.5 mm internal diameter PTFE tubing, corresponding to a volume of 15 mL. All connections are made by means of PVDF connectors, except cross-junction, which are made of methacrylate.

2.4 ICP-MS instrument and data processing

The ICP mass spectrometer used in the study was an Elan DRC-e (Perkin-Elmer). The system was fitted with a Scott spray chamber and a cross-flow nebulizer (Perkin-Elmer).

Data were acquired in transient peak hopping mode, which allows time resolved monitoring of multiple isotopes. Typical operating parameters of the ICP-MS are listed in Table 1. ²³²Th and ²³⁸U were selected to develop this method because of their environmental interest, since ²³²Th is the only natural occurring isotope of thorium, and ²³⁸U represents the 99.27% of natural uranium.¹ ²⁰⁹Bi (1.5 µg L⁻¹) was used as an internal standard to compensate for the instrument drift between runs.

Instrument control is performed using the software package AutoAnalysis 5.0 (Sciware, Spain). The distinctive feature of developed software based on dynamic link libraries (DLLs) at

Table 1 ICP-MS operating parameters

Radiofrequency power Gas flow	Forward	1100 W
	Plasma	15 L min ⁻¹
	Auxiliary Nebulizer	1.2 L min ⁻¹ 0.95 L min ⁻¹
Acquisition parameters (all analysis)	Dwell time	0.05 s
	Scan mode	Peak-hop transient
	Sweeps per reading	15
	MCA channels per spectral peak	1
	Resolution/amu 10% peak maximum	0.7
	Signal processing	Spectral peaks integrated; sum
	Readings per replicate	75
	Replicates	3
	Isotopes measured	²³² Th, ²³⁸ U
	Internal standard	²⁰⁹ Bi

32 bits is the possibility of using a single and versatile application without further modification for whatever instrumentation and detection system needed. The ICP-MS was controlled as a peripheral instrument of the LOV-MSFIA system using the software described above. The synchronism of ICP-MS with the LOV-MSFIA system was performed through the digital output of the multisyringe burette. A relay was used to trigger the events input of the ICP-MS.

2.5 Analytical procedure

The complete operational sequence for Th and U isolation and preconcentration with further on-line determination is listed in Table 2, and summarized as follows: first of all, the ICP-MS peristaltic pump is connected. Secondly, the column is loaded with 1 mL of saturated UTEVA-resin solution (30 g L⁻¹ of UTEVA resin in 3 mol L⁻¹ HNO₃). After that the resin needs to be conditioned with 1 mL of 3 mol L⁻¹ HNO₃. Once the column is ready, *x* mL of standard or sample are dispensed toward the column. Then 100 µL of 3 mol L⁻¹ HNO₃ are passed through the column to avoid interferences. After that, Th and U are eluted with 0.5 mL of 0.05 mol L⁻¹ H₂C₂O₄–0.01 mol L⁻¹ HNO₃. Later, 0.1 mL of bismuth (1.5 µg L⁻¹) is mixed with the eluent in the knotted reaction coil (KRC), prior to this plug being loaded at the HC₂. At this point, the injection valve is activated (IV-inject position) and the ICP-MS data acquisition is triggered. In order to avoid contamination between samples, 1 mL of the next sample is loaded into the holding coil (HC₁) and dispensed at the waste position. The resin was changed when required depending on the durability of the resin (as a function of the matrix sample).

2.6 Optimization of experimental conditions

In order to find the best operational conditions for separation, preconcentration and detection analysis of ultra-trace levels of thorium and uranium in the LOV-MSFIA-ICP-MS system a series of investigations were conducted. Amongst the various parameters affecting the performance of the sorbent bead-injection preconcentration in terms of sorption efficiency for Th and U, sample medium (3 mol L⁻¹ HNO₃), loading flow rate

Table 2 Automatic procedure for thorium and uranium separation, pre-concentration and determination using ICP-MS^a

Step	Flow rate/mL min ⁻¹	MSFIA-LOV				
		S ₁	S ₂	S ₃	LOV position	IV
1. ICP-MS	1.2	Off	Off	Off	1	Load
2. Column load						
(a) Loading 1 mL UTEVA resin	5	On	Off	Off	5	Load
(b) Filling the column	2	On	Off	Off	1	Load
3. Conditioning of UTEVA resin						
(a) Loading 1 mL HNO ₃ into HC ₁	5	On	Off	Off	2	Load
(b) Rinsing 1 mL on the column	2	On	Off	Off	1	Load
4. Sample loading						
(a) Loading <i>x</i> mL sample	5	On	Off	Off	4	Load
(b) Rinsing <i>x</i> mL on the column	0.8	On	Off	Off	1	Load
5. Interferences elimination						
(a) Loading 0.1 mL HNO ₃	5	On	Off	Off	2	Load
(b) Rinsing 0.2 mL on the column	2	On	Off	Off	1	Load
6. Elution of Th and U						
(a) Loading 0.5 mL eluent	5	On	Off	Off	3	Load
(b) Rinsing 0.625 mL on the column	0.8	On	Off	Off	1	Load
7. Internal standard addition (0.1 mL Bi)	2	Off	On	Off	1	Load
8. Loading into the holding coil (HC ₂)	2	Off	Off	On	1	Load
9. Injection into the ICP-MS	1.2	Off	Off	Off	1	Injection
10. Change of sample						
(a) Loading new sample into HC ₁	5	On	Off	Off	4	Load
(b) Discarding	5	On	Off	Off	6	Load
11. Beads replacing						
(a) Loading old beads into HC ₁	5	On	Off	Off	1	Load
(b) Discarding old beads	5	On	Off	Off	6	Load
(c) Loading new beads into HC ₁	5	On	Off	Off	5	Load
(d) Filling the column	2	On	Off	Off	1	Load

^a MSFIA: S₁: H₂O, S₂: Bi solution, S₃: H₂O; IV: load means to waste, injection to the detector.

(0.8 mL min⁻¹) and stripping conditions (0.8 mL min⁻¹) were optimized in previous works.^{16,17}

Three potentially critical variables for thorium and uranium determination were taken into consideration, namely, the nitric acid concentration (studied range: 0.01–0.05 mol L⁻¹), the oxalic acid concentration (0.01–0.05 mol L⁻¹), and the eluent volume (0.1–0.7 mL). Besides, tolerance to potential interfering species was investigated.

The computer statistics package Minitab (Minitab 15) was used to build a multivariate two-level full factorial design to screen the variables and second-order interactions between them having a significant influence upon the trace elements determination (analytical response) and to discard those with negligible effects on the response. Multivariate designs provide relevant knowledge on the effect of variables within the entire experimental domain selected, and the variance of the estimate of the response in every point of the domain is better than that obtained by univariate methods.¹⁸

The experimental design was built in a dimensionless coordinate system using factor coding, wherein the highest and lowest levels are given as +1 and -1, respectively. A randomized

Table 3 Optimized conditions

Optimized conditions	
Nitric acid concentration	0.01 mol L ⁻¹
Oxalic acid concentration	0.05 mol L ⁻¹
Eluent volume	0.50 mL
Sample load flow rate	0.8 mL min ⁻¹
Stripping flow rate	0.8 mL min ⁻¹

complete block amounting to a total number of 11 experiments was performed aimed at ensuring that the variability found in the response is on the account of the variables rather than the random error.¹⁹ Three center points were included, to identify any irregularities, such as the loss of linearity in the center of the interval. Results showed that the curvature and the three variables studied were significant.

Finally, a response surface face centered central composite experimental design with a total number of 17 experiments was resorted to find the critical value of the variables for the thorium and uranium determination. Optimized conditions are summarized in Table 3.

3. Results and discussion

3.1 Flow system set-up

MSFIA is a very versatile flow technique which allowed its easy hyphenation with LOV and with the ICP-MS. With the help of an injection valve, the plug of eluent is directed toward the detector (inject position) or toward the waste (load position), as required, with great precision and reproducibility.

The hyphenated LOV-MSFIA-ICP-MS system allows drastic reduction of reagents consumption and waste generation (*e.g.* with the proposed method less than half the volume of waste per peak is generated than using a FIA method²⁰ (10 mL sample volume and 8.75 mL HNO₃ per peak)), even loading the maximum sample volume, reduction of resin consumption and time saving in relation to manual methodologies, whose operations can last days against an injection frequency of 4–9 injection h⁻¹, depending on the sample volume, *e.g.* injection time (time required to obtain a peak) for 0.1 mL of sample is 6 min 50 s and for 8 mL of sample is 16 min 40 s. Furthermore, achieving the full automation of the proposed method by the on-line column regeneration is a noteworthy feature compared to other developed methods based on flow techniques.

In contrast to conventional inorganic solid mass spectrometric techniques, ICP-MS allows a simple sample introduction in an ion source operating at atmospheric pressure and an easy quantification procedure using aqueous standard solutions. So that once Th and U are simultaneously eluted, all the U and Th isotopes are detected in 90 seconds. Thus, a fast isotopic analysis can be performed with the proposed method. Instead, radiometric detectors which are also able to identify isotopes need a long time to do it, *e.g.* an alpha spectrometer needs in the order of days to reduce uncertainties and obtain a statistically significant measurement. The total dissolved solids (TDS) content was 0.07% allowing an accurate and safe performance for the ICP-

MS. Spectral peaks integrated was used as signal processing in peak-hop transient mode. The injection volume was 0.6 mL, injected at 1.2 mL min⁻¹.

3.2 Column properties

The direct determination of uranium and thorium by the instrumental techniques including inductively coupled plasma-mass spectrometry is still difficult because of the insufficient sensitivity, lack of selectivity, presence of complex matrix, poor precision and accuracy. To solve these problems, enrichment and separation techniques have been used in the analytical chemistry laboratories for uranium and thorium determinations. Solid phase extraction is one of the important preconcentration-separation procedures for trace heavy-metals ions, due to its simplicity and limited usage of the organic solvents.

UTEVA resin has been chosen because it is able to extract tetra- and hexa-valent actinides from HNO₃ solutions of high concentration (>1 mol L⁻¹) simultaneously and elute them with a small amount of stripping solution. The extractant in the UTEVA resin, DAAP, shows affinity for nitrate complexes of actinide elements. Formation of these complexes is driven by the concentration of nitrate in the sample solution. This resin has been widely used to isolate and preconcentrate actinide elements with a variety of detection systems. A large number of commonly occurring matrix elements show no or little retention in nitric acid media and can be separated from actinides during sample load and column wash steps. The resin needs to be conditioned with nitric acid. Thus, the concentration of nitric acid was optimized and for an acid concentration of 3 mol L⁻¹ uranium and thorium showed maximal retention on the resin. In fact the resin is prepared and left at the syringe mounted as a bead reservoir in port 5 of the LOV with 3 mol L⁻¹ HNO₃ solution.

Once the resin is ready, on-column extraction and preconcentration of analytes are carried out automatically, ensuring high repeatability between replicates. Automated preconcentration enables reduction of the detection limit in a remarkable and reproducible way.

As observed in the results shown in Table 4, up to a sample volume of 8 mL recoveries of thorium and uranium retained in the column are higher than 90%. Thus 8 mL would be the maximum preconcentrable volume to carry out the simultaneous Th and U determination, reaching a preconcentration factor of 13 (*i.e.* 8 mL of sample volume and 0.625 mL of final volume injected into the ICP-MS).

Table 4 Analytical parameters

Analytical parameters	Thorium	Uranium
Detection limit/ng L ⁻¹	2.8	0.4
Regression coefficient	0.9995	0.9999
Repeatability (%) (<i>n</i> = 10)	1.6	1.6
Reproducibility (%) (<i>n</i> = 5)	1.7	1.7
Resin durability (injections)	150	150
Preconcentration volume	Up to 8 mL	Up to 8 mL
Linear working range/ng	0–20	0–20
Injection throughput/h ⁻¹	4–9	4–9

Table 5 Comparison between different systems for uranium and thorium determination, using ICP-MS as a detector

Detection system	Flow system	Linear working range/ $\mu\text{g L}^{-1}$		LOD/ng L ⁻¹		RSD (%)		Reference
		²³⁸ U	²³² Th	²³⁸ U	²³² Th	²³⁸ U	²³² Th	
ICP-MS	FIA	0.001–0.1	—	0.3	—	3	—	10
	FIA	—	—	48	120	—	—	21
	FIA	0–10	0–10	15	6	4.3	5.8	22
	Batch method	—	—	6.3	4.5	2.3	4.5	23
	LOV-MSFIA	0–200 ^a	0–200 ^a	0.4	2.8	1.7	1.7	Proposed method

^a Upper limit calculated for 0.1 mL of sample.

3.3 Working range

Mass calibration curves (counts of analyte/counts of internal standard ratio *versus* mass in ng of Th and U) with a statistically satisfactory fit were obtained as $y = 2.3663x + 0.0400$ ($r^2 = 0.9995$, $n = 7$) for ^{232}Th and $y = 2.5903x + 0.0635$ ($r^2 = 0.9999$, $n = 7$) for ^{238}U . Under optimum conditions described above (Section 2.6) calibration curves are linear over the mass range 0–20 ng Th and 0–20 ng U. The proposed method provides high versatility allowing the loading of variable sample volumes (0.1–8 mL), admitting the analysis to a wide sample concentration range (0–200 $\mu\text{g L}^{-1}$ for Th and U), as can be seen in Table 5. The fact of using SPE allows preconcentration and dilution processes (depending on the loaded sample volume and the eluent volume). Thus, mass calibration is recommended since the volume to be loaded can be chosen by the analyst depending on the initial concentration of the sample. Furthermore preconcentration improves the detection limits, increases the sensitivity and enhances the accuracy of the results.

3.4 Limit of detection

The WHO recommends that natural U and ^{232}Th in drinking water should not exceed 15 $\mu\text{g L}^{-1}$ and 1 Bq L^{-1} (246 $\mu\text{g L}^{-1}$ ^{232}Th) respectively.² Taking into account that the described method is applied to environmental samples analysis, one of the main advantages is the LODs obtained. Thus, the limit of detections achieved are 0.003 ng and 0.02 ng for U and Th, respectively, both calculated from three times the standard deviation of ten replicates of the blank divided by the slope of the calibration curve. Considering the maximum preconcentrable sample volume LODs are 0.4 ng L^{-1} (ppt) for uranium and 2.8 ng L^{-1} (ppt) for thorium. Therefore, with this method the WHO reference values of uranium and thorium could be easily measured.

As can be seen in Table 5 the LODs of the current method are very low. Thus, the developed method is actually able to determine concentrations of uranium and thorium in a wide

concentration range including trace levels with a high and remarkable reproducibility compared with other developed methods.^{21–23}

3.5 Resin durability

The extraction column lifetime is intimately linked to the repeatability of the methodology and is indicative of the number of consecutive analyses feasible without changing the column packing. We estimate that the lifetime is 150 injections for the simultaneous determination of both analytes with recoveries higher than 95% and RSDs of 2.5% ($n = 150$). This long durability of such a small amount of resin (30 mg) makes the method very inexpensive compared with batch methods, which utilize single-use cartridges that contain 800 mg of resin. Moreover, the proposed LOV-MSFIA procedure for thorium and uranium preconcentration and isolation reduces the amount of resin and improves its reuse with respect to existing FIA methods which use diverse solid phase extraction materials, *e.g.* in the method proposed by Aldstadt *et al.*¹⁰ 500 mg of TRU resin are used and the durability of the resin is 100 injections and in the method developed by Godoy *et al.*⁵ 780 mg of resin are used in single use cartridges.

The reproducibility of the method, RSD 1.7% ($n = 5$), was determined from results obtained on different working days, changing the resin column and using a solution which contained 2.5 ng of thorium and uranium, including the resin replacement effect in the RSD calculated. As said above, this reproducibility is remarkable compared to other existing methods which determine uranium and thorium, as can be seen in Table 5.

3.6 Interferences

UTEVA resin (Uranium und TEtraValents Actinides) not only retains Th and U, but also Pu. Am is not retained in 3 mol L^{-1} HNO_3 solution. Thus, step 4 of the analytical procedure is necessary to strip the remaining potentially interfering metals from the resin before thorium and uranium are eluted. These

Table 6 Analysis of water samples^a

Sample ($n = 3$)	Added Th/ $\mu\text{g L}^{-1}$	Added U/ $\mu\text{g L}^{-1}$	Found Th/ $\mu\text{g L}^{-1}$	Found U/ $\mu\text{g L}^{-1}$	Recovery (%)	
					Th	U
Tap water	—	—	<LOD	<LOD		
	0.025	0.025	0.023 ± 0.001	0.023 ± 0.001	92	93
Mineral water	2.500	2.500	2.45 ± 0.01	2.42 ± 0.02	98	97
	—	—	<LOD	<LOD		
Freshwater	0.025	0.025	0.024 ± 0.001	0.024 ± 0.001	94	94
	2.500	2.500	2.51 ± 0.02	2.51 ± 0.02	100	99
Seawater	—	—	<LOD	0.845 ± 0.002		
	0.025	0.025	0.022 ± 0.001	0.869 ± 0.001	90	96
Wellwater	2.500	2.500	2.49 ± 0.01	3.29 ± 0.01	99	98
	—	—	<LOD	0.741 ± 0.007		
Wellwater	0.025	0.025	0.024 ± 0.002	0.765 ± 0.001	96	97
	2.500	2.500	2.51 ± 0.01	3.24 ± 0.01	100	100
Wellwater	—	—	<LOD	0.0046 ± 0.0001		
	0.025	0.025	0.022 ± 0.001	0.032 ± 0.002	90	109
	2.500	2.500	2.46 ± 0.02	2.46 ± 0.02	98	98

^a Results are expressed as the mean value \pm standard deviation ($n = 3$).

Table 7 Analysis of solid samples^a

Sample (<i>n</i> = 3)	Alpha spectrometry/mg kg ⁻¹		LOV-MSFIA-ICP-MS/mg kg ⁻¹	
	Th	U	Th	U
Phosphogypsum	1.23 ± 0.49	4.47 ± 0.16	1.45 ± 0.01	4.78 ± 0.23
Sample (<i>n</i> = 3)	Certified value/mg kg ⁻¹		Found/mg kg ⁻¹	
	Th	U	Th	U
Channel sediment BCR-320R	5.30 ± 0.40 ^b	1.56 ± 0.20 ^b	4.74 ± 0.32 ^b	1.88 ± 0.22 ^b

^a Results are expressed as the mean value ± standard deviation (SD) (*n* = 3). No significant differences at the 95% confidence level. ^b Results are expressed as the mean value ± 2 SD. No significant differences at the 95% confidence level.

possible interferences were studied and none resulted in a significant interference (differences in the analytical signal of ±10%). We even tested up to 2000 times the concentrations of plutonium that can be found in the environment^{24,25} and they did not significantly disturb Th or U determination.

It has to be taken into account that if a sample with a high phosphate content is analyzed, 0.5 mol L⁻¹ Al(NO₃)₃ has to be added to counteract its effects in order to determine thorium accurately. Phosphate anions readily complex tetravalent actinide and these phosphate complexes are not extracted by the DAAP. Addition of Al(NO₃)₃, which has higher stability constant with phosphate ions than Th, does improve extractability of Th.²⁶ These results seem to reflect a difference in the chemical properties of Th. In the sample solutions, Th cations are Th⁴⁺. Their charge is likely neutralized by counter anions. Since phosphate occurs quite commonly in a variety of biological and environmental samples and it is well known that the thorium nitrate formation is not dominant under the present experimental conditions, its effect is most relevant. To solve this addition of metal ions such as Al³⁺ is required. Al³⁺ ions complex with phosphate ions, and then, the effective concentration of phosphate ions would be decreased and thorium nitrates will prevail.

Uranium was effectively extracted on UTEVA resin. Under the present conditions, the U cations are UO₂²⁺, which are extracted on UTEVA resin as UO₂(NO₃)₂.

3.7 Application to real samples

The automatic methodology was evaluated by analyzing five different water matrixes (fresh, mineral, tap, well and seawater). For water matrices, the procedure was applied to spiked samples with known Th and U masses, obtained from the corresponding standards. Results revealed that recovery was fairly good, higher than 90% in all cases. Results of analyses for three replicates (*n* = 3) are shown in Table 6.

A phosphogypsum sample with natural thorium and uranium content and a reference material (channel sediment) were analyzed. The phosphogypsum sample was also analyzed by alpha spectrometry using a Canberra 7401 α spectrometer with an A450-18AM model passivated implanted planar silicon detector with 450 mm² of active area and 17 keV of energy resolution. The *t*-test for comparison of means revealed that there were no significant differences at the 95% confidence level between the results obtained by alpha spectrometry and the

results obtained with the proposed method. The channel sediment (BCR-320R) was obtained from the IRMM. The *t*-test for comparison of means revealed that there were no significant differences at the 95% confidence level between the certified value and the results obtained with the proposed method. Results of analyses for three replicates (*n* = 3) are shown in Table 7.

4. Conclusions

The proposed system has proved to be a versatile, fast and accurate analyzer for radioactive elements, which will be an interesting tool for further assays.

Combination of LOV and MSFIA techniques with UTEVA-resin coupled to ICP-MS enabled fully automated separation and detection, improving analyst safety. Inductively coupled plasma-mass spectrometry is ideally suited for the fully automated determination of the concentration and isotopic composition of the actinide elements.

The proposed procedure was successfully applied to the determination of trace levels of Th and U in environmental samples. In fact, with the proposed method it is possible to analyze drinking waters achieving the reference levels established by the WHO.

Main achievements of the proposed method are the LODs attained (ppt levels), the wide working range, the full automation of the column replacement provided by the BI, and the accuracy and precision of the results obtained.

The proposed method improves the timeliness of support operations for characterization and remediation. Moreover this method has several and remarkable advantages such as simplicity, sensitivity, selectivity, versatility, repeatability, minimization of sample handling and robustness compared with previous works.

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