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Lab on valve-multisyringe flow injection system (LOV-MSFIA) for fully automated uranium determination in environmental samples

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ABSTRACT

The hyphenation of lab-on-valve (LOV) and multisyringe flow analysis (MSFIA), coupled to a long path length liquid waveguide capillary cell (LWCC), allows the spectrophotometric determination of uranium in different types of environmental sample matrices, without any manual pre-treatment, and achieving high selectivity and sensitivity levels. On-line separation and preconcentration of uranium is carried out by means of UTEVA resin. The potential of the LOV-MSFIA makes possible the fully automation of the system by the in-line regeneration of the column. After elution, uranium(VI) is spectrophotometrically detected after reaction with arsenazo-III. The determination of levels of uranium present in environmental samples is required in order to establish an environmental control. Thus, we propose a rapid, cheap and fully automated method to determine uranium(VI) in environmental samples. The limit of detection reached is 1.9 ηg of uranium and depending on the preconcentrated volume; it results in ppt levels (10.3 ηg L^{-1}). Different water sample matrices (seawater, well water, freshwater, tap water and mineral water) and a phosphogypsum sample (with natural uranium content) were satisfactorily analyzed.

1. Introduction

Lab-on-valve (LOV) [1,2] brings to flow-based analysis the third generation, which significantly facilitates integration of various analytical units in the valve and provides great potential for miniaturization of the entire instrumentation. LOV is also a novel methodology for downscaling reagent based assays to micro- and submicroliter level. It is shown that sample handling in the sequential injection mode, which employs forward, reversed and stopped flow, can be programmed to accommodate a wide variety of assays within the same microfluidic device. It is noteworthy that LOV-based techniques [3–6] have not only been extensively employed in homogeneous solution-based assays, but have also shown promise in heterogeneous assays because flexible fluid manipulation is also suitable for delivering beads in flow-based manifolds (i.e. precise fluid manipulation by the LOV system and the channel configuration also make it a powerful platform for bead injection (BI)). In combination with the renewable surface concept, BI has been widely exploited for separation and preconcentration of analyte in the presence of complex matrix components. Most importantly, the automated transport of solid materials in such a system allows their renewal at will and thus provides measurement, packing and perfusion of beads with samples and reagents with a high degree of repeatability.

Multisyringe flow injection analysis (MSFIA) [7,8] profits simultaneously from the advantages offered by flow injection analysis (FIA) and sequential injection analysis (SIA) methodologies, combining the multi-channel operation and high injection throughput of FIA with the robustness and the versatility of SIA. Using this technique, several radioisotope automatic separations have been applied to environmental and biological samples [9].

Furthermore MSFIA and LOV are especially suitable for minimization of reagent consumption (green chemistry), because reagents are propelled to the system only when necessary, and they allow development of fully automated systems with high injection throughput. Besides these techniques improve reproducibility and achieve a significant decrease of both time and cost per analysis.

Determination of uranium in environmental and biological samples has considerable potential as a tool for assessing human exposure. Despite the relatively low specific activity of natural uranium isotopes, there exits an important health concern because of their chemical toxicity and ratio toxicity of their decay products. This element, present in soil, rocks water and other samples, can be incorporated into human food chain through various pathways. The simplest way for their intake is through water and beverages consumption. Therefore, WHO recommends that uranium in drinking water should not exceed 15 μg L^{-1} [10]. This recommendation requires a regular monitoring of uranium (as isotopes and element),

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and consequently, forces the analysts to find rapid, inexpensive and sensitive methods for its determination.

In the proposed method arsenazo-III has been chosen as a chromogenic reagent to detect uranium spectrophotometrically. This reaction has been successfully applied in prior works due to the high stability of its uranium complex [11]. Spectrophotometry is an acceptable detection method, due to its good precision and accuracy, associated with its lower cost compared with other techniques. The critical point against the use of spectrophotometry for determination of uranium is generally associated with low sensitivity of the spectrophotometric determinations and impossibility of direct determination without sample pretreatment. This is accomplished in this work by exploiting both uranium preconcentration on a chromatographic extraction resin and a long waveguide capillary cell (LWCC) for sensitivity enhancement.

Extraction chromatography is a technique that is ideally suited to the separation of radionuclides from a wide range of sample types. This technique combines the selectivity of liquid-liquid extraction with the ease of operation of column chromatography. Horwitz et al. [12,13] have developed several types of extraction chromatographic resins that can be used for enrichment and separation of uranium. So it is well known that uranium tetravalent actinide specific resin UTEVA [14–19] is very applicable for separation of U from various types of samples.

In order to enhance the sensitivity and improve limits of detection of optical instrumentation, a long path length liquid waveguide capillary cell (LWCC) has been coupled to the system. LWCCs have been widely used to determine environmental parameters at trace levels [20,21].

Thus the main aim of this work is the development of a simple and fully automated method for uranium preconcentration, separation and detection in environmental samples, easily adaptable to various types of sample matrices. Therefore, in this paper, selective and sensitive determination of uranium exploiting extraction chromatographic materials in LOV-MSFIA is presented.

2. Experimental

2.1. Reagents and standard solutions

All solutions were prepared from analytical grade reagents with Millipore quality water. All uranium solutions were obtained by appropriate dilution of the standard with 3 mol L^{-1} HNO_3. Reagents and materials included HNO_3 60% Scharlau (Barcelona, Spain), HCl 37% Scharlau, HF 40% Merck (Darmstadt, Germany), EDTA Scharlau, Arsenazo-III Fluka (Madrid, Spain), chloroacetic acid Scharlau, sodium chloroacetate Scharlau, uranium atomic absorption standard solution (1004 mg L^{-1} in 1.2 wt % HNO_3) Sigma–Aldrich (Madrid, Spain), thorium atomic absorption standard solution (1012 mg L^{-1} in 5.1 wt % HNO_3) Sigma–Aldrich, $^{239+240}$Pu (203 ± 1 ng L^{-1} standard in 1 mol L^{-1} HCl) Ciemat (Madrid, Spain), UTEVA (uranium and tetravalents actinides) resin 50–100 μm, Triskem Industries (France) and glass fibre prefilters Millipore (Madrid, Spain).

2.2. Samples

All samples were prepared in a final solution of 3 mol L^{-1} HNO_3.

For acid digestion of phosphogypsum, approximately 10 g of dry sample were dissolved in 150 mL 8 mol L^{-1} HNO_3 with constant boiling and stirring for 8 h.

A channel sediment standard reference material (BCR-320R) from the Institute for Reference Materials and Measurements (IRMM) was analyzed for validation of uranium determination. This sample was digested via a microwave digestor (MLS-1200 Mega) from Milestone (Sorisole, Italy). A weighed dried sample (*viz.*, 200 mg) was transferred to PTFE vessels to which an acid mixture containing 9 mL of concentrated HNO_3 and 2 mL of concentrated HF was added. The clear digests were heated again to near dryness and diluted to 20 mL in a final solution containing 3 mol L^{-1} HNO_3 and 2.5 g L^{-1} EDTA.

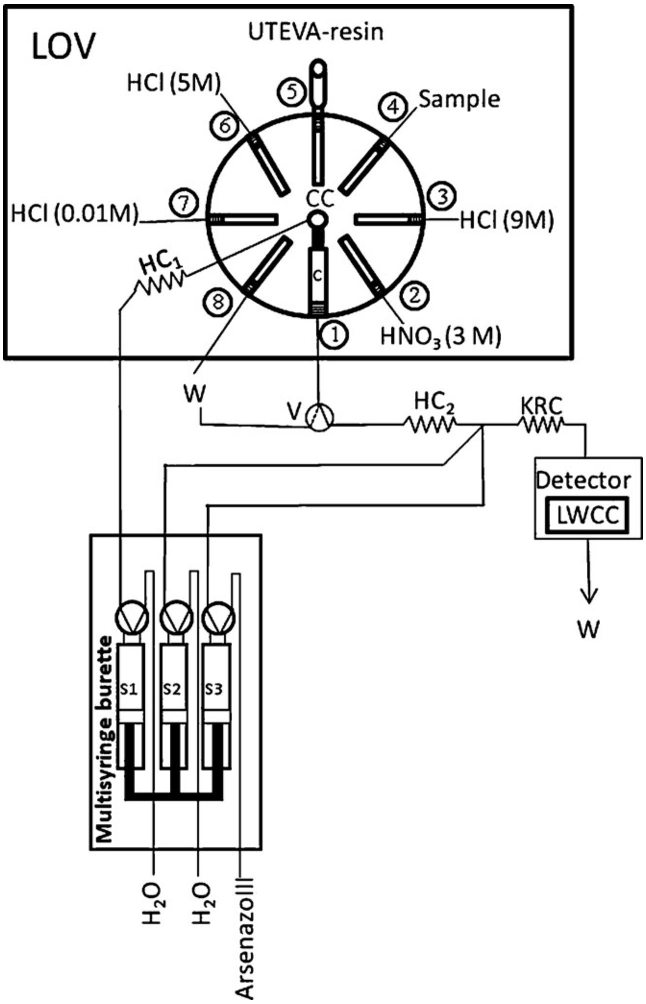

Fig. 1. Miniaturized LOV-MSFIA system for uranium(VI) isolation, preconcentration and detection. S: syringe, LOV: lab-on-valve, HC: holding coil, KRC: knotted reaction coil, V: solenoid valve, LWCC: Long path length waveguide capillary cell, C: column and W: waste.

2.3. Manifold and software

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

The LOV microconduit (Sciware, Palma de Mallorca, Spain), fabricated from methacrylate encompassing eight integrated microchannels (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 an eight-port multiposition selection valve (SV). 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 (1–8), for sequential aspiration of the various constituents for the 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

Table 1
Automatic procedure for uranium separation, preconcentration and spectrophotometric detection.

Step	Flow rate (mL min^{-1})	LOV-MSFIA				
		S1	S2	S3	LOV position	V
Conditioning of UTEVA resin						
(a) Loading 1 mL HNO_3 into HC_1	5	On	Off	Off	2	Off
(b)Rinsing 1 mL on the column	2	On	Off	Off	1	Off
Sample loading						
(a)Loading x mL sample into HC_1	5	On	Off	Off	4	Off
(b)Rinsing x mL on the column	0.8	On	Off	Off	1	Off
Interferences elimination						
(a)Loading 0.1 mL 3 mol L^{-1} HNO_3	5	On	Off	Off	2	Off
(b)Rinsing 0.1 mL on the column	2	On	Off	Off	1	Off
(c)Loading 0.1 mL 9 mol L^{-1} HCl	5	On	Off	Off	3	Off
(d)Rinsing 0.1 mL on the column	2	On	Off	Off	1	Off
(e)Loading 2 mL 5 mol L^{-1} HCl	5	On	Off	Off	7	Off
(f)Rinsing 2 mL on the column	2	On	Off	Off	1	Off
Elution of U						
(a)Loading 1 mL 0.01 mol L^{-1} HCl	5	On	Off	Off	6	Off
(b)Rinsing 1 mL on the column	0.8	On	Off	Off	1	On
Reaction						
(a)Simultaneous dispense: eluent (1 mL) and arsenazo-III (1 mL)	1	On	Off	On	1	On
Reaction plug to the detector.	2	Off	On	Off	1	Off
Change of sample						
(a)Loading 1 mL new sample	5	On	Off	Off	4	Off
(b)Discarding 2 mL	5	On	Off	Off	8	Off
Beads replacing						
(a)Loading old beads into HC_1	5	On	Off	Off	1	Off
(b)Discarding old beads	5	On	Off	Off	8	Off
(c)Loading new beads into HC_1	5	On	Off	Off	5	Off
(d)Filling the column	2	On	Off	Off	1	Off

MSFIA – S1: H_2O; S2: H_2O; S3: Arsenazo-III in buffer solution; V: Off means to waste, on to the detector.

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. The eluent and cleansing dissolutions reservoirs were attached to peripheral ports as follows: 2 (3 mol L^{-1} HNO_3), 3 (9 mol L^{-1} HCl), 6 (5 mol L^{-1} HCl) and 7 (0.01 mol L^{-1} HCl), whereas ports 4 and 8 were employed for sample disposal and waste, respectively.

MSFIA comprises basically a multisyringe burette (BU4S; Crison Instruments, Barcelona, Spain) with programmable flow rates. This burette is equipped with three 10 mL glass syringes (Hamilton, Switzerland) which are used as liquid drivers. Each syringe has a three-way solenoid valve (N-Research, Caldwell, NJ, USA) at the head, which facilitates the application of multicommutation schemes (on: in-line flow; off: to reservoirs). There is also one solenoid commutation valve V (on: in-line flow to the detector; off: to waste) (MTV-3-N 1/4 UKG; Takasago, Japan), which helps drive the flow in the desired way.

The flow network is constructed with 0.8 mm internal diameter poly(tetrafluoroethylene) (PTFE) tubing, including a 3-m holding coil (HC_2) and a 3-m knotted reaction coil (KRC). The holding coil connected with the LOV (HC_1) is constructed with 1.5 mm internal diameter poly(tetrafluoroethylene) (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.

The detection system is composed of a deuterium-halogen light source (Mikropack, Germany), two optical fibres of 400 and 600 μm internal diameter (Ocean Optics, USA), a flow cell made from a 100 cm type II Teflon AF 2400 long path-length liquid core waveguide capillary cell (World Precision Instruments, FL, USA) (internal diameter 550 μm, effective path length 100.0 ± 0.5 cm, internal volume 240 μL), and a USB 2000 miniaturized fibre optic CCD spectrometer (Ocean Optics), connected to a computer via an USB interface. LWCCs are based on the use of a capillary with a lower refractive index than the liquid core contained in it, so the light introduced into the liquid core of the capillary is totally internally reflected down the capillary towards the detector. Therefore, LWCCs can detect as much of the optical signal as possible while minimizing background noise. The absorbance is measured at 660 nm.

Instrument control and acquisition of spectrophotometric data are performed using the software package AutoAnalysis 5.0 (Sciware, Palma de Mallorca, Spain). The distinctive feature of developed software based on dynamic link libraries (DLLs) at 32 bits is the possibility of using a single and versatile application without further modification for whatever instrumentation and detection system needed. It involves a basic protocol which allows the implementation of specific and individual DLLs, addressing the configuration of the assembled flow analyzer.

2.4. Analytical procedure

The complete operational sequence for U(VI) isolation and preconcentration with further on-line determination is listed in Table 1,and summarized as follows:

1. Conditioning of UTEVA resin: The CC is connected to port 2 to aspirate 1 mL of 3 mol L^{-1} HNO_3 into HC_1, then it comes back to port 1 and the HNO_3 is propelled towards the column at a flow rate of 2.0 mL min^{-1}. V is deactivated (V-off, to waste) in order to bypass the LWCC, allowing higher flow rates.
2. Sample loading: once the column is ready, x mL of standard or sample (port 4) are dispensed toward the column (port 1) at a flow rate of 0.8 mL min^{-1}.
3. Elimination of interferences: The sequence used to eliminate interferences is the following: first 100 μL 3 mol L^{-1} HNO_3 (port 2) to avoid Pu interference, then 100 μL 9 mol L^{-1} HCl (port 3) are dispensed in order to change the resin to chloride system and finally 2 mL of 5 mol L^{-1} HCl (port 7) to eliminate thorium interference. The flow rate used in this step is 2 mL min^{-1}. All

Table 2
Optimized conditions.

Arsenazo-III concentration	0.001%
Arsenazo-III volume	1 mL
HCl (eluent) concentration	0.01 mol L^{-1}
HCl (eluent) volume	1 mL
Buffer concentration	0.5 mol L^{-1}
Loading flow rate	0.8 mL min^{-1}
Striping flow rate	0.8 mL min^{-1}
Sample medium (HNO_3)	3 mol L^{-1}

Table 3
Analytical parameters.

Analytical parameters	
Detection limit	10.3 ηg L^{-1}
Regression coefficient	0.9997
Repeatability (%) ($n = 10$)	1.6
Reproducibility (%) ($n = 5$)	1.7
Resin durability	100 injections
Preconcentration volume	Up to 30 mL
Sensitivity	3.6289 AU μg^{-1}
Linear working range	0–0.3 μg
Injection throughput	1.2–5.5 h^{-1}

these solutions are loaded into HC_1 and dispensed at port 1 sequentially.

4. Elution of U(VI): At this point all the uranium contained in the sample and nothing else is retained on the column. 1 mL 0.01 mol L^{-1} HCl (port 6) is loaded into HC_1 and V is activated (V-on) to propel the eluent (1 mL 0.01 mol L^{-1} HCl) through the column (port 1) towards the detector at a flow rate of 0.8 mL min^{-1}.
5. Reaction: S1 and S3 are activated (S1-on, S3-on) and 1 mL arsenazo-III is simultaneously mixed with the eluent in the knotted reaction coil.
6. Final dispense: S2 is activated (S2-on) and the reaction plug passes through the detector.
7. Change of sample: In order to avoid contamination between samples, 1 mL of the next sample is loaded into the holding coil (HC_1) and dispensed at the waste position (port 8).
8. Change of the resin: applicable when required depending on the sample matrix. The column is regenerated by replacing the resin automatically. First, the old resin is loaded into the holding coil (HC_1) and sent to waste (port 8), then 1 mL of resin is loaded into the holding coil from the resin reservoir (port 5) which contains a saturated solution of the resin (30 g L^{-1} of UTEVA resin in HNO_3 3 mol L^{-1}) and dispensed at port 1 with V-off (to waste) to fill the column.

2.5. *Optimization of experimental conditions*

In order to find the best operational conditions for separation, preconcentration and detection analysis of ultra-trace levels of uranium in the LOV-MSFIA flow 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 U(VI), sample medium (3 mol L^{-1} HNO_3), loading flow rate (0.8 mL min^{-1} was the optimum loading and stripping flow rate, as it was the highest in which the maximal sorption and elution efficiency was observed) and stripping conditions, tolerance to potential interfering species are regarded as the most crucial ones. Reaction of detection conditions such as type of reagent, acidity of the reaction plug and wavelength (660 nm) were optimized in a previous work [22].

The pH is an essential condition to carry out the colorimetric reaction in order to avoid interference from calcium and overlap of the arsenazo-III spectrum with the maximum of the complex formed. Thus, the optimum pH is 2, and the arsenazo-III is prepared in buffer solution (chloroacetic acid–sodium chloroacetate).

The computer statistics package StatGraphics (Stat-Graphics Centurion XV, Stat Point, Herndon, VA, USA, 2005) was used to build a response surface experimental design. A full factorial composite design with a total number of twenty-seven runs, including centre points, was carried out in order to optimize the experimental conditions.

Effects of individual factors (arsenazo-III volume and concentration, eluent volume and concentration, and buffer concentration) and their second order interactions were thus investigated. Optimized conditions are summarized in Table 2.

3. Results and discussion

3.1. *Flow system set-up*

In addition to compactness, the advantage of this "lab-on-valve" system is the permanent rigid position of the sample processing channels that ensures repeatability of microfluidic manipulations, controlled by conventional sized peripherals. This provides proven robustness and reliability of operation, and makes the microfluidic system compatible with real life samples and peripheral instruments.

MSFIA is a very versatile flow technique which allowed its easy hyphenation with LOV. With the help of a three-way solenoid valve, the plug of reagents is directed toward the detector (on position) or toward the waste (off position), as required, with great precision and reproducibility.

In this way both flow techniques LOV-MSFIA complement each other, improving their individual advantages according to the required analytical needs. This allows drastic reduction of reagents consumption, waste generation, reduction of resin consumption and time saving in relation to manual methodologies, whose operations can last days against an injection frequency of 1.2–5.5 injection h^{-1}, depending on the sample volume. Achieving the fully automation of the proposed method by the in-line column regeneration.

3.2. *Column properties*

The extractant in the UTEVA resin, diamyl, amylphosphonate (DAAP), forms nitrato complexes with uranium(VI) and tetravalent actinide elements. The 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. UTEVA resin is able to retain up to 100 mg of U per g of resin.

The resin needs to be conditioned with nitric acid of the same concentration as the samples medium. Thus, the concentration of nitric acid was optimized and for acid concentrations up to 3 mol L^{-1} uranium showed no retention on the resin. So, we decided to use 3 mol L^{-1} nitric acid for both processes because it is the lower concentration for total uranium(VI) retention. 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} HNO_3 solution.

Once the resin is ready, on-column extraction and preconcentration of the analyte 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 3, up to a sample volume of 30 mL recovery of uranium retained in the column is

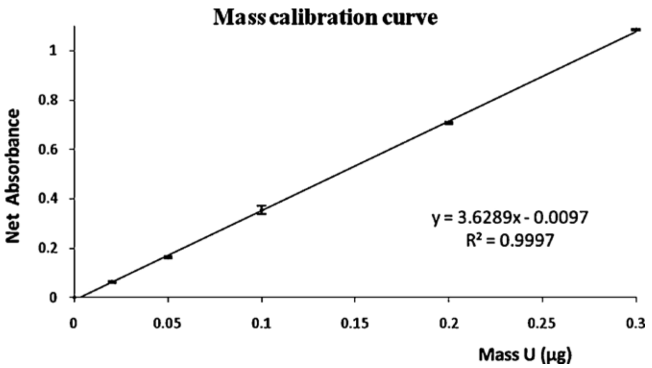

Fig. 2. Mass calibration curve. Net absorbance versus uranium(VI) mass in µg. It is represented the mean value ± standard deviation.

higher than 90%. Preconcentration of sample by a factor of 30:1 can be considered a fairly good result for this type of analysis. Evidently, the larger the volume capable of being preconcentrated the lower LOD attained.

3.3. *Working range*

A mass calibration curve (net absorbance versus mass in µg uranium(VI)), with a statistically satisfactory fit was obtained ($y = 3.6289x – 0.0097$, $r^2 = 0.9997$). Under the optimum conditions described above the calibration curve is linear over the concentration range 0–0.3 µg uranium(VI). A mass calibration curve is shown in Fig. 2. The fact of using a preconcentration process implies mass calibration, because the volume to be concentrated can be chosen by the analyst depending on the concentration of the sample. Therefore it provides high versatility to the proposed method allowing preconcentration of variable sample volumes, admitting the analysis to a wide concentration range.

3.4. *Limit of detection*

Taking into account that the described method is applied to environmental samples analysis, one of the main advantages is the LOD obtained passing through the column up to 30 mL of sample without disturbing significantly the response signal. Thus, the limit of detection achieved is 10.3 ηg L^{-1} (ppt), calculated from three times the standard deviation of ten replicates of the blank divided by the slope of the calibration curve. So with this method the WHO reference value of uranium could be easily measured.

As can be seen in Table 4 the LOD of the current method is very low, one to three orders of magnitude lower than those obtained with radiometric methods (LOD between: 18 and 0.40 µg L^{-1}) [23–25], furthermore requiring much less time. A radiometric determination can last 24 h versus the 11 min required by the proposed method for uranium determination. Another disadvantage of classical radiochemical methods is that these may generate significant quantities of secondary hazardous waste.

Table 4
LOD comparison between methods with different detection systems for uranium determination.

Detection systems	Flow system	LOD (ng L^{-1})	Ref.
Radiometric	Batch method	18000	[23]
	Batch method	2457	[24]
	Batch method	400	[25]
ICP-MS	FIA	690	[29]
	FIA	15	[28]
	Batch method	1	[27]
	FIA	0.2	[26]
Spectrophotometric	MSFIA-MPFS	12.6	[22]
	LOV-MSFIA	10.3	Our method

It should be emphasized that the proposed method is simple, compact, fully automated and low cost, since it requires less maintenance and inexpensive instrumentation and can easily be adapted for field measurements. Even so, the LOD achieved is similar to those obtained using ICP–MS [26–29] which vary in a range 0.2–690 ng L^{-1} (ppt).

The combination of UTEVA–resin, the sensitivity of the colorimetric reaction, and the LWCC made possible the achievement of such a low LOD. Without one of these essential components, results would not have been so good. Thus, the developed method is actually able to determine concentrations of uranium at real environmental levels.

3.5. *Resin durability*

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. Results obtained up to the hundredth replicate reveal recovery of the analyte higher than 90% with a RSD of 5.1%. In this way we estimate that the lifetime is 100 injections; replacement of the column is then recommended. This long durability (100 injections) of such 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. In addition, the proposed LOV-MSFIA system is able to renew the solid phase extraction at will in a fully automated way, without requiring the analyst intervention, resulting in higher reproducibility and repeatability, minimizing at the same time reagents consumption, even the amount of resin required is almost three times lower than the amount required in a previous work [22], in which the resin had to be renewed manually, what resulted also in lower reproducibility and repeatability. Moreover, the durability of the present column is more than the double, although containing less extraction chromatographic resin than in the previous work.

The reproducibility of the method, RSD 1.7%, was determined from results obtained on different working days, changing the resin column and using a solution which contained 0.2 µg uranium, the resin replacement effect was included in the RSD given.

3.6. *Interferences*

The main advantage of using arsenazo-III lies in the high stability of its uranium complex which makes possible its analytical utilization in strongly acidic media. The usefulness of the reactivity of arsenazo-III lies in the fact that metals whose complex formation depends on high pH, do not interfere with the determination of other elements. In other words by specifying the pH it is possible to use arsenazo-III very selectively [11,30,31].

UTEVA resin (uranium und tetravalents actinides) not only retains uranium(VI), but also Pu, and Th. Am is not retained in 3 mol L^{-1} HNO_3 solution. Step 3 of the analytical procedure is necessary to strip the remaining potentially interference metals (Pu and Th) from the resin before uranium(VI) is eluted. These possible interferences were studied and none resulted in significant interference (differences in analytical signal of ±10%). We even tested up to 2000 times the concentrations of plutonium [32,33] that can be found in the environment and they did not significantly disturb uranium(VI) determination.

Furthermore, it has been reported that arsenazo-III forms stable complexes with thorium [34] and calcium [35]. Thorium could be a great interference if it is not striped from the column prior to uranium(VI). In order to evaluate potential interferences on the target specie, both in the complexation reaction and in the

Table 5
Analysis of different types of sample.

Sample ($n = 3$)	Added U ($\mu g\,L^{-1}$)	Found U ($\mu g\,L^{-1}$)	Recovery (%)
Tap water	0	<LOD	
	20	19.8 ± 0.4	98
Mineral water	0	<LOD	
	20	19.9 ± 0.5	99
Freshwater	0	<LOD	
	20	20.80 ± 0.05	105
Seawater	0	<LOD	
	20	19.2 ± 1.5	93
Well water	0	<LOD	102
	20	21.0 ± 0.3	

Sample ($n = 3$)	Validation method[a] ($\mu g\,L^{-1}$)	Found U ($\mu g\,L^{-1}$)	Significant difference $\alpha = 0.05$
Phosphogypsum	179.2 ± 9.7	186.7 ± 6.6	Not found

Sample ($n = 3$)	Certified value ($\mu g\,L^{-1}$)	Found U ($\mu g\,L^{-1}$)	Significant difference $\alpha = 0.05$
Channel sediment BCR-320R	1.56 ± 0.20	1.59 ± 0.02	Not found

[a] Determined by ICP-MS.
Results are expressed as mean value ± standard deviation.

sorption process onto the surface of the packed column we tested up to 0.2 mg L^{-1} of Th, in a proportion of 4 to 1 respect to uranium, which is the maximum proportion of these elements found in the environment [34,36]. To overcome thorium and plutonium interference, it was necessary to pass through the column up to 2 mL of 5 mol L^{-1} HCl and 0.1 mL of 3 mol L^{-1} HNO_3, respectively. Calcium interference was overcome by fixing the pH at 2, at this pH calcium does not react with arsenazo-III.

3.7. Application to real samples

The automatic methodology was evaluated by analyzing five different water matrixes (fresh water, mineral water, tap water, well water and seawater), a channel sediment and a phosphogypsum sample with natural uranium content (phosphate fertilizer plant located in Huelva, Spain). Results of analyses for three replicates ($n = 3$) are shown in Table 5.

For water matrices, the procedure was applied to spiked samples with known U(VI) mass, obtained from the corresponding standard. Results revealed recovery was fairly good, higher than 93% in all cases.

In order to validate the proposed method a phosphogypsum sample was analyzed by the proposed method and by ICP–MS. The channel sediment standard reference material (BCR-320R) obtained from the IRMM was also analyzed by the proposed method. In both cases, the t-test for comparison of means revealed there were no significant differences at the 95% confidence level.

4. Conclusions

To the best of our knowledge, this is the first LOV-MSFIA fully automated method developed for ultra trace radioisotope determination. Combination of LOV and MSFIA techniques with UTEVA–resin enables fully automated sample treatment, separation and detection, improving analyst safety.

The proposed procedure was successfully applied to the determination of trace levels of U(VI) in environmental samples. Besides with the proposed method it is possible to analyze uranium(VI) in drinking waters achieving the reference level established by the WHO.

The main achievements of the proposed method are the LOD attained (ppt levels), the automation of the column replacement provided by the BI and the cost reduction per analysis due to the long durability of such small amount of resin. Thus our method is proposed as an alternative to existing methods which require more expensive instrumentation, such as radiometric counters or ICP-MS.

The proposed method reduces analytical costs and improves the timeliness of support operations for characterization and remediation. Moreover this method has several advantages such as simplicity, compactness, sensitivity, selectivity, low operational cost, versatility, repeatability, minimization of sample handling and robustness.

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References

[1] J. Ruzicka, Analyst 125 (2000) 1053–1060.
[2] J. Wang, E.H. Hansen, Trends Anal. Chem. 22 (2003) 225–231.
[3] M.D. Castro, J. Ruiz-Jiménez, J.A. Pérez-Serradilla, Trends Anal. Chem. 27 (2008) 118–126.
[4] I. Lahdesmaki, P. Chocholous, A.D. Carroll, J. Anderson, P.S. Rabinovitch, J. Ruzicka, Analyst 134 (2009) 1498–1504.
[5] Y. Wang, Z. Liu, G. Yao, P. Zhu, X. Hu, C. Yang, Q. Xu, Anal. Chim. Acta 649 (2009) 75–79.
[6] M. Alcalde-Molina, J. Ruiz-Jiménez, M.D. Luque de Castro, Anal. Chim. Acta 652 (2009) 148–153.
[7] V. Cerdà, J.M. Estela, R. Forteza, A. Cladera, E. Becerra, P. Altimira, P. Sitjar, Talanta 50 (1999) 695–705.
[8] C. Pons, R. Forteza, A.O.S.S. Rangel, V. Cerdà, Trends Anal. Chem. 25 (2006) 583–588.
[9] Y. Fajardo, L. Ferrer, E. Gómez, F. Garcias, M. Casas, V. Cerdà, Anal. Chem. 80 (2008) 195–202.
[10] Guidelines for Drinking-water Quality, vol. 1, 3rd ed., World Health Organization, WHO, Geneva, 2004.
[11] E.B. Sandell, H. Onishi (Eds.), Photometric Determination of Traces of Metals, 4th ed., John Wiley & Sons, New York, 1979.
[12] E.P. Horwitz, M.L. Dietz, R. Chiarizia, H. Diamond, Anal. Chim. Acta 266 (1992) 25–37.
[13] E.P. Horwitz, R. Chiarizia, M.L. Dietz, H. Diamond, Anal. Chim. Acta 281 (1993) 361–372.
[14] I.W. Croudace, P.E. Warwick, R.C. Greenwood, Anal. Chim. Acta 577 (2006) 111–118.
[15] I.W. Croudace, P.E. Warwick, R. Taylor, S. Dee, Anal. Chim. Acta 371 (1998) 217–225.
[16] H. Rameback, U. Nygren, P. Lagerkvist, A. Verbruggen, R. Wellum, G. Skarnemark, Nucl. Instr. Meth. Phys. Res. 266 (2008) 807–812.
[17] A. Fujiwara, Y. Kameo, A. Hoshi, T. Haraga, M. Nakashima, J. Chrom. A 1140 (2007) 163–167.
[18] E. Manickam, S. Sdraulig, R.A. Tinker, J. Enrviron. Radioact. 99 (2008) 497–501.
[19] L. Benedik, M. Vasile, Y. Spasova, U. Watjen, Appl. Rad. Isot. 67 (2009) 770–775.

[20] F. Maya, J.M. Estela, V. Cerdà, Anal. Bioanal. Chem. 394 (2009) 1577–1583.
[21] L.J. Gimbert, P.J. Worsfold, Trends Anal. Chem. 26 (2007) 914–930.
[22] J. Avivar, L. Ferrer, M. Casas, V. Cerdà, Anal. Bioanal. Chem. 397 (2010) 871–878.
[23] G. Jia, G. Torri, P. Innocenzi, J. Radioanal, Nucl. Chem. 262 (2004) 433–441.
[24] S. Antoniou, A. Tsiaili, I. Pashalidis, Rad. Meas. 43 (2008) 1294–1298.
[25] G. Van Britsom, B. Slowikowski, M. Bickel, Sci. Total Environ. 173 (1995) 83–89.
[26] M.L.D.P. Godoy, J.M. Godoy, R. Kowsmann, G.M. dos Santos, R.P. da, Cruz, J. Environ. Rad. 88 (2006) 109–117.
[27] A. Sabarudin, M. Oshima, T. Yakayanagi, L. Hakim, K. Oshita, Y.H. Gao, S. Motomizu, Anal. Chim. Acta 581 (2007) 214–220.
[28] E.R. Unsworth, J.M. Cook, S.J. Hill, Anal. Chim. Acta 442 (2001) 141–146.
[29] G. Daneshvar, A. Jabbari, Y. Yamini, D. Paki, J. Anal. Chem. 64 (2009) 602–608.
[30] J. Fries, H. Getrost, Organic Reagents for Trace Analysis, Merck, 1977, pp. 384–391.
[31] M.H. Khan, P. Warwick, N. Evans, Chemosphere 63 (2006) 1165–1169.
[32] J.A. Sanchez-Cabeza, J. Merino, P. Masqué, P.I. Mitchell, L.L. Vintró, W.R. Schell, L. Cross, A. Calbet, Sci. Total Environ. 311 (2003) 233–245.
[33] D.I. Struminska, B. Skwarzec, J. Environ. Radioact. 72 (2004) 355–361.
[34] M. Rozmaric, A.G. Ivsic, Z. Grahek, Talanta 80 (2009) 352–362.
[35] N. Malcik, J.P. Ferrance, J.P. Landers, P. Caglar, Sens. Actuators B 107 (2005) 24–31.
[36] C. Galindo, L. Mougin, A. Nourreddine, Appl. Rad. Isot. 65 (2007) 9–16.