Talanta 134 (2015) 674–680

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Uranium monitoring tool for rapid analysis of environmental samples based on automated liquid-liquid microextraction

Rogelio Rodríguez [a,b], Jessica Avivar [b,d], Laura Ferrer [b,*], Luz O. Leal [a], Víctor Cerdà [c]

[a] Energy and Environmental Department, Advanced Materials Research Center (CIMAV) S.C., Chihuahua, Chihuahua 31109, Mexico
[b] Environmental Radioactivity Laboratory-LaboRA, University of the Balearic Islands, Palma de Mallorca E-07122, Spain
[c] Laboratory of Environmental Analytical Chemistry, University of the Balearic Islands, Palma de Mallorca E-07122, Spain
[d] Sciware Systems, S.L., Spin-off from the University of the Balearic Islands, Bunyola E-07193, Spain

ARTICLE INFO

Article history:
Received 6 October 2014
Received in revised form
3 December 2014
Accepted 6 December 2014
Available online 15 December 2014

Keywords:
Uranium(VI) monitor
Cyanex-272
In-syringe liquid-liquid microextraction
Magnetic stirring assistance
Flow techniques
Environmental samples

ABSTRACT

A fully automated in-syringe (IS) magnetic stirring assisted (MSA) liquid-liquid microextraction (LLME) method for uranium(VI) determination was developed, exploiting a long path-length liquid waveguide capillary cell (LWCC) with spectrophotometric detection. On-line extraction of uranium was performed within a glass syringe containing a magnetic stirrer for homogenization of the sample and the successive reagents: cyanex-272 in dodecane as extractant, EDTA as interference eliminator, hydrochloric acid to make the back-extraction of U(VI) and arsenazo-III as chromogenic reagent to accomplish the spectrophotometric detection at 655 nm. Magnetic stirring assistance was performed by a specially designed driving device placed around the syringe body creating a rotating magnetic field in the syringe, and forcing the rotation of the stirring bar located inside the syringe.

The detection limit (LOD) of the developed method is 3.2 $\mu g\ L^{-1}$. Its good interday precision (Relative Standard Deviation, RSD 3.3%), and its high extraction frequency (up to 6 h^{-1}) makes of this method an inexpensive and fast screening tool for monitoring uranium(VI) in environmental samples. It was successfully applied to different environmental matrices: channel sediment certified reference material (BCR-320R), soil and phosphogypsum reference materials, and natural water samples, with recoveries close to 100%.

1. Introduction

Long-lived radioactive elements such as uranium, and any of their decay products, are considered as Naturally Occurring Radioactive Material (NORM). The term NORM refers to naturally occurring radioactive materials whose potential for exposure has been increased by human activities [1]. Certain industries handle significant quantities of NORM, which usually end up in their waste streams, or in the case of uranium mining, in their tailing dams. As potential NORM hazards have been identified, these industries have increasingly become subject to monitoring and regulation [2–4]. Moreover, uranium is present in soil, rocks and water being easily incorporated into the human food chain through various pathways. The simplest way for its intake is through water and beverages consumption. Thus, uranium is considered an element of great environmental interest, in both chemical and radiological aspects [5,6]. Organizations such as WHO (World Health Organization) and USEPA (United States Environmental Protection Agency) have specified a guideline value of 30 $\mu g\ L^{-1}$ uranium in drinking water [2,3]. For the foregoing reasons, there is a need for reliable methods, of easy handling, fast and low cost to enable uranium control in a large number of samples. Thus, we propose a rapid, high accuracy and precision, inexpensive, and automated method for determination of uranium (VI) in environmental samples.

In this context, spectrophotometric detection is a useful tool to develop simple and inexpensive methods for radioactive element monitoring. Thus, when the threshold value is exceed, the content of specific radioisotopes present in the sample should be analyzed [7]. In order to enhance the sensitivity and improve limits of detection in spectrophotometric methods, long path length liquid waveguide capillary cells (LWCCs) have been widely used to determine environmental contaminants at trace levels [8,9]. LWCCs are based on 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 toward the detector, detecting as much of the optical signal as possible while minimizing background noise. Arsenazo-III has been used as chromogenic reagent to form a highly stable uranium complex [10,11].

* Corresponding author.
E-mail address: laura.ferrer@uib.es (L. Ferrer).

http://dx.doi.org/10.1016/j.talanta.2014.12.007
0039-9140/

Provided the low concentration of uranium in environmental samples and the presence of interferences, sample pretreatment is almost unavoidable. Liquid–liquid extraction (LLE) was one of the earliest and is one of the most used sample pretreatment techniques for analyte preconcentration and sample clean-up. However, conventional LLE generally involves a tedious procedure with a lot of steps, increasing the risk of the analyst and of sample contamination or loss of analyte. Besides, LLE also requires large amounts of sample and commonly hazardous organic solvents. Therefore, many efforts have been focused to the miniaturization and automation of this extraction technique by a drastic reduction of the extractant phase volume with the development of liquid–liquid microextraction (LLME) techniques [12,13]. Various types of organophosphorous compounds and amides have been used to carry out separation of uranium in LLE [14,15]. The commercial extractant cyanex-272 containing predominantly bis(2,4,4 trimethylpentyl)phosphinic acid, available from Cytec [16], is mainly used for separation of cobalt and nickel and its extraction behavior with lanthanides and actinides has also been investigated while it has been scarcely applied for uranium extraction [17]. It has been recently used for the liquid-liquid extraction of uranium(VI) in sulfate, chloride, nitrate and sodium salicylate medium with different kinds of diluents [18,19]].

Flow techniques allow the development of fully automated methods achieving the minimization of sample handling, drastic reduction of reagent consumption, improvement of reproducibility and the sample throughput, together with a significant decrease of both time and cost per analysis [20]. The multisyringe flow injection analysis (MSFIA) offers multi-channel operation, high injection throughput, robustness and versatility [21]. Using this flow technique, several automatic separations of radionuclides and radioactive elements have been implemented and applied to environmental and biological samples analyses [7]. Moreover, lab-in-syringe (IS) is a powerful tool that has significantly improved LLME, allowing automation and miniaturization of the method and thus a drastic reduction of sample and reagents per analysis. Furthermore the syringe can be placed up or down in order to have the phase with the preconcentrated and isolated analyte located at the head of the syringe being ready to be automatically collected and injected into the detection system [22]. Moreover, extraction efficiency can be improved by using magnetic-stirring-assisted (MSA) in-syringe LLME.

Therefore, a fully automated in syringe LLME with assisted agitation coupled to a LWCC spectrophotometric detector is presented. Uranium is isolated and preconcentrated by IS-MSA-LLME previous arsenazo-III-uranium(VI) complex formation. The potential of the present system as screening tool for uranium determination has been studied by its application to a variety of environmental matrices.

2. Experimental

2.1. Reagents and standard solutions

All solutions were of analytical-reagent grade, and Milli-Q water provided by Direct-8 purification system (resistivity $>18\ \mathrm{M\Omega}$ cm, Millipore Iberica, Spain) was used throughout. All glassware was carefully cleaned, soaked in 10% (v/v) HNO_3 during 24 h and rinsed with Milli-Q water prior use.

Uranium solutions were prepared by appropriate dilution of the uranium standard ($1010 \pm 6\ \mu g\ mL^{-1}$, Sigma-Aldrich) with Milli-Q quality water. Organic phase solution was prepared by dissolving the appropriate amount of cyanex-272 in dodecane.

Specifications of the reagents used are given below:

- Cyanex-272, 90% produced by Cytec Industries, France.
- Dodecane 99%, from Sigma-Aldrich.
- HCl 37%, from Scharlau, Barcelona, Spain.
- Sodium formate 99%, from Scharlau, Barcelona, Spain.
- EDTA, from Scharlau, Barcelona, Spain.
- Ethanol, from Scharlau, Barcelona, Spain.
- Arsenazo-III, from Fluka, Madrid, Spain.
- Xylene 98.5% from Sigma-Aldrich.
- n-Hexane 96% from Scharlau, Barcelona, Spain.

2.2. Samples

Water samples (mineral water, sea water and tap water) were analyzed directly with the proposed system. Sea water was filtered through a membrane of 0.45 μm.

In order to validate the proposed method, a channel sediment certified reference material (BCR-320 R) from the Institute for Reference Materials and Measurements (IRMM) was analyzed. In addition, two other reference materials were also analyzed, i.e. soil and phosphogypsum samples from proficiency tests organized by the Centre for Energy, Environmental and Technological Research of Spain (CIEMAT) and the Spanish Nuclear Security Council (CSN). The phosphogypsum is a secondary residue from phosphate fertilizer plants which contains uranium, thorium and radium. The phosphogypsum sample came from residual ponds of a phosphate fertilizer plant located in Huelva (Spain).

Microwave-assisted acid digestion of solid samples was carried out via a microwave digestor (MLS-1200 Mega) from Milestone (Sorisole, Italy). Hence, a weighed dried sample (viz., 200 mg) was transferred to poly(tetrafluoroethylene) (PTFE) vessels to which 10 mL of concentrated HNO_3 (65%, Merck, Darmstadt, Germany) were added. The microwave digestion program consisted 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 supplied. The digests were heated again to dryness and diluted to 20 mL with Millipore water.

2.3. Manifold and software

The developed IS-MSA-MSFIA system is shown in Fig. 1. MSFIA comprises basically a 5000-step multisyringe burette (BU4S; Crison Instruments, Barcelona, Spain) with programmable flow rates, which has been placed upside down, for phase location convenience. This burette is equipped with 5 mL (S_1) and 10 mL (S_2) 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). The central port of a rotary eight-port selection valve (Crison) is connected to S_1, addressing the peripheral ports of the valve (1–8), for sequential aspiration of the various constituents for the LLME and complex formation processes, via the central communication channel (CC). There are also two additional three-way solenoid valves V_1 and V_2 (MTV-3-N 1/4 UKG; Takasago, Japan) to drive the flow in the desired way.

The flow network is constructed with 0.8 mm internal diameter PTFE tubing. All connections are made by means of PVDF connectors, except cross-junctions, which are made of methacrylate.

The detection system is composed of a deuterium–halogen light source (Mikropack, Germany), two optical fibers of 400 and 600 μm internal diameter (Ocean Optics, USA), a long path length liquid core waveguide capillary cell type II Teflon AF 2400 (World Precision Instruments, FL, USA), with an effective path length of 100.0 ± 0.5 cm, an internal diameter 550 μm, and an internal volume 240 μL; and a USB 2000 miniaturized CCD spectrophotometer (Ocean

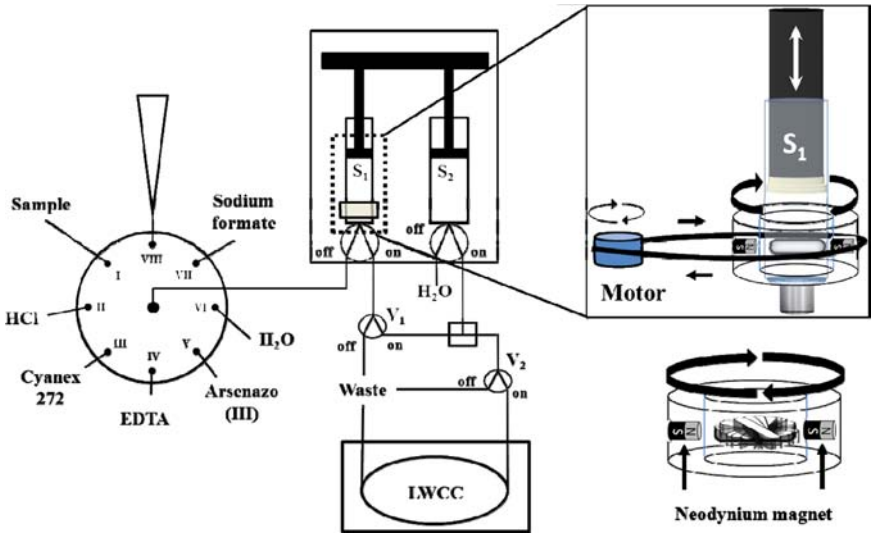

Fig. 1. IS-MSA-MSFIA system for uranium(VI) determination. Liquid waveguide capillary cell (LWCC), syringe ($S_{1,2}$), external solenoid valve ($V_{1,2}$).

Optics, USA), connected to a computer via an USB interface. The absorbance is measured at 655 nm.

Instrument control, data acquisition and processing are performed using the software package AutoAnalysis 5.0 (Sciware Systems, Bunyola, Spain). The distinctive feature of the 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.

The magnetic stirring system allows homogeneous and rapid mixing of sample and reagents without the requirement of additional mixing chambers [23]. A diagram of the magnetic stirring system is depicted in Fig. 1. It consists of four principal parts: a small magnetic stirring bar (10 mm length, 3 mm diameter) placed inside the syringe, a acetal ring with two neodymium magnets (4 od x 5 mm length) placed around the glass barrel of the syringe, a motor that forces the magnetic stirring bar driver to rotate, and a regulation circuit board (Sciware Systems) connected to the syringe pump for revolution control. The top position of the syringes was adjusted to leave a space of about 0.5 mm when emptying the syringe in order to avoid any damage and to allow free rotation of the stirring bar even when the piston was in the upper position. A rubber band was used to connect the motor rotation and the bottom ring of the magnetic stirring bar driver.

The statistical software Statistica 7.0 was used for the optimization of the method via multivariate approach.

2.4. Analytical procedure

Table 1 depicts the general scheme of the method with the corresponding flow rates and volumes used. The steps of the process can be summarized as follow:

1. Sample loading: 4 mL of standard/sample are loaded (port I) inside S_1 (S_1-off) at a flow rate of 15 mL min^{-1}.
2. Uranium extraction: 0.5 mL of cyanex-272/dodecane (port III) are loaded inside S_1 (S_1-off) at a flow rate of 15 mL min^{-1}. The magnetic stirring is activated for 10 s, improving the contact between the standard/sample and the organic solvent, leading to the uranium stripping. Afterwards, the stirring is stopped and we wait 40 s for phase separation. When the two phases are separated, the aqueous phase is discarded (S_1-on) at a flow rate of 5 mL min^{-1}.
3. Elimination of interferences: 0.5 mL of 0.02 mol L^{-1} EDTA / 3.5% ethanol (port IV) are loaded inside S_1 (S_1-off) while stirring at a flow rate of 15 mL min^{-1}. A waiting time of 10 s is used for phase separation. In this step, thorium if present in the organic phase is stripped and it is discarded with the aqueous phase (S_1-on) at a flow rate of 5 mL min^{-1}.
4. Uranium back-extraction: 0.5 mL of 2 mol L^{-1} HCl (port II) are loaded inside S_1 (S_1-off) while stirring at a flow rate of 15 mL min^{-1}. A waiting time of 10 s is used for phase separation. In this step, the uranium is transferred to the aqueous phase and it is dispensed at a flow rate of 5 mL min^{-1} toward the holding tank (selection valve, port VIII).
5. Uranium reaction: 0.5 mL of 2 mol L^{-1} sodium formate (port VII) are loaded inside S_1 (S_1-off) at a flow rate of 15 mL min^{-1}. After that, the aqueous phase is loaded from the holding tank while stirring, achieving a pH close to 2 for an efficient reaction between uranium and arsenazo-III. Thus, a volume of 0.25 mL of 0.001% arsenazo-III (port V) is loaded inside S_1 (S_1-off) while stirring at a flow rate of 15 mL min^{-1}. After 5 s, the colored complex is dispensed with the same syringe (S_1-on, V_1-on) up to the cross-junction. Then the colored complex is dispensed toward the liquid waveguide capillary cell (LWCC) with water (S_1-on, V_1-off, S_2-on, V_2-on).
6. Change of sample: In order to avoid contamination between samples, 1 mL of the next sample (port I) is loaded inside S_1 and then the same volume is dispensed to waste (S_1-on, V_1-off).
7. Syringe and manifold washing: first 5 mL of deionized water (port VI) are loaded while stirring and then these are discarded to waste. Finally, the process is repeated again, dispensing the 5 mL through all the system including the LWCC at a flow rate of 3 mL min^{-1}.

3. Results and discussion

3.1. Flow system set-up

The use of a selection valve permits the design of a system with the capability of commuting automatically between various ports, as many as reagents involved in the chemical analysis. Thus, reagents may be selected at the appropriate time quickly and accurately.

Table 1
Automated procedure for uranium extraction, back-extraction and spectrophotometric detection.

Step	Flow rate (mL min^{-1})	Selection valve	S_1	S_2	V_1	V_2	Stirring
Sample loading							
(a) Load 4 mL of standard or sample	15	I	off	off	off	off	off
Uranium extraction							
(a) Load 0.5 mL of cyanex-272/dodecane	15	III	off	off	off	off	off
(b) Magnetic stirring activation (10 s)	15	III	off	off	off	off	on
(c) Waiting time for phases separation (40 s)	15	III	off	off	off	off	off
(d) Aqueous phase discarding	5	III	on	off	off	off	off
Elimination of interferences							
(a) Load 0.5 mL of EDTA/ethanol	15	IV	off	off	off	off	on
(b) Waiting time for phases separation (10 s)	15	IV	off	off	off	off	off
(d) Aqueous phase discarding	5	IV	on	off	off	off	off
Uranium back-extraction							
(a) Load 0.5 mL of 2 mol L^{-1} HCl	15	II	off	off	off	off	on
(b) Waiting time for phases separation (10 s)	15	II	off	off	off	off	off
(c) Dispense the aqueous phase toward the retention tank	5	VIII	off	off	off	off	off
Uranium reaction							
(a) Load 0.5 mL of 2 mol L^{-1} sodium formate	15	VII	off	off	off	off	off
(b) Load aqueous phase	15	VIII	off	off	off	off	on
(c) Load 0.25 mL of 0.001% arsenazo-III	15	V	off	off	off	off	on
(d) Wait to complete reaction (5 s)	15	V	off	off	off	off	off
Uranium spectrophotometric detection							
(a) Dispense colored complex until cross- junction	3	V	on	off	on	off	off
(b) Dispense colored complex toward the LWCC and start detection (655 nm)	3	V	on	on	off	on	off
Change of sample							
(a) Load 1 mL of new sample	15	I	off	off	off	off	off
(b) Dispense 1 mL of new sample	15	I	on	off	off	off	off
Cleaning system							
(a) Load 5 mL of deionized water	15	VI	off	off	off	off	on
(b) Dispense 5 mL of deionized water	15	VI	on	off	off	off	off
(c) Load 5 mL of deionized water	15	VI	off	off	off	off	on
(b) Dispense 5 mL of deionized water	15	VI	on	off	on	on	off

MSFIA combined with a selection valve forms a robust system that allows the rigorous control of volumes and flow rates of reagents and sample. Also, with the help of three-way solenoid valves, the plug of reagents-sample is directed toward the detector or toward the waste as required, with great precision and reproducibility. Another advantage to highlight of the proposed system is that the magnetic stirring assistance makes possible the homogeneous mixing of sample and reagents within seconds. Thus, the liquid-liquid microextraction of uranium is accomplished, removing interferences and ensuring the correct uranium determination.

The use of spectrophotometric detection exploiting a LWCC provides high sensitivity, good precision and the full automation of the system, being an excellent tool for uranium monitoring even as portable system.

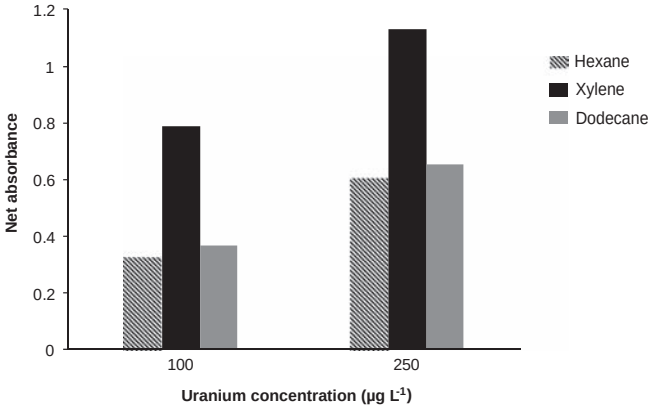

Fig. 2. Comparison of organic diluents for cyanex-272 used in uranium extraction for two concentration levels of uranium(VI).

3.2. Optimal working conditions

Uranium extraction was studied, and three organic solvents, viz., xylene, dodecane and hexane, were tested as diluents of cyanex-272. Different solutions of cyanex-272 were prepared at the same concentration (5×10^{-4} mol L^{-1}) according to a previous work [24]. Under this condition, two levels of standard concentration were analyzed by triplicate with the proposed method (Fig. 2). As can be observed, xylene gives better results for uranium extraction, whilst using hexane the net absorbance is the lowest. However, laborious cleaning cycles were required when xylene was used as diluent, in order to maintain the reproducibility, and also taking into account its higher toxicity, xylene was discarded. Comparing dodecane and hexane, the net absorbance remained stable and the cleaning cycle was simpler and faster. So, dodecane was selected as diluent of cyanex-272 given it provided slightly higher analytical signals.

In order to avoid the interference from calcium and the overlap of the arsenazo-III spectrum with the maximum of the complex formed, a pH nearly 2 was adjusted adding sodium formate at the same volume and concentration of HCl [10,25].

Sodium salicylate medium was assayed in a previous work to improve uranium LLE using cyanex-272 as extractant [24]. Thus, the sodium salicylate effect was tested in the screening step.

To find the best operational conditions for liquid-liquid microextraction of uranium with the proposed system, optimization was performed using multivariate analysis. The optimization methodology started with a screening to study the independent variables and their possible interactions by a fractional factorial design (2^{7-2}) [26]. In all cases, three center points were included, to identify any curvature and to estimate the error. The independent variables studied were: cyanex-272/dodecane concentration (0.25–0.5 mmol L^{-1}), cyanex-272/dodecane volume (0.5–1.5 mL),

HCl concentration (0.5–2.5 mol L^{-1}), HCl volume (0.5–1.5 mL), arsenazo-III concentration (0.0001–0.001%), arsenazo-III volume (0.25–1 mL), and sodium salicylate concentration (0–0.002 mol L^{-1}). Results showed that the curvature and three of the seven variables studied, i.e. cyanex-272/dodecane concentration, arsenazo-III volume and concentration, were significant in the studied experimental domain. Then, these significant variables were optimized with a response surface design [26], using a face centered central composite design. A total of 17 experimental runs were conducted to optimize the experimental conditions. All experimental responses were statistically analyzed, showing satisfactory results (i.e. good adjust coefficient for the 3-way interaction model, normal distribution of the residuals histogram and good fit between observed vs. predicted values). Thus, critical values were obtained for these three variables, namely: 0.4 mmol L^{-1} cyanex-272/dodecane, 0.25 mL arsenazo-III and 0.001% arsenazo-III which were used for further assays. The volume of cyanex-272/dodecane was fixed at 0.5 mL since it didn't have a significant effect upon the response and a higher enrichment factor could be accomplished selecting the lowest volume. The sodium salycilate didn't show a significant effect upon the response, being not necessary. Thus, it was not used in further assays simplifying the sample pretreatment. The HCl concentration wasn't significant. Therefore, it was fixed at 2 mol L^{-1} according to bibliography [24]. A volume of 0.5 mL of HCl was selected because it did not improve the net signal when increasing it and the uranium was diluted in a larger volume which then had to be neutralized with sodium formate. Table 2 summarizes the working conditions of the system.

3.3. Analytical parameters

Analytical parameters are summarized in Table 3. Under the selected operational conditions described above, concentration calibration curves (net absorbance versus μg L^{-1} uranium(VI)), with a statistically satisfactory fit were obtained ($y=0.00253 \pm 0.00006$ x – 0.0056 ± 0.0002, $R^2=0.9985$). The calibration curve is linear over the concentration range 10.7–400 μg L^{-1} of uranium.

The method detection limit (LOD) was calculated as three times the standard deviation of ten replicates of the blank divided by the slope of the calibration curve [27,28]. Thus, the LOD achieved is 3.2 μg L^{-1} which is similar than that calculated by other authors (2.4 μg L^{-1}) exploiting dispersive-LLME with spectrophotometric detection [29]. The corresponding limit of quantification (LOQ) was calculated as ten times the standard deviation of ten replicates of the blank divided by the slope of the calibration curve, obtaining a LOQ of 10.7 μg L^{-1}. Moreover, the present method allows to attain the reference value for uranium suggested by WHO and USEPA [2,3]. Furthermore, the automated method presented is capable to directly perform water analysis without any pretreatment. This fact, together with the portable size of the total system makes of it a powerful and efficient tool for field analysis, being an excellent screening tool in times of emergency and environmental contingency. In the event that the uranium content exceeds the threshold value, the radioisotopes of uranium present in the sample should be analyzed, which is laborious, expensive and time-consuming.

The present work requires a sample volume of 4 mL, which is up to 12.5 times lower than that used in previously reported manual methods (up to 20 mL of sample) [30]. The enrichment factor (EF) accomplished, i.e. EF=8, can be estimated from the ratio between the volume of the sample and the volume of the final extraction solution (0.5 mL of HCl). The volume and concentration of cyanex-272 were also reduced considerably, compared with a previous work allowing significant savings in the use of this extractant [24].

Intra and interday precision of the method were evaluated by analyzing ten extractions in one day and over a period of five working days, respectively. The relative standard deviations (RSDs) were 3.0 and 3.3%, respectively.

The analysis frequency of the proposed method is also higher than that reported by other authors [29], since an analysis requires a maximum of 10 min, which allows analyzing up to six samples per hour providing a rapid response. Since all chemical procedures were carried out in a syringe, and given the tendency of dodecane to stick to hydrophobic surfaces such as the piston's head and the stirring bar (PTFE) and the possible adsorption of the dye on the wall of the syringe, a cleaning step was implemented after every analysis avoiding contamination between samples. Furthermore, the stirring speed of the automatic stirring system allows an efficient washing of the walls inside the syringe and removing reagent residues adhered to the wall from previous analysis. Thus, good results obtained for the intra- and inter-day precision indicated no crossover contamination between samples of different concentrations.

Table 2
Optimized working conditions.

Reagent	Concentration	Volume
Cyanex-272 / Dodecane	0.4 mmol L^{-1}	0.5 mL
HCl	2 mol L^{-1}	0.5 mL
Arsenazo-III	0.001%	0.25 mL

Table 3
Analytical parameters of the proposed method.

Analytical parameters	
Detection limit (LOD)	3.2 μg L^{-1}
Quantification limit (LOQ)	10.7 μg L^{-1}
Regression coefficient	0.9985
Intraday precision ($n=10$)	3%
Interday precision ($n=5$)	3.3%
Sample volume	4 mL
Enrichment factor (EF)	8
Sensitivity	0.0025 UA μg L^{-1}
Linear working range	10.7–400 μg L^{-1}
Injection throughput	6 h^{-1}

3.4. Interferences

According to a previous work, the affinity of cyanex-272 for uranium and thorium as extractant is similar [24]. Therefore, to prevent any thorium interference, a step to eliminate interferences with 0.02 mol L^{-1} EDTA / 3.5% ethanol was included in the analytical protocol. EDTA back-extracts thorium retained in the extractant but not uranium. Hence, to determine the possible influence of thorium on the measurement of uranium, a solution of 50 μg L^{-1} of uranium was assessed in relation with thorium until a ratio of 1:300. Results showed that thorium interferes at ratios above 1:200 (uranium:thorium). However, thorium did not interfere during the analysis of environmental samples and reference certified materials that also contained thorium.

Furthermore, in the derivatization step by controlling the pH of the reaction uranium-arsenazo-III complex, it becomes highly selective and stable [10,31]. This was accomplished by the use of sodium formate in the same concentration and volume as the hydrochloric acid used in the back-extraction step, allowing a pH close to 2 for an efficient reaction with arsenazo-III.

Table 4
Analysis of environmental samples.

Sample*	Added U (μg L^{-1})	Found (μg L^{-1})	Recovery (%)
Tap water	0	< LOD	
	20	20 ± 1	101
Mineral water	0	< LOD	
	20	21 ± 1	104
Seawater	0	< LOD	
	20	20 ± 2	99
Sample*		**Certified value (mg kg^{-1})**	**Found (mg kg^{-1})****
Phosphogypsum sample[a]		4.5 ± 0.8	4.2 ± 0.4
Soil sample[b]		1.7 ± 0.3	1.60 ± 0.10
Channel sediment (BCR-320 R)[c]		1.6 ± 0.2	1.4 ± 0.2

* (n=3)
** The t-test of comparison of means revealed no differences at the 95% confidence level.
Thorium content: [a] 1.5 ± 0.3 mg kg^{-1}, [b] $3.5 \times 10^{-5} \pm 6.35 \times 10^{-6}$ mg kg^{-1}, [c] 5.3 ± 0.4 mg kg^{-1}

3.5. Validation and application to environmental samples

The automated methodology was validated by analyzing a channel sediment certified reference material (BCR-320 R) and two reference materials, i.e. soil and phosphogypsum samples. In addition, the method was applied to different water matrices (mineral, tap and sea water). Results of analyses for three replicates (n=3) are shown in Table 4.

For the channel sediment certified reference material as well as soil and phosphogypsum reference materials, the t-test for comparison of means revealed that there were no significant differences at the 95% confidence level. In the case of water matrices, the procedure was applied to samples and spiked samples with known U(VI) concentration, obtained from the corresponding standard. Results revealed that recovery was fairly good, close to 100% in all cases. Although the uranium concentration is commonly very low in seawater, it should be highlighted the good performance of the developed method in such type of complex matrix.

4. Conclusions

An accurate, precise, reliable and rapid analytical method for uranium determination in a wide variety of environmental matrices is presented, proving to be a robust, fast and useful screening tool for uranium monitoring.

The developed method takes advantage of the automation offered by flow analysis techniques, which combined with in-syringe magnetic stirring assisted exploits the full potential of the liquid-liquid microextraction as extraction technique.

The use of cyanex-272 for uranium extraction and its posterior derivatization with arsenazo-III allowed the satisfactory uranium determination in environmental samples with high variability in uranium(VI) content. Moreover, the implementation of a liquid waveguide capillary cell made possible to achieve the uranium reference value established by several regulatory organizations in drinking water.

Thus, the figures of merit of this methodology together with the equipment used provides various advantages such as simplicity, selectivity, sensitivity, low operational and instrumentation costs and robustness. Thus, the present method is a completely new and automated methodology that reduces significantly the use of sample and reagents, contributing to significantly reduce the environmental impact per analysis.

Acknowledgments

This work was funded by the Spanish Ministry of Economy and Competitiveness (MINECO, project CTM2013-42401-R), the Balearic Government (project 43/2011) both cofinanced by FEDER funds and by the National Council of Science and Technology in Mexico (CONACYT) and the Government of Chihuahua State (project FOMIX CHIH-2013-C03-194659). R. Rodríguez acknowledges to CONACYT for the allowance of a grant. J. Avivar acknowledges to MINECO for the financial support through the Torres Quevedo Programme (PTQ-12–05755). Authors acknowledge to Cytec Industries France SARL for donating cyanex-272 to make possible this research.

References

[1] D. Larivière, N. Guérin, Natural radioactivity, in: D.A Atwood (Ed.), Radionuclides in the Environment, John Wiley & Sons, Chichester, UK, 2010, pp. 1–17.
[2] World Health Organization (WHO), Guidelines for drinking water quality, fourth ed., World Health Organization, Geneva, Switzerland, 2011.
[3] Radiation Protection: Uranium, Environmental Protection Agency (EP). 〈http://www.epa.gov/radiation/radionuclides/uranium.html〉 (accessed date 12.18.14).
[4] Toxicological Profile for Uranium, Agency for Toxic Substances and Disease Registry (ATSDR). 〈http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=440&tid=77〉 (accessed date 12.18.14).
[5] L.R. Morss, N.M. Edelstein, J. Fuger (Eds.), The Chemistry of the Actinide and Transactinide Elements, Springer, Netherlands, 2006.
[6] J. Emsley, Uranium, in: Nature's Building Blocks: an A to Z Guide to the Elements, Oxford University Press, Oxford, UK, 2001.
[7] Y. Fajardo, J. Avivar, L. Ferrer, E. Gómez, M. Casas, V. Cerdà, Trend Anal. Chem 29 (2010) 1399–1408.
[8] L.J. Gimbert, P.J. Worsfold, Trend Anal. Chem 26 (2007) 914–930.
[9] F. Maya, J.M. Estela, V. Cerdà, Anal. Bioanal. Chem. 394 (2009) 1577–1583.
[10] Photometric Determination of Traces of Metals, in: E.B. Sandell, H. Onishi (Eds.), fourth ed.,JohnWiley & Sons, New York, USA, 1979.
[11] J. Avivar, L. Ferrer, M. Casas, V. Cerdà, Anal. Bioanal. Chem. 397 (2010) 871–878.
[12] F. Pena-Pereira, I. Lavilla, C. Bendicho, Spectrochim. Acta B. 64 (2009) 1–15.
[13] C.I.C. Silvestre, J.LM. Santos, J.L.F.C Lima, E.A.G. Zagatto, Anal. Chim. Acta 652 (2009) 54–65.
[14] M. Eskendari Nasab, S.A. Milani, A. Sam, J. Radioanal. Nucl. Ch. 288 (2011) 677–683.
[15] A. Senol, J. Radioanal. Nucl. Ch. 258 (2003) 361–372.
[16] Cytec Industrial Materials, France, www.cytec.com.
[17] V.A. Cocalia, M.P. Jensen, J.D. Holbrey, S.K. Spear, D.C. Stepinski, R.D. Rogers, Dalton T. 11 (2005) 1966–1971.
[18] S.D. Dogmane, R.K. Singh, D.D. Bajpai, J.N. Mathur, J. Radioanal. Nucl. Ch. 253 (2002) 477–482.
[19] B. Rajeswari, B.A. Dhawale, T.R. Bangia, J.N. Mathur, A.G. Page, J. Radioanal. Nucl. Ch. 254 (2002) 479–483.
[20] V. Cerdà, L. Ferrer, J. Avivar, V. Cerdà, Flow Analysis: a Practical Guide, Elsevier, Amsterdam, The Netherlands, 2014.

[21] V. Cerdà, J.M. Estela, R. Forteza, A. Cladera, E. Becerra, P. Altimira, P. Sitjar, Talanta 50 (1999) 695–705.
[22] F. Maya, B. Horstkotte, J.M. Estela, V. Cerdà, Anal. Bioanal. Chem. 404 (2012) 909–917.
[23] C. Henriquez, B. Horstkotte, P. Solich, V. Cerdà, Anal. Bioanal. Chem. 405 (2013) 6761–6769.
[24] N.S. Madane, K.R. Nikam, K.R. Mahanwar, B.S. Mohite, J. Radioanal. Nucl. Ch. 288 (2011) 285–290.
[25] N. Malcik, J.P. Ferrance, J.P. Landers, P. Caglar, Sensor Actuat. B 107 (2005) 24–31.
[26] D.C. Montgomery, Design and Analysis of Experiments, seventh ed., John Wiley and Sons, Asia, 2009.
[27] G.L. Long, J.D. Winefordner, Anal. Chem. 55 (1983) 712–724.
[28] J.N. Miller, J.C. Miller, Statistics and Chemometrics for Analytical Chemistry, fourth ed., John Wiley and Sons, New York, USA, 2000.
[29] M. Kaykhaii, E. Ghasemi, Anal. Method 5 (2013) 5260–5266.
[30] N. Jalbani, M. Soylak, J. Radioanal. Nucl. Ch. 301 (2014) 263–268.
[31] J. Fries, H. Getrost, Organic Reagents for Trace Analysis, Merck, Darmstadt, 1977.