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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*

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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 $3.2 \mu\text{g L}^{-1}$. 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%.

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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 $30 \mu\text{g L}^{-1}$ 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 exceeded, 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).

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 MΩ cm, Millipore Iberica, Spain) was used throughout. All glassware was carefully cleaned, soaked in 10% (v/v) HNO₃ during 24 h and rinsed with Milli-Q water prior use.

Uranium solutions were prepared by appropriate dilution of the uranium standard ($1010 \pm 6 \mu\text{g mL}^{-1}$, 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 digester (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 HNO₃ (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 (S₁) and 10 mL (S₂) 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 S₁, 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 V₁ and V₂ (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

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