



A novel aeration-assisted homogenous liquid–liquid microextraction for determination of thorium and uranium in water and hair samples by inductively coupled plasma-mass spectroscopy



Somayeh Veyseh, Ali Niazi*

Department of Chemistry, Faculty of Science, Arak Branch, Islamic Azad University, Arak, Iran

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ABSTRACT

A novel method based on aeration-assisted homogeneous liquid–liquid microextraction using high density solvent is presented, which is combined with inductively coupled plasma-mass spectroscopy in which simultaneous preconcentration and determination of thorium and uranium with arsenazo III as the chelating reagent is carried out. To achieve optimum conditions, several parameters such as pH, concentration of arsenazo III, extraction and homogenous solvent types and their volumes, salt concentration and extraction time were investigated. Under which, the calibration graphs were linear in the range of 0.5–600.0 ng L⁻¹ for thorium and 0.3–550.0 ng L⁻¹ for uranium. Good linearities were obtained for both analytes with *R*² values larger than 0.9990. The limits of detection (LOD, 3*S*_b/*m*, *n*=5) of this method were 0.12 and 0.09 ng L⁻¹, and the enrichment factors were estimated to be 370 and 410 for thorium and uranium, respectively. The proposed method was applied to determine the thorium and uranium in human hair and different environmental water samples. Acceptable recoveries ranged from 99.4% to 100.7% with standard deviation of 0.05 to 0.17.

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1. Introduction

Determining heavy metals at trace levels in environmental samples is an important part of chemistry because of their positive or negative effects on the human body [1,2]. Micro-concentrations of heavy metals in water harmfully influence the environment and cause changes in their biochemical balances as they accumulate in certain parts of animal and plant organisms. Thorium and uranium play important roles in industry, especially as energy sources. Several methods have already been developed for the determination of thorium and uranium.

So far, various analytical methods have been employed to determine thorium and uranium in different samples, such as inductively coupled plasma atomic emission spectrometry (ICP-AES) [1], inductively coupled plasma-mass spectrometry (ICP-MS) [2,3], ion chromatography (IC) [4], capillary zone electrophoresis (CZE) [5], flow injection analysis (FIA) [6], fluorimetry [7,8], spectrophotometric [9] and electrochemistry [10]. Among them, ICP-MS is widely employed because of its high sensitivity, wide linear range, multi-element and multi-isotope detection. ICP-MS is also applied for the quantitative measurement of 1–10 ng L⁻¹ analytes. The

sensitivity of ICP-MS for direct determination of the elements of periodic table is more than most other techniques. Using this technique, it is even possible to analyze non-metal elements with good sensitivity. Thus, ICP-MS is used as an effective analytical tool to measure very low concentrations. Some of its other advantages include high linear dynamic range, high precision and accuracy in measurement and minimum interferences [11–13].

In analyzing environmental samples, sample pretreatment plays an important role in obtaining accurate and sensitive results. However, conventional extraction and preconcentration techniques such as liquid–liquid extraction (LLE), solid phase extraction (SPE) [14,15] and matrix solid-phase dispersion (DPSE) [16] require large amounts of organic solvent and are time-consuming, laborious, and relatively expensive methods [17–20].

As a sample preparation technique, the homogeneous liquid–liquid extraction (HLL) method utilizes phase separation phenomenon from a homogeneous solution, and target solutes are extracted into a separated phase. A method for homogeneous liquid–liquid microextraction via flotation assistance (HLLME-FA) was developed by Haji Hosseini et al., based on the application of low density organic solvents without centrifugation [20,21]. The method avoids centrifugation; thus, it simplifies operations and speeds up the extraction process. The purpose of the current study was to investigate, the possibility of using aeration-assisted homogeneous liquid–liquid microextraction for simultaneous

* Corresponding author. Fax: +98 86 33670017.

E-mail addresses: a-niazi@iau-arak.ac.ir, ali.niazi@gmail.com (A. Niazi).

determination of thorium and uranium by ICP-MS in human hair and different environmental water samples, for the first time. In order to optimize conditions, the effects of different parameters on the extraction efficiency such as pH, concentration of chelating agent, type and amount of extraction and homogenous solvents, extraction time and salt effect were investigated.

2. Experimental

2.1. Chemicals and reagents

All reagents used were of analytical reagent grade. Arsenazo III, acetic acid, phosphoric acid, boric acid, hydrochloric acid, sodium hydroxide, uranyl nitrate hexahydrate, thorium nitrate hexahydrate and all solvents, such as chloroform, carbon tetrachloride, dichloromethane, acetone, acetonitrile, ethanol and methanol were purchased from Merck. Standard stock solutions of 1000 $\mu\text{g mL}^{-1}$ thorium (IV) and uranium (VI) were prepared by dissolving appropriate amounts of thorium nitrate and uranyl nitrate hexahydrate in distilled water, respectively. Working solution standards were made by appropriate daily dilution as required. A stock arsenazo III solution ($1.0 \times 10^{-5} \text{ mol L}^{-1}$) was prepared by dissolving reagent in distilled water. A buffer solution was prepared using universal buffer solutions, which were prepared by mixing phosphoric, acetic, and boric acid [22]. All solutions were prepared with deionized water.

2.2. Apparatus

A Perkin Elmer SCIEX ELAN 9000 ICP-MS (Perkin-Elmer, Inc., Wellesley, MA, USA) was used to determine thorium and uranium levels. The instrumental operating conditions selected as recommended by the manufacturer are summarized in Table 1. The pH values were controlled by a Metrohm pH-meter (Model 780, Swiss) supplied with combined electrode.

2.3. Extraction procedure

The experimental procedure used for AA-HLLME is illustrated in Fig. 1. A volume of 50 mL of the sample solution containing 50 ng L^{-1} of each ion (thorium and uranium), arsenazo III ($1.0 \times 10^{-5} \text{ mol L}^{-1}$) as chelating agent, and 5.0 mL of buffer solution (pH 1.8) were added to the sample. A mixture of 1.5 mL ethanol as homogeneous solvent and 100 μL chloroform as

extraction solvent was added to the extraction cell (Fig. 1(a)). A volume of 50.0 mL of sample solution was injected rapidly into the extraction cell by syringe (Fig. 1(b)) to make a homogeneous solution (Fig. 1(c)). Then, 3.0 mL aqueous salt solution ($\text{NaCl } 1.0 \text{ mol L}^{-1}$) was added into the cell by syringe (Fig. 1(d)); aeration was used in this step in order to increase contact surface (Fig. 1(e)). After about 3 min, the organic solvent on the bottom of the tube was collected (Fig. 1(f)). Finally, the extracted phase was diluted with ethanol and injected into ICP-MS for subsequent measurements.

2.4. Real sample preparation

Environmental water samples, such as, tap, well, river and lake surface water were collected from different cities, immediately filtered through 0.45 μm membrane filters and stored at 4 °C. The certified reference material GSB 07-1376-2001 (standard environmental water sample) was obtained from the National Research Center for Certified Reference Materials (China). Human hair samples were collected from 10 donors, 25–35 years old, of both genders living in different environmental contexts in Markazi province (Iran). The collected hair samples were kept in separate plastic envelopes for each participant and marked with identification numbers. To investigate spiked samples a pool of hair from volunteers who had not taken illicit or therapeutic drugs was prepared. The hair was washed for 5 min with deionized water and acetone in an ultrasonic bath, dried, cut into pieces of 2–5 mm length, and carefully mixed. Scalp hair samples weighing approximately 1.0 g were taken from the occipital region of the head, using stainless steel scissors without vanadium, and stored in plastic bags. More specifically, hair samples were immersed in 20 mL of ultrapure water and stirred in an ultrasonic bath for 15 min (3 times). However, ultrapure water was proven to be a more suitable washing agent for efficiently removing surface dirt and grease in this work. The washed samples were individually placed in glass beakers and dried at about 50 °C to constant weight. Dried samples were stored separately in polyethylene bags until acid digestion in a microwave system prior to microextraction, and ICP-MS [23] was performed.

3. Results and discussion

3.1. Optimization of experimental conditions

To optimize different experimental parameters, the pH of samples, concentration of arsenazo III, type and volume of extraction and homogenous solvents, the extraction times and, salt effect for the extraction were investigated. Samples containing 50 ng L^{-1} of thorium and uranium were selected to be used for extraction under different conditions. Experiments were performed in three replicates by modifying one parameter at a time while keeping the remaining parameters constant. It should be noted that the memory effect was prevented by washing the glass cell extraction with acetone and distilled water prior to the next microextraction.

3.2. Effect of pH

The separation of metal ions by the presented method involved the prior formation of metal complexes with enough hydrophobicity to be extracted in the organic phase; as already well known, pH plays an essential role in metal complex formation. The complex formation reactions of thorium and uranium with arsenazo III are pH dependent. A range of pH 1–8 was used to test the influence of sample pH on extraction efficiency. Fig. 2 shows

Table 1
Operating conditions for ICP-MS (ELAN 9000).

RF power	1000 W
Plasma gas flow	15 L min^{-1}
Auxiliary gas flow	1 L min^{-1}
Nebulizer gas flow	0.81 L min^{-1}
Solution pump rate	1.50 mL min^{-1}
Sample introduction system	Cross-flow with Scott spray chamber
Rinse time	35 s @ 48 rpm
Sample uptake time	25 s @ 48 rpm
Equilibration time	10 s @ 24 rpm
Analysis time (total)	2:06 min
Detector mode	Dual mode
Lens	6.25
Sampler/Skimmer cones	Nickel
Scanning mode	Peak Hopping
Number of points/peak	1
Dwell time	100 ms per point
Number of sweeps/reading	8
Number of readings/replicate	1
Number of replicates	3
Total acquisition time	3: 16 min

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