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Combination of solid phase extraction and dispersive liquid–liquid microextraction for separation/preconcentration of ultra trace amounts of uranium prior to its fiber optic-linear array spectrophotometry determination

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HIGHLIGHTS

- By combination of SPE and DDLME a high preconcentration factor of 2500 was obtained.
- Development of SPE-DDLME-Spectrophotometric method for det. of trace amounts of uranium.
- Ultra trace amount of uranium in water samples was det. by the proposed method.
- The detection limit of the proposed method is comparable to the most sensitive method.
- The proposed method is a free interference spectrophotometric method for uranium det.
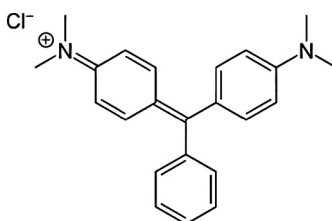
GRAPHICAL ABSTRACT

Pass the sample through the basic alumina column ⇒ elute retained uranium along with the cations ⇒ convert the uranium to its anionic benzoate complex ⇒ extract its ion pair with malachite green into small volume of chloroform by DLLME ⇒ measure its absorption at 621 nm using fiber optic-linear array detection spectrophotometry.

Malachite green

ABSTRACT

A simple and sensitive method for the separation and preconcentration of the ultra trace amounts of uranium and its determination by spectrophotometry was developed. The method is based on the combination of solid phase extraction and dispersive liquid–liquid microextraction. Thus, by passing the sample through the basic alumina column, the uranyl ion and some cations are separated from the sample matrix. The retained uranyl ion along with the cations are eluted with 5 mL of nitric acid ($2 \, mol \, L^{-1}$) and after neutralization of the eluent, the extracted uranyl ion is converted to its anionic benzoate complex and is separated from other cations by extraction of its ion pair with malachite green into small volume of chloroform using dispersive liquid–liquid microextraction. The amount of uranium is then determined by the absorption measurement of the extracted ion pair at 621 nm using flow injection spectrophotometry. Under the optimum conditions, with 500 mL of the sample, a preconcentration factor of 1980, a detection limit of $40 \, ng \, L^{-1}$, and a relative standard deviation of 4.1% ($n = 6$) at $400 \, ng \, L^{-1}$ were obtained. The method was successfully applied to the determination of uranium in mineral water, river water, well water, spring water and sea water samples.

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1. Introduction

Uranium is a naturally occurring element and is widely spread throughout the environment. Naturally it can be found in very small amount in soils, rocks, air and water. However, larger amounts of

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uranium have entered into the environment through the human activities such as mining, milling, and nuclear industry processes [1]. The worldwide demand for uranium is high and stimulates the development of new procedures for the separation and preconcentration of uranium from sources with low uranium content such as natural water [2,3]. On the other hand, uranium and its compounds are highly toxic and can cause progressive or irreversible renal injury and in acute cases may lead to kidney failure and death [4]. World Health Organization (WHO) recommended that the level of uranium in drinking water should not exceed $15 \mu g L^{-1}$ and United States Environment Protection Agency (USEPA) has set the value of 30 as the safe limit of uranium in public water supplies [5]. Thus, development of a sensitive, low cost and easy operation method for the monitoring of the low level of uranium in the natural water samples is a challenging task. The most sensitive methods used for the determination of trace amounts of uranium is fission-track registration (FTR) [6], neutron activation analysis (NAA) [7], and inductively coupled plasma–mass spectrometry (ICP–MS) [1]. However, the FTR and NAA require access to a nuclear reactor, and ICP–MS is not suitable for measurement of uranium in samples with high salt content. Spectrophotometery is one of the most popular analytical techniques for the determination of uranyl ions due to its low cost, operational facilities and high analytical frequency, but it lacks the required selectivity and sensitivity for direct determination of low level of uranium. Thus, a separation and preconcentration step prior to its spectrophtometric determination is required. The most widely techniques used for the separation and preconcentration of uranium prior to its spectrophotometric determination are liquid–liquid extraction [8–10], solid phase extraction [11–19] and cloud point extraction [20–24]. However, the separation and preconcentration factors obtained by most of these methods are not sufficient for spectrophotometric determination of ultra trace amounts of uranium, some of them use expensive reagent [12–15,23] and usually require high volume of sample. In order to achieve a low detection limit and good selectivity with the spectrophotometric determination of uranium, herein, the solid phase extraction and dispersive liquid–liquid microextraction is combined and a simple and selective method for the determination of ultra trace amounts of uranium is developed. The factors influencing the separation and preconcentration steps were optimized and the method was successfully applied to determination of ultra trace amounts of uranium in natural water samples.

2. Experimental

2.1. Apparatus

An Avantes photodiode array spectrophotometer model AvaSpec-2048 equipped with a source model of Ava Light-DH-S-BAL and a 10-mm Z shape micro flow cell, an Ismatec peristaltic pump model MS-REGLO/8-100 (Switzerland), and a rotary injection valve (Rheodyne, CA, USA) with $60 \mu L$ loop were used. The measurements were made against a reagent blank solution. The pH was measured using a Metrohm pH meter (model 691, Switzerland) equipped with a combined glass calomel electrode. For the phase separation a centrifuge (Hitachi, Universal 320, Tuttlingen, Germany) was used.

2.2. Reagents

All chemicals were of the highest purity available from Merck Company and were used as received, except otherwise stated. Doubly distilled water was used during the study. A stock solution of $1000 \, mg \, L^{-1}$ of uranium was prepared by dissolving appropriate

amount of $UO_2(NO_3)_2 \cdot 6H_2O$ in water. Working solutions were prepared daily from the stock solution by serial dilutions with double distilled water. Malachite green ($1.8 \times 10^{-3} \, mol \, L^{-1}$) was prepared by dissolving 0.2 g of the reagent in 100 mL water. Alumina particles (γ type, 10–50 μm, chromatographic grade, Merck, Darmstadt, Germany) was purified by shaking with $5 \, mol \, L^{-1}$ nitric acid and washing three times with double distilled water. The buffer of pH 5.5 was prepared using sodium benzoate and benzoic acid. All glassware was kept in 10% nitric acid during the night and then was rinsed several times with double distilled water before use.

2.3. Preparation of water samples

The water samples collected was treated according to the standard procedure [25,26]; i.e. it was filtered through 0.45 μm Millipore filter and acidified with AR nitric acid (pH $\sim$ 2) before use. Then the pH of the samples were adjusted and treated according to the given procedure.

2.4. Preparation of standard reference material

An appropriate amount of the standard material of stream sediment, IAEA-313 (International Atomic Energy Agency, Austria) was weighed into a beaker, 10 mL concentrated nitric acid was added and the mixture was heated to near boiling point. Next 2 mL of hydrogen peroxide (30% v/v) was added, and the excess amount of hydrogen peroxide was removed by heating the mixture to near dryness. Then $\sim$20 mL of doubly distilled water was added to the residue, the solution was filtered and diluted with water to 300 mL. Finally, 100 mL of the solution was treated according to the given procedure.

2.5. Preparation of the column and its regeneration

A small amount of glass wool was placed on the disk of a glass column (10 cm $\times$ 1.0 cm i.d.) to prevent the loss of the sorbent during sample loading. Then the column was packed with γ-alumina (to the height of 1.5 cm) and was covered with small amount of glass wool. The passage of 5 mL of ammonia solution ($2 \, mol \, L^{-1}$) was necessary to make the column basic and to regenerate the column basicity before processing of the next sample.

2.6. Procedure

The sample or standard solution containing not more than 1.0 μg of uranium was made 0.16 $mol \, L^{-1}$ with respect to sodium acetate solution, the pH was adjusted to approximately 9 by addition of ammonia solution and the sample was passed through the column at a flow rate of $15.0 \, mL \, min^{-1}$ with the aid of a suction pump. The retained uranium was eluted into a conical tube, with 5.0 mL of $2.0 \, mol \, L^{-1}$ of nitric acid at a flow rate of $2.0 \, mL \, min^{-1}$. The eluent was neutralized and 1.5 mL of buffer solution of benzoate ($9.8 \times 10^{-3} \, mol \, L^{-1}$) was added which cause adjustment of the pH to $\sim$5.5 and formation of the anionic complex of uranium benzoate. Then 500 μL of malachite green solution ($1.8 \times 10^{-3} \, mol \, L^{-1}$) was added and a mixture of 500 μL of ethanol (as dispersive solvent) and 200 μL of chloroform (as extraction solvent) was rapidly injected into the solution. In this stage the solution became cloudy and the ternary adduct of uranium–benzoate–malachite green was extracted into the fine droplet of chloroform. The mixture was then centrifuged for 3 min (2000 rpm) and the organic solvent (about 187 μL) was settled down in the bottom of the tube. Finally, the extract was introduced into a quartz micro flow-cell of a spectrophotometer via the sample loop of injection valve, the pump was then stopped for 2 s and the measurement was carried out at 621 nm.