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M. KONSTANTINOY, I. PASHALIDIS

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Speciation and spectrophotometric determination of uranium in seawater

M. KONSTANTINOOU and I. PASHALIDIS

Department of Chemistry, University of Cyprus,
P.O. Box 20537, 1678 Lefkosia, Cyprus

e-mail: pspasch@ucy.ac.cy

Abstract

A series of ion-exchange and extraction procedures for the separation of uranium from seawater samples and subsequent spectrophotometric determination of uranium in seawater by means of arsenazo(III) is described. According to the measurements performed by means of traced samples at every stage of separation, the yield of the pre-analytical procedures is generally over 90% and the separation of uranium very selective. The mean uranium concentration in seawater samples collected from five different coastal areas in Cyprus was found to be $3.2 \pm 0.2 \mu\text{g L}^{-1}$. Uranium in seawater is stable in its hexavalent oxidation state and $\text{UO}_2(\text{CO}_3)_3^{4-}$ is the predominant species under normal coastal conditions ($\text{pH} \geq 8$, $E_H \geq 0.35 \text{ mV}$, 1 atm and 0.03% CO_2).

Keywords: Uranium; Seawater; Cationexchange; Extraction; Spectrophotometry.

Introduction

In the last decades there has been enormous interest in the environmental chemistry of uranium due to its increased use for nuclear-energy production and in armour-penetrating bullets. Migration of uranium from the mining and processing facilities into natural systems occurs through leaching by rain and distribution of uranium-bearing dust by wind. On the other hand, uranium can be released into the environment upon impact or by corrosion of used bullet mantle materials (BLEISE *et al.*, 2003).

Uranium is a ubiquitous, primordial radionuclide the concentration of which in the environment strongly depends on the

geological matrix and varies between 0.1 and 500 ppm. In seawater the uranium concentration is $(3.3 \pm 0.2) \mu\text{g L}^{-1}$, which corresponds to a total uranium amount of about $4.5 \cdot 10^{12}$ tons. The uranium concentration and distribution is almost uniform because the amount of the element delivered to the sea by rivers and atmospheric particles is compensated by the diffusion of hexavalent uranium into anoxic sediments and its interaction with colloidal particles, which represent the main mechanisms of uranium removal from seawater. On the other hand, the long residence time of uranium in the ocean (about $4 \cdot 10^5$ years) suggests that particulate scavenging capability is inefficient. This can be attributed to a reversible binding of uranium

to particles and the competition by carbonate resulting in the formation of very stable uranium(VI) carbonate species under surface seawater conditions. (CHEN *et al.*, 1986)

The chemical behaviour of uranium in aqueous systems is strongly influenced by the redox potential (E_H) and the acidity (pH) of the medium, which determine the most stable oxidation state and chemical species of uranium in seawater. In situ measurements indicate that the redox potential of aerated seawater is not governed by the oxygen/water couple but can be calculated by an empirical equation, that gives an estimated E_H value of about 0.35 V (SILVER, 2001). The acid-base chemistry of seawater is dominated by the interaction of the carbonate ion (CO_3^{2-}) with the weak carbonic acid (H_2CO_3^*). A predominant source of carbonate ions is calcium carbonate, whereas carbonic acid results from the dissolution of atmospheric carbon dioxide gas and the decomposition of organic matter in seawater (PILSON, 1998).

Primarily, changes in pH induce hydrolysis reactions of uranium which may affect its redox stability, lead to the formation of mono- and polynuclear hydroxo- species and ternary complexes, and induce (co)precipitation or sorption. Although hydrolysis, particularly at higher uranium concentrations, can lead to the formation of polynuclear species in seawater, because of the increased salinity and the relatively low uranium concentrations ($[\text{U}]_{\text{tot}} \approx 3 \mu\text{g L}^{-1}$), mononuclear species are expected to be predominant (CHOPPIN and STOUT, 1998).

On the other hand, carbonate ions (CO_3^{2-}) present in seawater even at relatively low concentrations ($[\text{CO}_3^{2-}] = 125 - 220 \mu\text{mol Kg}^{-1}$) significantly influence the chemistry of uranium. Calculations based on thermodynamic data for hydrolysis and carbonate complexation indicate that in seawater the uranium-carbonate species, $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$, are the dominating uranium(VI) species in solution. (PASHALIDIS *et al.*, 1997) The formation

affinity of the two uranium-carbonate complexes is high enough to stabilize uranium in aquatic solutions at concentrations ($> 10^{-4} \text{ mol L}^{-1}$, 3.3 mg L^{-1}) which are orders of magnitude above the uranium concentration found in seawater ($10^{-8} \text{ mol L}^{-1}$, $3.3 \mu\text{g L}^{-1}$), indicating that the uranium carbonate complex anions govern the chemical behaviour of uranium(VI) in seawater.

The present paper discusses a simple methodology for uranium determination in seawater after selective separation of uranium from the matrix by cationexchange and extraction pre-analytical procedures. The methodology has been applied in order to determine uranium concentrations in seawater samples from five different coastal areas in Cyprus. Furthermore, speciation of uranium in seawater is briefly discussed.

Materials and Methods

In all experiments analytical grade reagents and deionised water was used. The Chelex-100 resin (100-200 mesh, Bio-Rad Labs) was used as received. Arsenazo(III) solutions were prepared by dissolving appropriate amounts of arsenazo(III) salt (obtained from Aldrich Co) in aquatic 0.01 M HClO_4 . HNO_3 solutions of various concentrations (e.g. 2 and 8 M HNO_3) were prepared by diluting a concentrated solution (68% HNO_3). 30% v/v TBP solution was freshly prepared by mixing the appropriate volumes of tributyl phosphate (TBP) and dodecan, both obtained from Aldrich Co. $(\text{NH}_4)_2\text{SO}_4$ solutions were prepared by dissolving ammonium sulphate (99.999%, Aldrich Co) in deionised water.

Sample collection included surface seawater from five different coastal areas of Cyprus (Figure 1). Samples were collected in screw capped PE bottles, transferred to the laboratory and analysed immediately. A schematic overview of the pre-analytical procedures (e.g. sample collection, pre-concentration and uranium separation) is given in Figure 2. For the separation of uranium

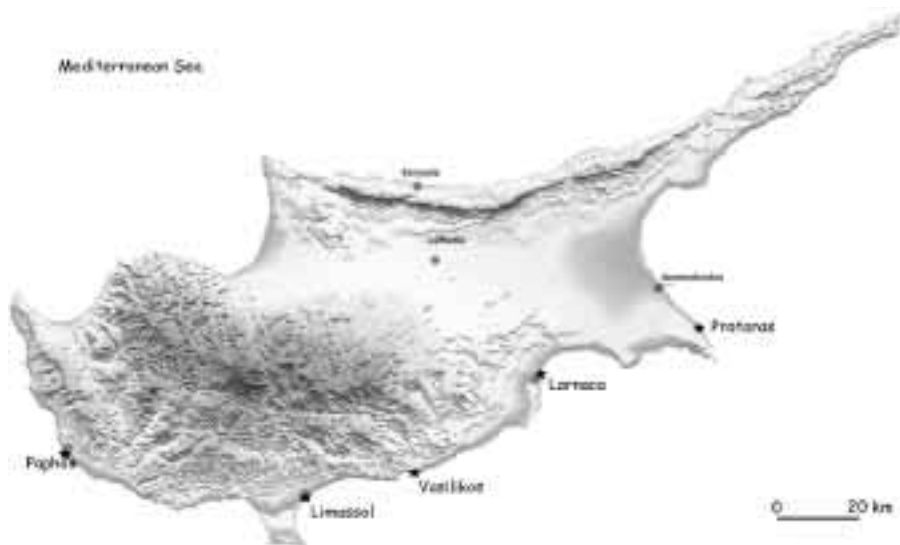


Fig. 1: Map of Cyprus. Asterisks on the map indicate locations where sampling of seawater was carried out.

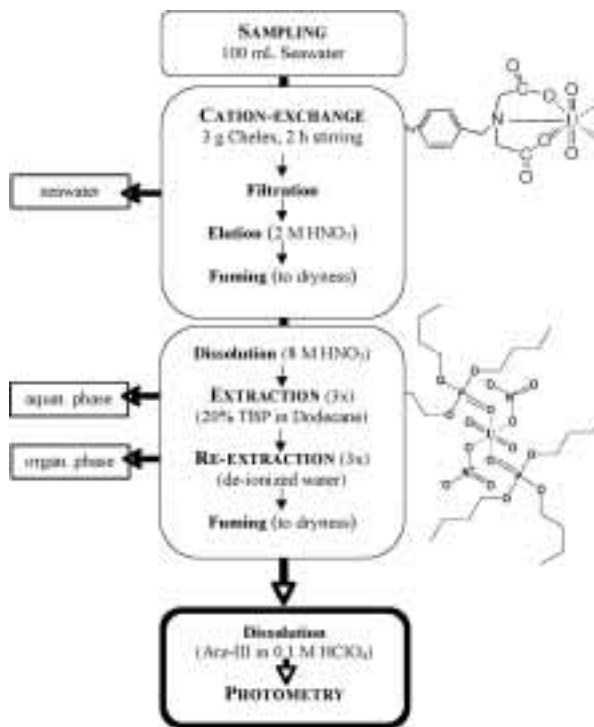


Fig. 2: Schematic overview of the pre-analytical procedures associated with uranium determination in Seawater. Chemical structures on the right present possible uranium(VI) chelation by adjacent carboxylic groups on chelex 100 (upper structure) and the uranium(VI)-tributylphosphate complex ($\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$) (structure below).

from the aqueous matrix, 1 g of Chelex-100 resin and 3 g of ammonium acetate were added to 100-mL seawater samples contained in 200-mL polypropylene beaker and stirred on a magnetic stirring table. After pH adjustment (pH = 5.3) using 2 M HNO₃, the beakers were sealed and stirred for at least an hour. The resin was separated from the solution by filtration and washed with 10 mL of distilled water.

Following this initial separation, the uranium was eluted from the Chelex-100 resin with 15 mL of 2 M HNO₃ solution. The acidic solutions were evaporated to incipient dryness and the residual was dissolved in 10 mL of 8 M HNO₃ solution. The latter and 10 mL of the 30% TBP solution were added in a 50 mL, short stemmed, separatory funnel, and the content was shaken vigorously for about 30 seconds. This extraction procedure was repeated once more and the aqueous phase was discarded. The uranium was removed from the organic phase by extracting successively two times with 20 mL of distilled water and collecting the aqueous phase in a 100 mL beaker.

The aqueous solutions were evaporated to incipient dryness and the residual was dissolved in arsenazo(III) / 0.01 M HClO₄ solution and determined by spectrophotometry using a Shimadzu UV-2401 spectrophotometer.

Results

Prior to the photometric determination of uranium with arsenazo(III), the method was calibrated using standard uranium solutions. Spectra of the uranyl-arsenazo(III) complex at various concentrations and the corresponding calibration curve are shown in Figure 3a and 3b, respectively. Based on the calibration data the lowest detection limit for the method was estimated to be 7.0 µg L⁻¹ of uranium in the aqueous solution. Taking into account that uranium concentration in seawater is about 3.3 µg L⁻¹ and that due to the pre-concentration the volume of the seawater sample is reduced down to 10 mL, 100 mL of seawater result in a solution of about 33 µg L⁻¹ of uranium. This value is by far above the

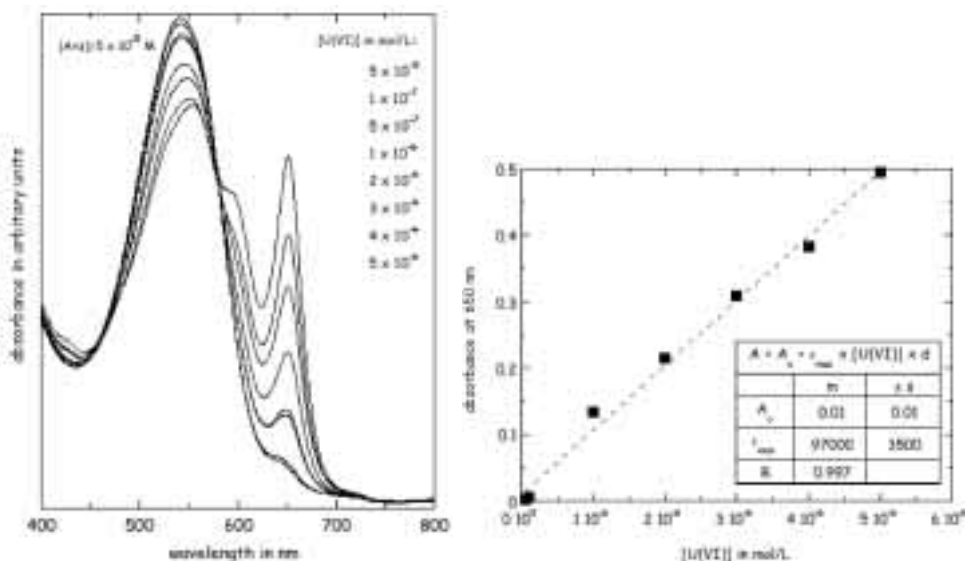


Fig. 3: Absorption spectrum (a) and the calibration curve of the absorbance vs concentration of the uranyl-arsenazo(III) complex (b).

detection limit of uranium estimated for the present method.

The uranium recovery after the cationexchange and extraction procedures was followed by spectrophotometry using arsenazo(III) (SAVVIN, 1961) and was estimated to be $(97 \pm 2) \%$ and $(93 \pm 2) \%$, respectively. Analysis of seawater samples from five different coastal areas in Cyprus was performed as described previously and resulted in a mean uranium concentration of $(3.2 \pm 0.2) \mu\text{g L}^{-1}$. This value is close to the average value of uranium concentration given in the literature (CHEN *et al.*, 1986). The separate uranium concentrations determined in the five different seawater samples are given in Table 1.

Discussion

Figure 4 illustrates in an E_H/pH diagram the common oxidation states in which uranium species are encountered in aquatic solutions. In surface seawater uranium exists predominantly in its hexavalent state and the uranium-carbonate species, $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$, are expected to be the dominant uranium(VI) species in solution. Acidification ($\text{pH} < 6$) of seawater samples results in the destabilisation of the carbonato-species and the formation of uranium(VI)-hydroxo- or uranium(VI)-aquo- complexes (PASHALIDIS *et al.*, 1997). Hence, prior to pre-concentration of uranium from seawater the samples have to

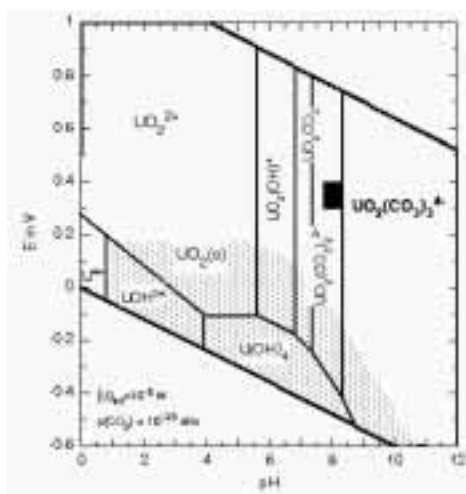


Fig. 4: E_H/pH diagram of uranium in aqueous solution ($[\text{U}]_{\text{tot}} = 10^{-8} \text{ mol L}^{-1}$, $p(\text{CO}_2) = 10^{-3.5}$). The black rectangle indicates the E_H and pH values estimated for surface seawater.

be acidified. Thus, the separation and pre-concentration of uranium by the cationexchange resin Chelex-100 was performed at $\text{pH} 5.3$, since at this pH the cationic uranium(VI) species, UO_2^{2+} and UO_2OH^+ , are predominant in solution and the competition of protons, regarding cationexchange, relatively low (equation 3).

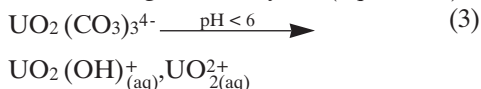


Table 1
Uranium concentration and radioactivity determined in seawater samples from five different coastal areas in Cyprus.

sampling area	uranium concentration in mg L^{-1}	uranium radioactivity in mBq L^{-1}
Paphos	3.1	79
Limassol	3.3	85
Vasiliko	3.4	87
Larnaca	2.9	74
Protaras	3.2	81
mean value	3.2 ± 0.2	81 ± 5

Chelex-100 is a styrene-divinylbenzene copolymer based resin containing paired iminodiacetate ions which act as strong chelating groups in binding polyvalent metal ions. Figure 1 shows a possible binding mode of uranyl ion in Chelex-100. After the cationexchange procedure, the samples are largely free of extraneous ions. However, their content of heavy metal ion is still high enough to disturb the correct spectrophotometric determination of uranium, since these cations also form stable complexes with arsenazo(III). Therefore, the samples were purified further by a standard tributyl-phosphate extraction procedure (EBERLE & LERNER, 1957), which removes almost all interferences. This extraction is based on the formation of a hydrophobic uranyl complex containing two nitrate ions, which neutralise the charge of the uranyl moiety, and two tributyl-ligands, which increase the hydrophobicity of the complex due to the aliphatic chains (Figure 1).

The spectrophotometric determination of uranium is based on the characteristic absorption at 650 nm of the 1:1 complex formed between the uranyl cation and arsenazo(III). The method is very reliable and sensitive for uranium and its detection limits can be reduced easily down to few nanomoles per liter of seawater. In addition, this procedure is very selective for uranium, as confirmed by alpha spectroscopy and results in the production of pure uranium samples, which are suitable not only for UV-Vis spectrophotometric, but also alpha spectroscopic analysis as well. (PASHALIDIS & TSERTOS, 2004). However, since the photometric detection by means of arsenazo(III) is not uranium specific, the method is sensitive to cross-contamination. Moreover, in contrast to alpha spectroscopy, the photometric method does not give any information about the isotopic composition of uranium. Nevertheless, because of its lower detection limits, cost effectiveness and simplicity, it can be easily used as routine method for the determination of total uranium

concentration in seawater and other natural aquatic samples.

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