Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.21747

112 (2018) 94–98
April

Uranium monitoring in ground- and wastewaters

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Received 25 August 2017; Accepted 30 November 2017

ABSTRACT

Uranium in ground- and wastewater samples has been analyzed by alpha-spectroscopy after pre-concentration and separation by means of a chelating resin Lewatit TP 207, and following electrodeposition of the radioelement on stainless steel discs. The effect of the amount of resin used on the uranium recovery and the spectra quality has been investigated using 200 mL aliquots of a groundwater sample. In addition, the method has been successfully applied to detect depleted uranium (DU) contamination in wastewater samples obtained from a local wastewater treatment plant. The radiometric analysis has indicated DU contamination, which was restricted to certain wastewater storage reservoirs and hence was only a localized environmental problem.

Keywords: Uranium; Groundwaters; Lewatit; Alpha-spectroscopy; DU-contaminated wastewaters

1. Introduction

Analysis of uranium in surface and groundwaters is of particular interest regarding environmental contamination from anthropogenic activities such as the nuclear fuel cycle processes and the use of depleted uranium (DU) in civil and military applications [1]. In addition, accurate knowledge of the uranium isotopic ratio in the studied waters is of particular interest because it may indicate the source of contamination [2].

Alpha-spectroscopy is a widely used radiometric method for the quantitation and determination of the isotopic composition of uranium in natural and technical samples, because it is a low-cost and robust method. However, prior alpha-radiometric analysis, uranium has to be pre-concentrated and separated from the matrix and subsequently electrodeposited on stainless steel discs [3–6]. Pre-concentration and separation of uranium are necessary because of its relatively low levels in environmental water samples and the interference of the emitted alpha-particles with solids/salts deposited on the stainless steel discs, that eventually leads to lower spectral resolution and higher detection limits [7].

Pre-concentration and separation procedures including various pre-analytical techniques (e.g., co-precipitation, extraction and ion-exchange) are usually time and material consuming. Nevertheless, alpha-spectroscopy is the method of choice compared with other radiometric methods for uranium analysis (e.g., liquid scintillation counting [8]) because of the increased spectral resolution that allows isotopic activity ratio determinations. Ion-exchange techniques are widely used because of their advantages such as relatively low running costs and energy consumption, easy regeneration and maintenance. In addition, ion-exchange resins can be modified to increase their ion-exchange capacity [9,10].

In this study, we present a relatively low-cost and effective method for the pre-concentration and separation of uranium from ground- and wastewaters and the alpha-spectrometric determination of the uranium isotopes after electrodeposition on stainless steel discs. In contrast to a previously presented method, which uses Chelex 100, in the present method the cation-chelating resin Lewatit TP 207 is used. In this context, alpha-spectra obtained using varying amounts of the resin at constant groundwater volume and DU-contaminated wastewater samples are presented and discussed.

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Presented at the 5th International Conference on Sustainable Solid Waste Management (ATHENS 2017), 21–24 June 2017, Athens, Greece.

1944-3994/1944-3986

2. Experimental

Sample collection and treatment prior to alpha-spectroscopic analysis have been carried out similar to previous studies related to uranium analysis in ground- and seawaters [4–6]. The groundwater studied here has been sampled from a local groundwater system, which is hosted by sedimentary rock formations and has been previously studied [11,12]. For the selective extraction of uranium from the acidified samples, the cation-exchange resin Lewatit TP 207 (Fluka) that possess chelating iminodiacetate groups has been used. It has to be noted that the resin was washed thoroughly prior to usage in order to remove any soluble/suspended resin particles, which negatively affect uranium pre-concentration and recovery from aqueous solutions. The resin was suspended in 2 M HNO_3 and washed several times with de-ionized water until the washing solutions had a weak acidic pH ($3 < pH < 5$). Following, a pre-defined amount of the resin and 0.5 g of ammonium acetate were added to a 200 mL sample contained in a polypropylene beaker and stirred on a magnetic stirring table. The pH of the solution was adjusted to pH 4.5 and the suspension was stirred for 2 h. Acidification of the sample solution is a pre-condition to perform the cation-exchange separation of U(VI), because uranium in the studied ground- and wastewaters exists basically in the form of anionic carbonato complexes ($UO_2(CO_3)_n^{(2n-2)-}$). Upon acidification (pH 4.5), the anionic carbonato complexes are converted to the cationic UO_2^{2+}, which is strongly bound by the complexing cation-exchange resin [4–6]. Then, the resin was separated from the solution by filtration and washed with 20 mL of distilled water. After this initial separation, the radionuclides were eluted from the resin with 15 mL of 2 M HNO_3. The acidic solution was evaporated to incipient dryness and the residue was dissolved in 20 mL of 0.15 M $(NH_4)_2SO_4$ solution. From this solution, uranium was directly electrodeposited for 2 h on a stainless steel disc at a voltage of 17 V and a current of 0.4 A.

Alpha-spectroscopic analysis was performed using the Alpha Analyst Integrated Alpha Spectrometer (Canberra), which was equipped with several semiconductor detectors. The alpha-spectrometric system was calibrated using a mixed nuclide standard reference source (Eckert & Ziegler Analytics, USA) and the method efficiency was determined by tracing the samples under investigation with known amounts of a ^{232}U standard solution [4–6]. Prior to sample measurement, the background was measured under identical conditions and was found to be about 5 counts per day within the energy range of 3–8 MeV. By using blank solutions, the minimum detectable activity of the method was calculated to be 7 mBq L^{-1} at the 95% confidence limit, and the uncertainty of the uranium activity concentration and the $^{234/238}U$ ratio about 10%. The efficiency of the electrodeposition of uranium on stainless steel discs was excellent and reached values close to 99%. The electrodeposition process is only insignificantly affected by the composition of the studied water sample. After cation-exchange only polyvalent metal ions are present in solution (e.g., Fe(III)), which are electrodeposited together with uranium (U(VI)) on the stainless steel plate. On the other hand, the counting efficiency is affected dramatically due to the increased self-adsorption of the sample. Nevertheless, the efficiency is determined by using the tracer solution.

The effect of the amount (0.1, 0.25, 0.5 and 1.0 g) of the Lewatit resin on the uranium recovery and the spectral resolution was investigated using a locally sampled groundwater, which was traced with a ^{232}U standard solution (NPL, UK). The volume of the groundwater, which has been previously studied and extensively characterized [11,12], was 200 mL and was traced with 50 mBq of a ^{232}U standard solution. Separation and analysis of uranium in the groundwater samples have been carried out as described above.

The applicability of the resin has been tested using 5 g per 1-L samples of a local (Cypriot) groundwater and three different wastewater samples obtained from a municipal wastewater treatment plant and traced with 100 mBq of a ^{232}U standard solution. Uranium in the representative samples exists basically in the form of carbonato complexes [5,6,8]. Wastewater reservoirs of the wastewater treatment plant had been contaminated because DU-contaminated effluents from a military vehicle cleaning facility had been released into the associated processes stream. The uranium separation and pre-concentration was performed using the Lewatit resin as described above and the analysis was carried out in triplicate by alpha-spectroscopy [4–6].

3. Results and discussion

Lewatit TP 207 is a cation-exchange resin with chelating iminodiacetate groups and is used for the removal of polyvalent metal ions from natural waters and process solutions [13]. Although chelating iminodiacetate groups present within a certain pH range ($4 < pH < 5$) increased selectivity for the uranyl-cation [14], binding of other polyvalent metal ions from natural water and wastewater solutions is also possible, particularly at increased resin amounts. The composition of the groundwater samples studied here is described elsewhere [11], indicating that the metal ions competing uranium binding by the resin are mainly Ca^{2+} and Fe^{3+} ions. The effect of increased resin amounts on the quality and resolution of the alpha-spectra, as well as the uranium recovery is graphically shown in Fig. 1 and the corresponding data are summarized in Table 1.

According to the experimental data (Fig. 1 and Table 1) using higher amounts of resin results in increased yields of uranium recovered. However, as the resin amount increases a systematic decrease of the spectral resolution is observed. This is because using higher amounts of resin for the recovery of uranium from the matrix solution (e.g., groundwater) results in the binding of increased amounts of other cationic species (e.g., Fe^{3+} and Ca^{2+}) by the resin due to excess of cation binding sites. Subsequently, during acidic elution of uranium from the resin, all cationic species are released along with uranium and transferred into the electrolyte solution (e.g., 0.15 M $(NH_4)SO_4$, pH 2) and may form during electrodeposition a precipitate film (such as $CaSO_4$ or $Fe(OH)_3$) on the disc. The thickness of the salt film on the disc depends on the amount of metal ions transferred from the groundwater into the electrolyte solution and affects diversely the energy of the alpha-particles reaching the detector. As a result, the energy of the alpha-particles shifts to lower energies and the corresponding alpha-peak becomes significantly broader [15].

Since peak broadening is associated with lower spectral resolution and higher detections limits [7], the amount of resin

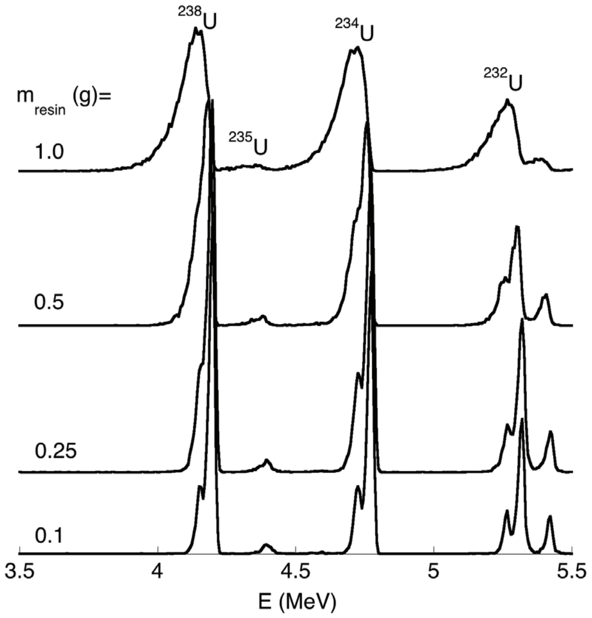

Fig. 1. Uranium alpha-spectra obtained for a groundwater sample after separation and pre-concentration of the element using different amounts of the Lewatit TP 207 resin and following electrodeposition on stainless steel discs.

Table 1
Spectral resolution (FWHM) of the alpha-spectra and recovery of uranium obtained for a groundwater sample after separation and pre-concentration of the element using different amounts of the Lewatit TP 207 resin

Amount (g)	0.1	0.25	0.5	1.0
(%) U recovery	62 ± 10	78 ± 10	85 ± 10	100 ± 10
FWHM (keV)	25 ± 1	32 ± 3	57 ± 5	118 ± 7

FWHM, full width at half maximum.

has to be chosen properly to achieve the desired uranium recovery yields and acceptable spectral resolution. Regarding uranium analysis by alpha-spectroscopy in groundwaters, similar to the one studied here, the amount of 0.25 g resin for a 200 mL sample seems to be an ideal combination for obtaining reasonable yields and good-quality spectra (Fig. 2).

The interaction of U(VI) with the iminodiacetic moieties of cation chelating resins (e.g., Chelex 100) has been extensively described elsewhere [14]. A schematic illustration of the complexation of U(VI) by the chelating iminodiacetic moieties of the resin is shown in Fig. 3.

The method has been applied to a local groundwater and three different waste waters samples delivered from a local municipal wastewater treatment plant to determine the concentration of uranium and its isotopic composition. This analysis has been performed because there was a suspicion that DU-contaminated effluents from a vehicle cleaning facility had been released into the processes stream of the respective wastewater treatment plant. In addition, the analysis has been carried out to prove the applicability of the method to a complex system such as municipal wastewater samples [16]. The analysis of the groundwater sample had been carried out for comparison reasons. The alpha-spectra corresponding to the groundwater and the wastewater samples obtained from three different treatment units/reservoirs are shown in Fig. 4 and the data evaluated from the alpha-spectra of the corresponding samples are summarized in Table 2.

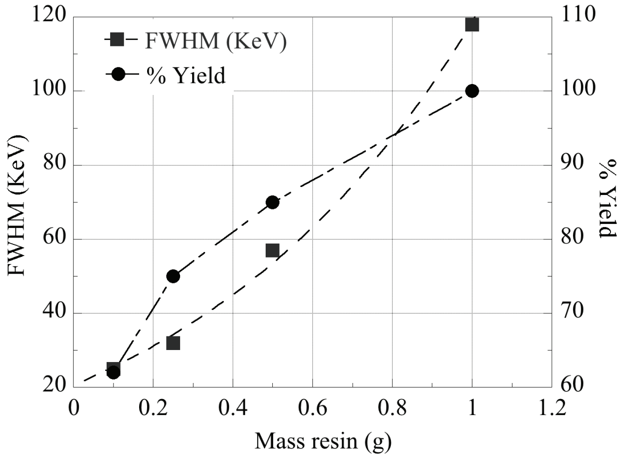

Fig. 2. Effect of the amount of resin used on the uranium recovery and spectral resolution.

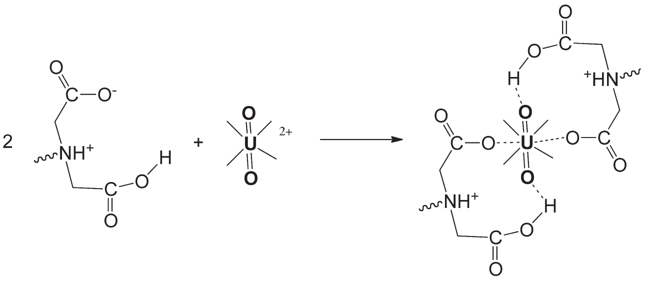

Fig. 3. Schematic illustration of the of U(VI) complexation by the iminodiacetic moieties of the Lewatit TP 207 resin.

The experimental data (Fig. 4 and Table 2) indicate significant differences between the samples regarding the activity concentration and the isotopic composition of uranium. Regarding the groundwater sample, the uranium concentration amounts 148 mBq L^{-1} and the isotopic ratio close to unity (1.1), which is generally within the range of uranium levels and isotopic ratios expected for groundwater samples in Cyprus [4–6]. On the other hand, the WW1 sample, which corresponds to non-contaminated wastewater, has a significantly lower uranium content because it corresponds to a non-contaminated municipal wastewater. The municipal wastewaters originate primarily from the municipal water supply system that delivers basically desalinated water (>70%), which is characterized by its low uranium content. In addition the isotopic ratio of this wastewater sample is about 1.2, which is a characteristic isotopic ratio value for local seawater and groundwater samples [3,4,6].

On the contrary, the wastewater samples WW2 and WW3 present significantly higher uranium content and isotopic ratios that are well below unity (≤0.5). This indicates pollution with uranium and particularly DU contamination of the respective wastewater reservoirs. The radioanalytical

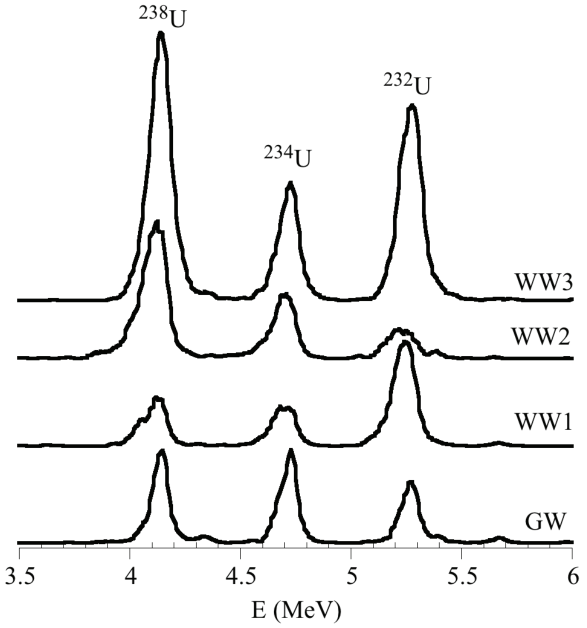

Fig. 4. Uranium alpha-spectra obtained for a groundwater (GW) and three different wastewater (WW) samples after separation and pre-concentration of the element by means of the Lewatit TP 207 resin and following electrodeposition on stainless steel discs.

Table 2
Uranium activity concentrations and isotopic ratios evaluated from the alpha-spectra obtained for a groundwater (GW) and three different wastewater (WW) samples after separation and pre-concentration of the element by means of the Lewatit TP 207 resin

Sample	[^{238}U]/(mBq L^{-1})	[^{238}U]/(µg L^{-1})	^{234}U/^{238}U ratio
GW	148 ± 15	12 ± 1.2	1.1 ± 0.16
WW1	37 ± 10	3 ± 0.8	1.2 ± 0.46
WW2	742 ± 150	60 ± 12	0.4 ± 0.11
WW3	185 ± 15	15 ± 1.2	0.5 ± 0.06

data have shown that DU contamination of the wastewater treatment reservoirs from effluents of the vehicle cleaning facility had been occurred. The contamination was basically restricted within the first wastewater reservoir (WW2) and was about five times above the uranium levels found in the studied groundwater. It is noteworthy, that in the second reservoir (WW3), the uranium levels decrease significantly most probably due to dilution and precipitation processes indicating that the treated wastewater does not pose a serious environmental concern and is not expected to have any implications for public health. However, the significant decrease of the ^{234}U/^{238}U ratio value in WW3 indicates rather dilution with waters of lower ^{234}U/^{238}U ratio (e.g., non-contaminated waters). In addition, the data indicate that the uranium recovery of the wastewater sample WW2 is significantly lower and this can be attributed to the increased organic load of this sample, which dramatically affects the uranium recovery. Furthermore, it is obvious that the spectra of the wastewater samples are of lower quality, which is ascribed to the presence of higher amounts of polyvalent metal ions (e.g., Ca^{2+} and Fe^{3+}). These metal ions are electrodeposited along with the U(VI) ions on the stainless steel discs, affecting the quality of the alpha-spectra.

4. Conclusions

Following conclusions can be drawn from the experimental results of the present study:

- After appropriate pre-treatment, the Lewatit resin can be successfully applied for the separation and pre-concentration of uranium from ground- and wastewater samples.
- The amount of resin used affects inversely uranium recovery and spectral resolution and hence there is a range that leads to acceptable recovery yields and useful spectral resolution.
- Uranium can be separated and pre-concentrated effectively even from complex matrices such as municipal wastewaters.
- The case study has shown DU contamination of the investigated wastewater treatment plant, which, however, was basically restricted within the first wastewater reservoir and is not expected to pose any further environmental concern.

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