

Uranium monitoring in ground and waste waters by alpha-spectroscopy after its separation by *Lewatit TP207* resin

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ABSTRACT

Monitoring of radioactive contamination including uranium contamination of solid waste and wastewater streams is of particular interest because radioactive waste can affect human health and the environment. Moreover, early detection of radioactive waste enhances safety and reduces the costs of further treatment processes and management stages. In this study, uranium in ground- and wastewater samples has been analyzed by alpha spectroscopy after pre-concentration and separation by means of a chelating resin *Lewatit TP207*, and following electrodeposition of the radionuclide 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. Generally, using 0.25 g resin for a 200 ml groundwater sample results in reasonable yields and good quality spectra. In addition, the method has been successfully applied to detect depleted uranium contamination in wastewater samples obtained from a local wastewater treatment plant. The alpha-spectroscopic analysis has shown significant depleted uranium (DU) contamination in certain wastewater reservoirs. The DU contamination could be attributed to effluents from a vehicle cleaning facility, which had been released into the processes stream of the respective wastewater treatment plant.

Keywords: Uranium; ground waters; Lewatit; alpha-spectroscopy; DU contaminated wastewaters

INTRODUCTION

Analysis of uranium in surface and groundwater samples is of particular interest for understanding environmental contamination from anthropogenic activities related to nuclear fuel cycle processes and the use of depleted uranium (DU) in civil and military applications [1]. In addition the accurate knowledge of uranium isotopic ratio in the studied water systems is of particular interest because it may indicate the source of contamination [2].

Alpha-spectroscopy is a widely used for the quantitation and determination of the isotopic composition of uranium in natural and technical samples, because it is a low-cost and robust radioanalytical method. However, prior alpha-radiometric analysis, uranium has to be pre-concentrated and separated from the matrix and subsequently electro-deposited on stainless steel discs [3-6]. Pre-concentration and separation of uranium is 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 to other radiometric methods for uranium analysis (e.g. liquid scintillation counting [8]) because of the increased spectral resolution that allows isotopic ratio determinations.

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 TP207* is used. In this context, alpha spectra obtained using varying amounts of the resin at constant ground water volume and DU contaminated wastewater samples are presented and discussed.

EXPERIMENTAL

Sample collection, preparation and treatment prior to alpha-spectroscopic analysis, as well as system calibration and data evaluation has been carried out as described elsewhere [4-6]. However, in this study the commercially available, cation-exchange resin with chelating iminodiacetate groups *Lewatit[®] MonoPlus TP 207* has been used for the selective extraction of uranium cations from weakly acidic solutions. 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 HNO₃ and washed several times with de-ionized water until the washing solutions had a weak acidic pH (3 < pH <5). Alpha-spectroscopic analysis was performed using the high resolution 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) and the method efficiency by tracing the samples under investigation with known amounts of a ²³²U standard solution [6].

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 has been investigated using a locally sampled groundwater, traced with a ²³²U standard solution (NPL, UK). The volume of the groundwater, which has been previously studied and extensively characterized [9, 10], was 200 ml and was traced with 50 mBq of a ²³²U standard solution.

The applicability of the resin has been tested using 1-liter samples of a local (Cypriot) groundwater and three different wastewater samples obtained from a municipal wastewater treatment plant. 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 similar to a procedure described elsewhere [4-6] and the analysis was carried out in triplicate.

RESULTS AND DISCUSSION

Lewatit[®] *MonoPlus 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 [11]. Although chelating iminodiacetate groups present within a certain pH range increased selectivity for the uranyl-cation [12], binding of other polyvalent metal ions from natural water and wastewater solutions is also possible, particularly at increased resin amounts. The effect of increasing the resin amount 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.

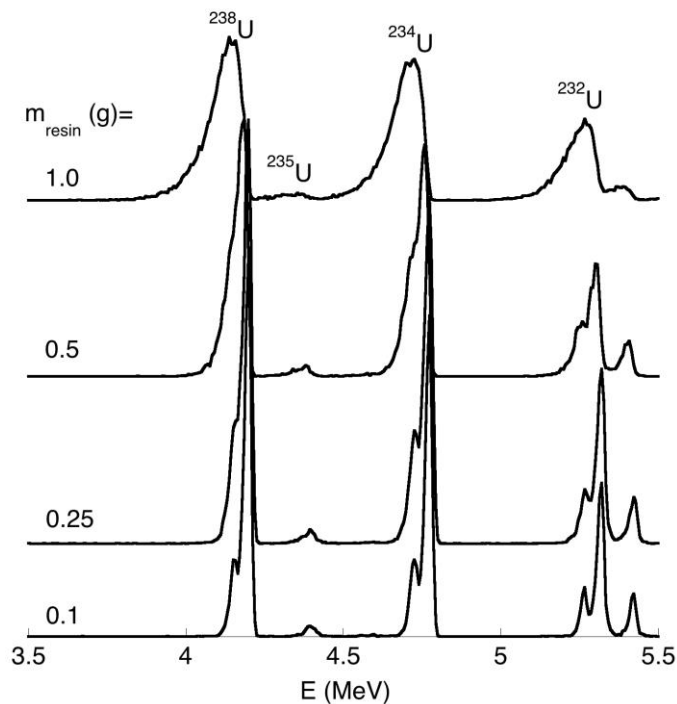


Fig. 1 Uranium alpha-spectra obtained for a groundwater sample after separation and pre-concentration of the element using different amounts of the Lewatit TP207 resin and following electrodeposition on stainless steel discs.

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 TP207 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

The experimental data (Fig.1 and Table 1) clearly show that using higher resin amounts results in increasing yields of uranium recovered from a certain sample volume. However, as the resin amount increases a dramatic decrease of the spectral resolution is observed. Using higher amounts of resin during uranium recovery from the matrix solution (e.g. groundwater) is associated with the binding of higher amounts of other cationic species (e.g. Fe^{3+} and Ca^{2+}) by the resin and subsequently released along with uranium into the electrolyte solution (e.g. 0.15 M $(\text{NH}_4)\text{SO}_4$ solution, pH 2). During electrodeposition besides uranyl cations, also other cations (e.g. Fe^{3+} and Ca^{2+}) are attracted by the cathode (stainless steel disc) and because of the existing conditions may form a precipitate film (such CaSO_4 or $\text{Fe}(\text{OH})_3$) on the disc. The thickness of the salt film on the disc depends obviously from the amount of metal ions transferred from the groundwater into the electrolyte solution and already mentioned from the amount of resin used. On the other hand, alpha-particles emitted from the electrodeposited uranium isotopes interact with the salt/solid film formed on the disc surface (self-absorption) and alter diversely the energy of the alpha-particles reaching the detector. As result, the energy of the alpha-particles shifts to lower energies and the corresponding alpha-peak becomes significantly broader.

Since, peak broadening is associated with lower spectral resolution and higher detections limits [7] the amount of resin has to be chosen properly to achieve the desired uranium recovery yields and acceptable spectral resolution. Regarding uranium analysis in ground waters, like 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. 1s, Supplementary information) .

The method has been applied to a local groundwater (GW) and three different wastewaters 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 like municipal wastewater samples [13]. The analysis of the ground water sample has been carried out for comparison reasons. The alpha spectra corresponding to the groundwater (GW) and the wastewater samples (WW) obtained from three different treatment units/reservoirs are shown in Fig. 2 and the data evaluated from the alpha-spectra of the corresponding samples are summarized in Table 2.

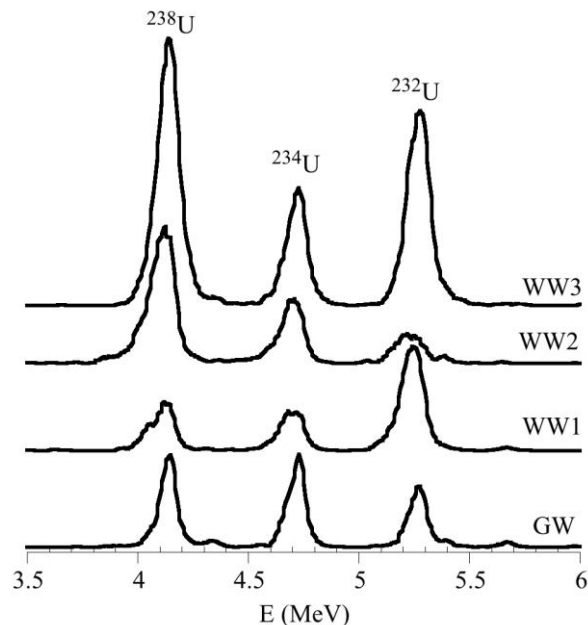


Fig. 2 Uranium alpha-spectra obtained for a groundwater (GW) and three different wastewater (WW) samples after separation and pre-concentration of the element by means of the Lewatit TP207 resin and following electrodeposition on stainless steel discs.

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 TP207 resin.

Sample	$[^{238}\text{U}] / (\text{mBq l}^{-1})$	$[^{238}\text{U}] / (\mu\text{g l}^{-1})$	$^{234}\text{U}/^{238}\text{U}$ ratio
GW	148 ± 15	12 ± 1	1.1 ± 0.1
WW1	37 ± 10	3 ± 1	1.2 ± 0.2
WW2	742 ± 150	60 ± 12	0.4 ± 0.2
WW3	185 ± 15	15 ± 1	0.5 ± 0.2

The experimental data (Fig. 1 and Table 1) clearly indicate significant differences regarding the activity concentration and isotopic composition of uranium. 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 ground waters 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 municipal wastewaters. These 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) and indicate pollution with uranium and particularly DU contamination of the respective wastewater reservoirs.

CONCLUSIONS

Following conclusions can be drawn from the experimental results of the present study: a) after appropriate pre-treatment the *Lewatit* resin can be successfully applied for the separation and pre-concentration of uranium from ground and wastewater samples.

b) 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.

c) uranium can be separated and pre-concentrated effectively even from complex matrices like municipal wastewaters.

REFERENCES

1. Bleise A., Danesi P.R., Burkart W.: Properties, use and health effects of depleted uranium (DU): a general overview. *J Environ Radioact* 64, 93–112 (2003)
2. Thomson J.: A total dissolution method for determination of the α -emitting isotopes of uranium and thorium in deep-sea sediments. *Anal Chim Acta* 142, 259-268 (1982)
3. Pashalidis I., Tsertos H.: Radiometric determination of uranium in natural waters after enrichment and separation by cation-exchange and extraction techniques. *J Radioanal Nucl Chem* 260, 439-442 (2004)
4. Killiari T., Pashalidis I.: Simplified alpha-spectroscopic analysis of uranium in natural waters after its separation by cation-exchange. *Radiat Measurem* 45, 966–968 (2010)
5. Ioannidou A., Samaropoulos I., Efstathiou M., Pashalidis I.: Uranium in ground water samples of Northern Greece. *J Radioanal Nucl Chem* 289, 551–555 (2011)
6. Charalambous C., Aletrari M., Piera P., Nicolaidou-Kanari P., Efstathiou M., Pashalidis I.: Uranium levels in Cypriot groundwater samples determined by ICP-MS and α -spectroscopy. *J Environ Radioact* 116, 187-92 (2013)
7. Sill C.W.: Determination of thorium and uranium isotopes in ores and mill tailings by alpha spectrometry. *Anal Chem* 49, 618–621 (1977)
8. Antoniou S., Tsiali A., Pashalidis I.: Alpha-radiometry of uranium in surface and ground waters by liquid scintillation counting after separation of the radionuclide by cation-exchange. *Radiat Meas* 43, 1294-1298 (2008)
9. Georgiou G., Pashalidis I.: Boron in ground waters of Nicosia (Cyprus) and its treatment by reverse osmosis. *Desalination* 215, 104-110 (2007)
10. Efstathiou M., Aristarchou T., Kiliari T., Demetriou A., Pashalidis I.: Seasonal variation, chemical behavior and kinetics of uranium in an unconfined groundwater system. *J Radioanal Nucl Chem* 299, 171-175 (2014)

11. Hubicki Z., Koodyska D.: In: Kilislioglu A (Ed) Ion Exchange Technologies, InTechPublishers, (2012). DOI: 10.5772/51040
12. Kiliari T., Pashalidis I.: Selective separation of actinyl(V,VI) cations from aqueous solutions by Chelex-100. *Radiochim Acta* 100(7), 439–444 (2014)
13. Henze M., Harremoës P., la Cour Jansen J., Arvin E.: *Wastewater Treatment: Biological and Chemical Processes*, 3rd ed, Springer-Verlag, Berlin (2002)

Supplementary information

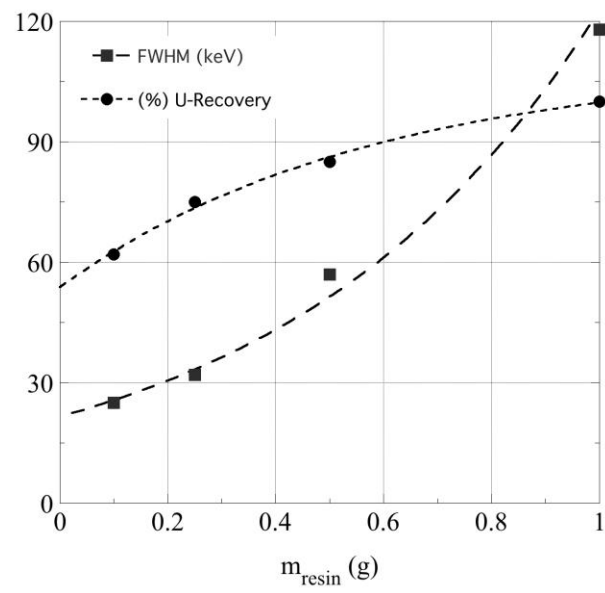


Fig. 1s The effect of the amount of resin used on the uranium recovery and spectral resolution.