EPJ Web of Conferences **24**, 03005 (2012)
DOI: 10.1051/epjconf/20122403005

Determination of uranium concentration in ground water samples of Northern Greece

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Abstract

The activity concentration of ^{238}U and ^{234}U has been determined in groundwater samples of hot springs and deep wells from the region of Northern Greece. The analysis was performed by alpha spectroscopy after pre-concentration and separation of uranium by cation exchange (Chelex 100 resin) and finally its electro-deposition on stainless steel discs. The uranium concentration in deep wells and springs varies strongly between 0.15 and 7.66 μg l^{-1}. Generally the springs present higher uranium concentration than the deep wells, except of the Apollonia spring, which has shown the lowest value of 0.15 mg l^{-1}. ^{238}U and ^{234}U activity concentration ranged between 1.8-95.3 mBq l^{-1} and 1.7-160.1 mBq l^{-1}, respectively. The obtained isotopic ratio ^{234}U/^{238}U varies between 0.95 and 1.74 which means that the two isotopes are not in radioactive equilibrium. The highest ^{234}U/^{238}U activity ratio values correspond to the Langada springs, indicating most probably old-type waters. On the other hand, ground waters from wells with relatively low uranium activity concentration and low ^{234}U/^{238}U isotopic ratios, point to the presence of younger waters with a stronger contribution of a local recharge component to the groundwater.

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1 Introduction

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 Uranium in water results from the weathering of rocks and soil. In groundwater, the nuclide activities are governed by a number of processes, including recoil supply and absorption-desorption [1]. This results in isotopic fractionation of this element, which is unique among the heavy elements, and has been useful in identifying waters, tracing them in the hydrologic cycle and estimating mixing ratios when surface waters merge. Accurate knowledge of uranium isotopic ratios in natural systems is of particular interest regarding geochronology, paleothermometry and pollution budgets.

Furthermore, knowledge of the uranium concentration in ground and surface waters is important in performing radiological impact assessment of various anthropogenic activities and aims to secure the increased standard of life in modern societies.

In the present work activity concentration of ^{238}U and ^{234}U has been determined in two different types of groundwater systems *i.e.* deep wells and hot springs of the region of Northern Greece, in order to define the levels of their concentrations. The analysis was performed by alpha spectroscopy after pre-concentration and separation of uranium by cation exchange and finally its electro-deposition on stainless steel discs.

2 Instrumentation and analysis

In the present work a relatively simple and effective method for the preconcentration and separation of uranium by cation exchange (Chelex 100 resin) and its alpha radiometric determination after electrodeposition on stainless steel discs was used. The employment of high-resolution alpha-spectroscopy allows an accurate determination of the activity of the ^{238}U and ^{234}U radioisotopes, even though they appear at very low concentrations. The measurements have been carried out in the Laboratory of Radioanalytical Chemistry of the University of Cyprus.

From each sampling position 1.5 l of groundwater samples were obtained. 500 ml of each groundwater sample was pre-treated by cation-exchange using Chelex 100 as described elsewhere [2]. This pre-analytical procedure is selective for uranium and was carried out in parallel for every sample.

Alpha-spectroscopic analysis of selected samples was performed using a high-resolution alpha-spectrometer (STC Amplituda, Doza) equipped with

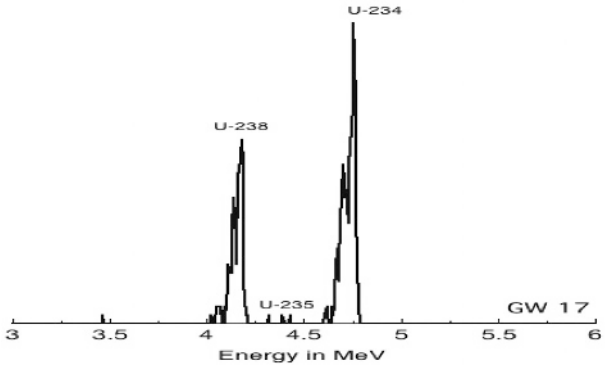

Figure 1: Typical alpha-spectrum of a groundwater sample displaying the alpha peaks of the corresponding uranium isotope ^{238}U and its daughter nuclide ^{234}U.

semiconductor detectors. Prior to the sample measurement, the background was carefully measured under identical conditions and was found to be about 50 counts per day within the energy range of 3 to 8 MeV.

Method calibration using cation exchange separation shows an efficiency of 85%. The electrodeposition of uranium on stainless steel discs resulted in excellent yields, generally over 99% [3]. The uranium activities were measured by alpha spectrometry with a detection counting efficiency of 8%. The Minimum Detectable Activity (MDA) reached in the measurements is about 1 mBq l^{-1} at the 95% confidence limit.

A typical α–spectrum of a groundwater sample is presented in fig. 1. The two main alpha peaks due to the ^{238}U and ^{234}U radioisotopes with energies of 4.198 MeV and of 4.776 MeV, respectively, are clearly shown. The small contribution of the ^{235}U radioisotope (below the experimental detection limit) does not give a statistically significant alpha peak.

3 Results and discussion

3.1 Uranium activity concentration

Sample collection included groundwater samples of springs and deep wells from ten different areas of the region of Northern Greece. All samples were collected at the end of the spring period and the beginning of the summer period. The activity concentration of the different uranium radioisotopes of the analyzed samples are shown in table 1. The ratio and the sum of the radioisotope activity concentration are also given for each measured sample. For ^{238}U, the activity concentration varies between 4.08 and 95.32 mBq l^{-1}.

Table 1: Concentration of ^{238}U and its daughter nuclide ^{234}U in groundwater samples collected from the region of Northern Greece. The uncertainties of ^{238}U and ^{234}U activity values is about 10%.

Area	^{238}U mBq	^{234}U mBq	^{238}U mBq l^{-1}	^{234}U mBq l^{-1}	^{238}U μg l^{-1}	^{234}U/^{238}U
Thermal hot springs						
Lagada-1	26.4	39.8	52.8	79.5	4.25	1.51
Lagada-2	28.9	50.1	57.7	100.2	4.64	1.74
Pozar-Aridaia	28.1	34.3	56.1	68.6	4.51	1.22
Thermi	16.9	17.4	33.8	34.9	2.71	1.03
Apollonia	2.0	1.9	4.1	3.9	0.33	0.95
Deep wells						
Ptolemaida-1	2.7	4.4	5.5	8.7	0.44	1.60
Ptolemaida-2	47.7	80.1	95.3	160.1	7.66	1.68
Ptolemaida-3	6.8	8.2	13.6	16.3	1.09	1.20
Ptolemaida-4	13.1	16.6	26.1	33.2	2.10	1.27
St Ioannis	11.9	17.9	23.9	35.9	1.93	1.50

For ^{234}U the activity concentration varies between 3.88 and 160.13 mBq l^{-1}. The ^{234}U/^{238}U ratio varies between 0.95 and 1.74. Generally the springs present higher uranium concentration than the deep wells, except of the Apollonia spring, which has shown the lowest value of 0.15 mg l^{-1}. Our results are in agreement with other investigators. Labidi *et al.* [4], measured uranium isotopes in thermo-mineral water springs in Tunisia and they found that the ^{234}U activity concentration varies between 1.1 and 82.2 mBq l^{-1}and that the ^{238}U concentration varies between 1.5 and 42.7 mBq l^{-1}. However, values are general higher than the concentrations of ^{238}U and ^{234}U in drinking waters in Greece. Kehagia *et al.* [5] found that ^{238}U and ^{234}U in the drinking water samples in Greece ranges from 0.91 to 17.27 mBq l^{-1} and from 2.13 to 22.01 mBq l^{-1}, respectively.

There is a correlation between the ^{234}U activity concentration values and those corresponding to ^{238}U (fig. 2). This observed correlation is related to the leaching of uranium isotopes with a high rate to the underground water flowing through the faults and fissures between the grains of reservoir rocks [6].

In naturally occurring uranium radioisotopes, the activity ratio ^{234}U/

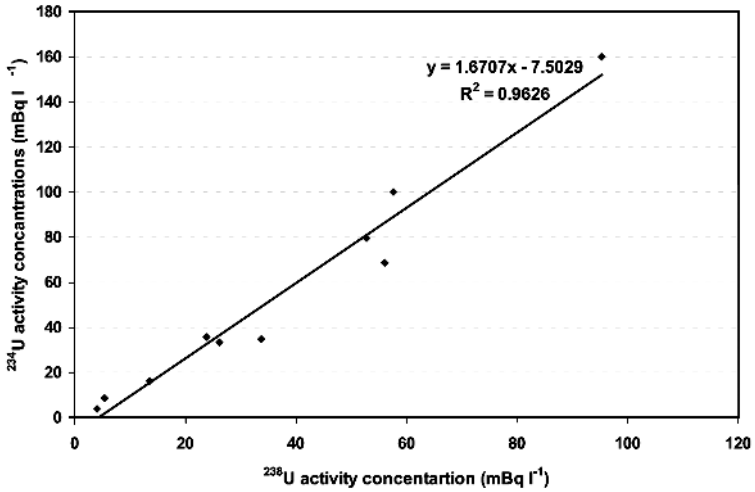

Figure 2: ^{234}U activity concentration values correlated with those corresponding to ^{238}U.

^{238}U can be about 1.05. In the present investigation, all the analyzed groundwater samples (except Thermi hot spring) show a radioactive disequilibrium between the two isotopes ^{234}U and ^{238}U. This disequilibrium occurs, because ^{234}U is more soluble than ^{238}U. In fact, it is established that ^{234}U recoil, crystal damage and leaching are the main mechanisms for ^{234}U/^{238}U disequilibrium in ground water [7, 8]. The determination of the ^{234}U/^{238}U ratio in disequilibrium is of importance in understanding hydrological, geochemical and chemical processes in terrestrial studies.

The observed disequilibrium in samples of this investigation might be correlated with the different geological formations and water flow paths in the studied areas. The highest ^{234}U/^{238}U activity ratio values correspond to Langada springs, indicating most probably old-type waters. On the other hand, groundwater from wells with relatively low uranium activity concentration and small ^{234}U/^{238}U isotopic ratios, point to the presence of younger waters with a stronger contribution of a local recharge component to the groundwater. However, further studies are required to establish the relationship between the disequilibrium activity ratio and the source of uranium in the water.

From the radiological point of view, using ground waters for human consumption would result in significantly increased radiation doses and their utilization for irrigation purposes would not imply an excessive radiation exposure to population, in cases of high uranium concentration. However,

the studied groundwater samples do not exhibit uranium content, above the limits of $15\,\mu g\,l^{-1}$ suggested by WHO (2004) for uranium concentration in waters.

4 Conclusion

^{234}U and ^{238}U uranium isotopes concentration was measured using alpha spectrometry in ten different groundwater samples from Northern Greece. In general, rather low activity concentration of the ^{238}U and ^{234}U radioisotopes exists, exhibiting values of $95.32\,mBq\,l^{-1}$ and $160.13\,mBq\,l^{-1}$, respectively. In only one sample the activity ratio of $^{234}U/^{238}U$ was found to be consistent with the value of 1.05, which is expected from naturally occurring uranium. In order to define the reasons for this disequilibrium, further investigation is needed, including at least the lithostratigraphic formation of the points of investigation. From the radiological point of view the studied groundwater does not exhibit an uranium content above the limits suggested by [9] for uranium concentration in waters, which is $15\,\mu g\,l^{-1}$

References

[1] PORCELLI D. and SWARZENSKI P.S., *Mineralogy and Geochemistry*, **52** (2003) 317.

[2] KILIARI T. and PASHALIDIS I., *Radiat. Measurem.*, **45**(8) (2010) 966.

[3] PASHALIDIS I. and TSERTOS H., *J. Radioanal. Nucl. Chem.*, **260** (2004) 439.

[4] LABIDI S., DACHRAOUI M., MAHJOUBI H., LEMAITRE N., BEN SALAH R. and MTIMET S., *J. Environ. Radioactivity*, **62** (2002) 87.

[5] KEHAGIA K., KOUKOULIOU V., BRATAKOS S., SEFERLIS S., TZOUMERKAS F. and POTIRIADIS C., *Desalination*, **213**(1-3) (2007) 98.

[6] KOZLOWSKA B., WALENCIK A., DORDA J. and PRZYLIBSKI T.A., *Poland Radiation Measurements*, **42** (2007) 1380.

[7] IVANOVICH M. and HARMON R.S., *Uranium-series Disequilibrium: Application to Earth, Marine and Environmental Sciences* (Clarendon Press, Oxford, 1992) pp. 910.

[8] KRONFELD J., GRADSTAJN E., MULLER H.W., RADIN J., YANIV A. and ZACH R., *Earth and Planetary Sci. Lett.*, **27** (1975) 342.

[9] WORLD HEALTH ORGANISATION, WHO, *Guidelines for drinking-water quality, Third edition, Recommendations*, Geneva, Vol. **1** (2004).