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DETERMINATION OF URANIUM AND THORIUM IN SOILS AND PLANTS BY ICP-MS. CASE STUDY OF BUHOVO REGION

Veronika Mihaylova, Boyan Todorov, Rumyana Djingova

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Abstract

ICP-MS was used for determination of U and Th in soil and plant samples from Buhovo mining area. The results proved considerably higher concentrations of both elements and higher isotope ratios ($^{238}U/^{232}Th$ and $^{235}U/^{238}U$) in the investigated soils and plants in comparison to background samples. U and Th were concentrated mainly in the seeds of the plants in contrast to background plants. Highest uptake of the elements was established for the dandelion and lowest for the wheat sample.

Key words: uranium, thorium, ICP-MS, Buhovo, dandelion (*Taraxacum officinale*), wheat (*Triticum aestivum L.*), soil

Introduction. Uranium mining and processing involve the removal of large amounts of accompanying materials and decay products which might increase exposure to natural radiation through different pathways. Uranium is characterized by both radiotoxicity and chemical toxicity [1], whereas thorium is to be considered as only radiotoxic. In recent years, the concentration and distribution of U and Th in soils and plants have been extensively studied [2–4]. The investigation of their distribution in different soil and sediment phases by applying sequential extraction procedures (SEP) may help to predict U and Th behaviour, giving information about the mobility and possible transfer along the food chain.

Various analytical techniques have been successfully applied for determining the uranium and thorium concentrations in different environmental samples [5–7], but inductively-coupled plasma mass spectrometry (ICP-MS) with its high sensi-

tivity, good accuracy and precision, isotope ratio measurements and a relatively simple sample preparation procedure [8–10] is one of the most suitable methods for determination of long-lived radionuclides in environment samples.

In order to assess possible contamination by U and Th, soil and plant samples from the abandoned mining area "Buhovo" located in Western Bulgaria were collected. Extensive mining was conducted in this region between 1938 and 1992. The mine was closed in 1992 and recultivation of the abandoned mining area started ten years later. The aim of this study is to investigate the distribution of U and Th in soils and plants in Buhovo region and the seasonal variations in the mobility of U, applying SEP.

Materials and method. ***Instrumentation.*** ICP-MS (Perkin Elmer SCIEX DRC-e) was used for the U and Th determination (Nebulizer gas flow – 0.90 l/min, Auxiliary gas flow – 1.20 l/min, Plasma gas flow – 15.00 l/min, Lens voltage – 6.00 V , ICP-RF power – 1100.00 W, Pulse stage voltage – 950.00 V, Dwell time – 50 ms, Washing solution – 5% HNO_3, Washing time – 180 s).

Samples. Soil and plant samples were taken from the abandoned mining area "Buhovo" located in Western Bulgaria. Soil sample 1 was collected at the tailing (0.6–1.0 µSv/h). Soil sample 2 was collected at the recultivated area planted with wheat (0.4–0.6 µSv/h). The soil samples were collected during spring and summer at a depth of 10 cm. Three common plants in the area, dandelion (*Taraxacum officinale*), wheat (*Triticum aestivum*) and grass were the main species collected. For comparison, soil and plant (dandelion) samples were taken from Gorno Uyno background region.

For evaluation of the accuracy stream sediment, reference materials STSD-1, STSD-3, STSD-4 (Canadian Certified Reference Project) were used for soil analysis. DC-73348, DC-73349 (China National Analysis Center) and NIST-1547 (National Institute of Standards and Technology) were used for plant analysis. A very good agreement between experimental and certified values was established.

Sample preparation. Plant samples. In the laboratory, the plant samples were oven-dried at 80 °C for 3 h. Digestion of the CRM-s and plant samples was done according to the following procedure: 0.5 g of the sample was mixed with 6 mL HNO_3 and the mixture was left for 24 h. Afterwards, 3 mL H_2O_2 in PTFE vessels 1 mL HF was added and microwave digestion (Anton Paar) was performed. After that, the solution was evaporated on a sand bath. The residue was dissolved in 5% v/v HNO_3. The solution was diluted to 50 mL with double deionized water. After that, the analysis of radionuclides was performed using ICP-MS.

Soil samples. The samples were air-dried, sieved through a 2 mm sieve. The soil samples and CRM-s were digested using HF/HNO_3, according to [11]. After digestion, the samples were evaporated to dryness. Then the residues were dissolved in 5%v/v HNO_3. After that, the analysis of radionuclides was performed using ICP-MS.

Sequential extraction. NIST standard sequential extraction for identifying the fractionation of radioactive elements in soil and sediments [12] was employed with slight modifications [13].

Results and discussion. ***Acid concentration of standard solutions.*** Uranium and thorium might adhere to sample vessel walls as well as to the internal components of the ICP-system [14]. To check these fresh solutions of ^{238}U and ^{232}Th in 2% v/v HNO_3 and 5% v/v HNO_3 with concentration of 0.5 ng mL^{-1}, 1 ng mL^{-1}, 10 ng mL^{-1} and 100 ng mL^{-1}were analyzed immediately and re-analyzed two and four weeks later (Fig. 1). Significant deviations in the measured concentrations were established. The results showed that uranium and thorium easily adhere to sample vessel walls and probably to the internal components of the ICP system. This can lead to an apparent loss of Th and U, especially at low concentrations. A constant thorium and uranium signal was not reached below 5% v/v HNO_3. Below this level, the U and Th concentrations were unpredictable. It is recommended that all U and Th analyses were performed in at least 5% HNO_3 and suggested that a 5% acid wash solution must be used.

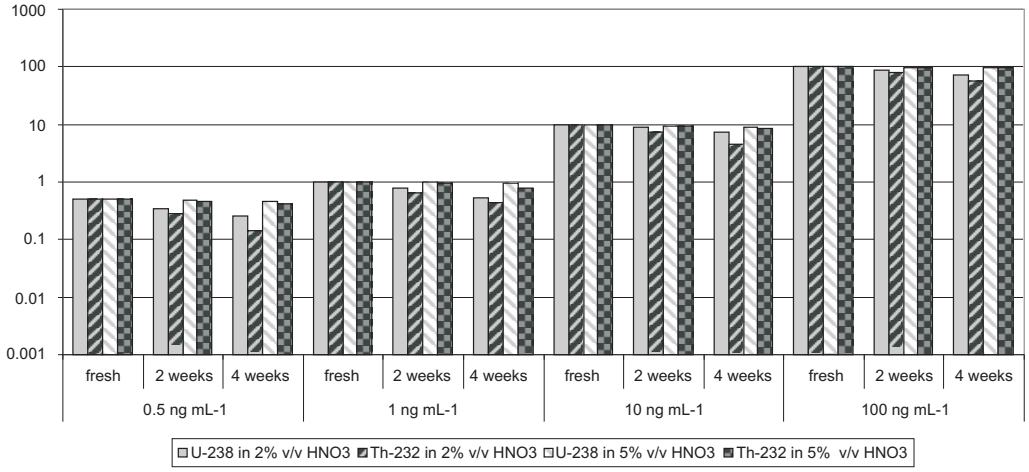

Fig. 1. Changes in model solutions of ^{238}U and ^{232}Th in 2% v/v HNO_3 and 5% v/v HNO_3

Uranium and thorium in soil and plant samples. The typical concentration range of Th in soils is 2–12 mg kg^{-1} with an average value of 6 mg kg^{-1} [15]. The world wide mean U concentration in non-contaminated soils ranges from 0.4 to 6.0 mg kg^{-1} [16]. The analytical results for plant and soil samples are summarized on Table 1. Uranium concentration in soil collected from Buhovo uranium mine ranged from 45 to 65 mg kg^{-1}. The concentration of Th was about 70 mg kg^{-1}. Generally, the Th and U concentrations of the soils were over 50 times higher than background concentration. ^{238}U/^{232}Th ration and ^{235}U/^{238}U were calculated for each soil. The result for the ratio ^{238}U/^{232}Th in the unpol-

Table 1

Uranium and thorium content in plant and soil samples, transfer factors, $^{235}U/^{238}U$ and $^{238}U/^{232}Th$ ratio

Plant samples	Part	Concentration ^{238}U ±SD/ (mg kg^{-1})	Concentration ^{232}Th ±SD/ (mg kg^{-1})	TF(U)	TF(Th)
Grass	—	0.128 ± 0.010	0.021 ± 0.002	$2.3*10^{-3}$	$0.3*10^{-3}$
Wheat	seeds	0.007 ± 0.002	0.026 ± 0.003	$0.2*10^{-3}$	$0.36*10^{-3}$
	stems	0.035 ± 0.003	0.004 ± 0.001	$0.8*10^{-3}$	$0.5*10^{-4}$
Dandelion	seeds	0.166 ± 0.013	0.121 ± 0.012	$0.37*10^{-2}$	$1.7*10^{-3}$
	stems	0.147 ± 0.012	0.073 ± 0.007	$0.33*10^{-2}$	$1.0*10^{-3}$
	leaves	0.137 ± 0.011	0.081 ± 0.009	$0.31*10^{-2}$	$1.1*10^{-3}$
Dandelion-background region (GU)	seeds	0.011 ± 0.008	0.013 ± 0.003	$1.16*10^{-2}$	$0.3*10^{-2}$
	stems	0.019 ± 0.007	0.033 ± 0.006	$2.0*10^{-2}$	$0.8*10^{-2}$
	leaves	0.031 ± 0.003	0.078 ± 0.008	$3.2*10^{-2}$	$1.9*10^{-2}$
Soil samples				Ratio $^{238}U/^{232}Th$	Ratio $^{235}U/^{238}U$
Soil sample 1		62 ± 3	70 ± 5	0.88	0.00785
Soil sample 2		45 ± 2	72 ± 6	0.62	0.00824
Soil sample background region (GU)		0.78 ± 0.05	4.49 ± 0.4	0.17	0.00724

luted region was 0.17, for the soil samples from Buhovo this ratio was markedly higher (0.62 and 0.88). The excess of uranium relative to Th indicated that U was introduced in addition to the soil. Data obtained for $^{235}U/^{238}U$ atom ratio in soil samples collected from Buhovo are higher than the natural $^{235}U/^{238}U$ (0.00725) value (Table 1). The $^{235}U/^{238}U$ atom ratio for the unpolluted region was 0.00724. It can be observed that the concentrations of the radionuclides in the soil samples collected from the mining area are strongly enhanced with respect to the non-polluted area.

The sampled plants (dandelion, wheat and grass) were divided into different parts and then analyzed by ICP-MS (Table 1). For comparison dandelion was collected from Gorno Uyno unpolluted region. The results showed that the concentrations of U and Th determined in dandelion, wheat and grass collected near the radioecologically problematic area were found to be higher in comparison with plant samples from unpolluted area. The U concentration in the dandelion leaves, stems and seeds from Buhovo were 5 times, 8 times and 15 times higher respectively in comparison with dandelion from Gorno Uyno. The Th concentrations were 9 times higher in seeds, 2 times higher in stems and in the same order in the leaves of dandelion from Buhovo in comparison with the background

Table 2

Season variations in U and Th forms

U and Th fractions	Spring		Summer	
	% #of U forms		% #of U forms	
	Soil sample 1	Soil sample 2	Soil sample 1	Soil sample 2
Water soluble	0.5	0.6	1.0	0.7
Organic	2.7	1.1	6.1	7.4
Carbonates	7.5	1.2	13.5	4.6
Oxides	1.1	0.8	0.2	0.9
total %	11.8	3.7	20.8	13.6

#-values are per cent of total U and Th

region. The data on Table 1 indicate, however, that in contrast to other elements – see e.g. [17,18], U and Th are concentrated in the seeds, which means that they are further transferred in the newly-growing plants. Analyzed plant samples from Buhovo have concentration ratio of $^{238}U/^{232}Th$ higher (from 0.27 to 8.75) in comparison to the unpolluted region (0.39–0.84) and "global values" of corresponding elements in the upper part of the Earth's crust [19]. A transfer factor (TF) for U and Th from soil to plants was calculated (Table 1). TF was slightly decreased compared with the control values. In spite of this the lower TF could not compensate the high concentration of U and Th in the soil. The highest uptake was established for the dandelion and the lowest for the wheat sample. Similar results were obtained by Stangeeva [20].

Seasonal change in the mobility of uranium. Since U is the primer pollutant in the area, its mobility was investigated using SEP. Uranium was extracted from the soil samples collected during spring (15 °C) and summer (27 °C) and then determined by ICP-MS (Table 2). Uranium concentration in the soil fractions varied depending on the sampling place and season of sample. In spring the highest concentration of U in soil 1 was established in the carbonate fraction, followed by the organic fraction with total extracted uranium of 11.2%. In soil 2, total extracted U was low – 3.7%. In summer in both soils the total extracted uranium was considerably increased. In soil 1, uranium was found mostly in the carbonate fraction, while in soil 2 – in the organic fraction.

Conclusions. Uranium and thorium were determined in soil and several plant species were taken from Buhovo abandoned uranium mining area. Generally, the Th and U concentrations of the soils were over 50 times higher than background values. The U/Th ratio was markedly higher than the control value, suggesting contamination with uranium. The $^{235}U/^{238}U$ atom ratios in soil samples were higher than the natural ratio. Plants grown in Buhovo have increased concentrations of Th and especially U in different plants and plant parts. Seasonal dependence on the mobility of uranium in the soil was established.

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Laboratory of Trace Analysis
Department of Analytical Chemistry
Faculty of Chemistry and Pharmacy
St. Kliment Ohridski University of Sofia
1, J. Bourchier Blvd
1164 Sofia, Bulgaria
e-mail: ahvm@chem.uni-sofia.bg