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ICP-MS DETERMINATION OF URANIUM AND THORIUM IN WATER SAMPLES TAKEN ALONG RIVER KURA

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Abstract: The uranium and thorium concentration in water samples collected from along River Kura has been measured using inductively coupled plasma mass spectrometry. The Agilent 7700x Series ICP-MS applied to analysis of water samples. The uranium concentration lies in the range of 0.697–7.035 ug L^{-1} with a mean value of 1.812 ug L^{-1}. The values of thorium on all sampling point less than 0.01μg/L. The measured uranium content in all water samples were less than the limit of 30 ug/L recommended by the World Health Organization (WHO) and US Environmental Protection Agency.

Keywords: Uranium, Thorium, ICP-MS, radionuclides.

1. Introduction

The largest proportion of human exposure to radiation comes from natural sources – from external sources of radiation, including cosmic and terrestrial radiation, and from inhalation or ingestion of radioactive materials. It is a ubiquitous radioactive trace element found in almost all terrestrial substances in different levels of concentration. Water plays an important role in the geophysical and geochemical processes, which slowly recycles the trace elements to and biosphere. Determination of natural radio nuclides such as U and Th in water samples are also important [1].

Uranium occurs in a dispersed state in the Earth's crust reaching an average concentration almost $4 \cdot 10^{-4}$ percent by mass. Uranium of natural isotopic composition consists of three isotopes: 238U, 235U and 234U, all of them are radioactive. The groups of uranium isotopes are found in the earth's crust with an abundance of 4 × 10-4 % and are found in rocks and minerals such as granite, metamorphic rocks lignite's, monazite sand, and phosphate deposits as well as in uranium minerals such as uraninite, carnotite and pitchblende. Uranium present in the Earth is transferred to water, plants, food supplements and then to human beings. Uranium nuclides emit alpha rays of high ionization power and therefore it may be hazardous if inhaled or ingested in higher quantity. Adverse health effects from natural uranium can be due to its radioactive and chemical properties. Radioactive effects are very small from natural uranium; chemically it can be harmful to the kidneys from large exposure. Uranium is a very reactive element readily combining with many elements to form a variety of complexes. The need of estimation of uranium concentration in water is multifold: it is an important fuel for nuclear power reactors, the hydro geochemical prospecting for uranium is essential and the assessment of risk of health hazards due to high concentration of uranium in water is most important [2-4].

Thorium is a naturally occurring radioactive metal that is found at low levels in soil, rocks, water, plants and animals. Almost all naturally occurring thorium exists in the form of either radioactive isotope thorium-232, thorium-230 and thorium-228. There are more than 10 other thorium isotopes that can be artificially produced. Smaller amounts of these isotopes are usually produced as decay products of other radionuclides and as unwanted products of nuclear reactions.

Studies of workers have shown that inhaling thorium dust will cause an increased risk of developing lung disease, including lung cancer, or pancreatic cancer. Liver disease and some types of cancer have been found in people injected in the past with thorium in order to take special X-rays. Bone cancer is also a potential health effect due to the storage of thorium in the bone [5]. The determination of uranium and thorium concentrations in geological samples is very important for the exploration of the natural resources of these elements. These geological samples, natural waters have special importance as indicators of uranium and thorium anomaly.

Brown et al. (1983) found uranium concentrations of 0.5-1.0 ppb in the waters of South Greenland [6]. In his survey of radioactivity in Boyuk Menderes River, Turkey, Kumru (1995) detected uranium and radium concentrations of 0.24-17.65 ppb and 0.016- 0.751 Bq/l respectively [7]. Bolivar et al. (1983) conducted a hydrogeochemical and stream-sediment reconnaissance in the Montrose quadrangle (Colorado) and determined that the uranium concentration in waters there varied within the range 0.02-856 ppb [8].

River Kura and Aras, its main tributary, constitute the main waterways of South Caucasus. Kura and its tributaries receive inputs of water from at least five countries: Armenia, Azerbaijan, Georgia, Iran, and Turkey, before it finally reaches the Caspian Sea. This provides a potential for transboundary water pollution within the Kura–Aras watershed. Azerbaijan, situated along the lower stretches of Kura–Aras, may be particularly exposed to pollution from countries located further up along the rivers [9].

In the present investigations, uranium and thorium concentration in water samples taken along river Kura has been measured using inductively coupled plasma mass spectrometry (ICP-MS) [7]. The Agilent 7700x Series ICP-MS applied to analysis of water samples. The method is based on the direct introduction of samples, without any chemical pre-treatment, into an inductively coupled plasma mass spectrometer (ICP-MS). Uranium and thorium was determined at the mass numbers of 238 and 232 respectively using Bi-209 as internal standard. The main purpose of the study is to measure the level of uranium and thorium in water samples taken along river Kura.

2. Materials and methods

Water samples were collected by means of a standard polyethylene water sampler, which was rinsed a few times with river water from the sampling point before representative sampling from 30 cm below water surface. Two hundred milliliters of water was filtered through a 0.45-μm membrane filter using a plastic filtration assembly without pump. A few drops of high-purity nitric acid were added to the filtrate to adjust to pH<2. The sample was stored at 4°C during transportation to the laboratory. Between each sampling, the water sampler was soaked with 10% v/v nitric acid and rinsed with ultrapure water. All plastic-ware sample bottles, pipette tips, filtration unit and flasks were soaked in 10% v/v HNO3 for 24 h and rinsed with ultra pure water before being used. Milli-Q ultra pure water (resistivity 18.2 MΩ cm, pH (5.5–6.5) was used throughout, and all laboratory operations. In the laboratory by adding an appropriate volume of nitric acid the acid concentration of the samples are adjusted to approximate at 1% (v/v) nitric acid solution.

An Agilent 7700x ICP-MS system was used to measure each sample in helium mode, using standard Agilent-recommended auto tuning for robust tuning conditions (around 1.0 % CeO/Ce). Before to start the analytical measurements, the plasma instrument was allowed to thermally equilibrate for at least 30 minutes and conducted mass calibration and resolution checks in the mass regions of interest.

The samples were analyzed for U and Th using an Agilent model 7700x inductively coupled plasma -mass spectrometry. Multi-element calibration working standards solutions were prepared by appropriate dilution of from 10 mg /L multi-element stock standard solutions- Environmental Calibration Standard- Part # 5183-4688 in 5% HNO3 in /1%HNO3 correspondingly. The evaluation of the analytical curves linearity was done based on injections of the standard solutions prepared in HNO3 1% at the concentration 0.25-0.5-1-5-10 μg/L where this sequence was measured.

The blank and calibration solutions were measured under optimized conditions. The calibration curve was automatically plotted by the instrument. Linear correlation coefficient (r) in all calibration curves were better than 0.9995. Instrument drift and matrix effects during measurement were corrected by using the internal standards include Tb and Bi were prepared by appropriate dilution from stock ICP-MS Internal Standard Mix Part# 5188-6525 after appropriate dilution and added on-line at the time of analysis using a second channel of the peristaltic pump. For quality control purposes, duplicate samples, matrix-spike sample were analyzed. 7700x ICP-MS

Operating Condition used for He mode

Operating condition	Mode
RF power	1550 W
Plasma gas flow	15 L/min
Carrier gas flow	1.05 L/min
Nebulizer pump	0.1 rps
Smp. depth	8 mm
S/C temp	2 degC
Discriminator	4.5 mV
Pulse HV	1149 V
Analog HV	1697 V
He Gas flow	5 mL/min

3. Results and discussion

A total of 15 water samples, have been analyzed for uranium and thorium concentration using ICP-MS. The dissolved uranium and thorium were defined from samples filtered through membranous the filter pore size 0, 45 μm , without preliminary sample preparation. All plastic-ware (sample bottles, pipette tips, filtration unit and flasks were soaked in 10% v/v HNO3 for 24 h and rinsed with ultra-pure water before being used. Milli-Q ultra-pure water (resistivity 18.2 MΩ cm), was used throughout, and all laboratory operations. In the laboratory by adding an appropriate volume of nitric acid the acid concentration of the samples are adjusted to approximate at 1% (v/v) nitric acid solution.

CRM purchased from the National Research Council of Canada (NRCC) were analyzed to validate our procedure: SLRS-5 (river water).

The values of uranium and thorium in samples are presented in Table 1.

Table 1. The measurement concentrations of Thorium and Uranium.

NN	Sampling Points	Th, ug/L	U, ug/L	NN	Sampling Points	Th, ug/L	U, ug/L
1	Jandargol Reservoir	<0.01	1.410	9	Varvara Reservoir	<0.01	1.211
2	River Khrami, Red Bridge	<0.01	0.709	10	Elijan River	<0.01	1.409
3	River Kura, Bridge Poylu	<0.01	0.697	11	River Kura, Till of Aras River	<0.01	1.815
4	River Kura, Girzan village	<0.01	0.716	12	River Aras, Novruzlu village bridge, post	<0.01	7.035
5	Shemkir Reservoir	<0.01	1.481	13	River Kura, Down of Aras Rive, bridge	<0.01	2.919
6	Yenikend Reservoir	<0.01	1.161	14	Duzdag lake	<0.01	2.277
7	Mingacheur Reservoir	<0.01	1.216	15	River Kura, Banka settlement	<0.01	1.914
8	River Kura, Bridge Mingacheur	<0.01	1.209				

The values of thorium on all sampling point less than 0.01µg/L. The quantity of uranium in samples taken from River Kura ranges from 0.697 µg/L in Bridge Poylu to 2.919 µg/L in Down of Aras River bridge with an average value of 1.434 µg/L.

As can be seen from the Table 1, the concentration of uranium in Shamkir, Yenikand, Mingachevir and Varvara reservoirs,and outlet of Mingachevir reservoir, are higher than its value until to Shamkir water reservoir. For our opinion this is due to the fact that the element uranium-is koservativ type element. The observation growth of the uranium concentration after Mingechevir water reservoir till to reaches the river Araz, it can be related to of phosphorus fertilizers used in agriculture in these areas, while the discharge of drainage water in the Kura River and on the north side of the rivers, which mixed with river Kura. It is known that the phosphorous fertilizers consist some uranium. Since it is a relatively large concentration of uranium in the Araz River, lead to rise of the concentration of uranium in Kura reaver. Changes the concentration of uranium along the river Kura schematically shown in the Fig.1.

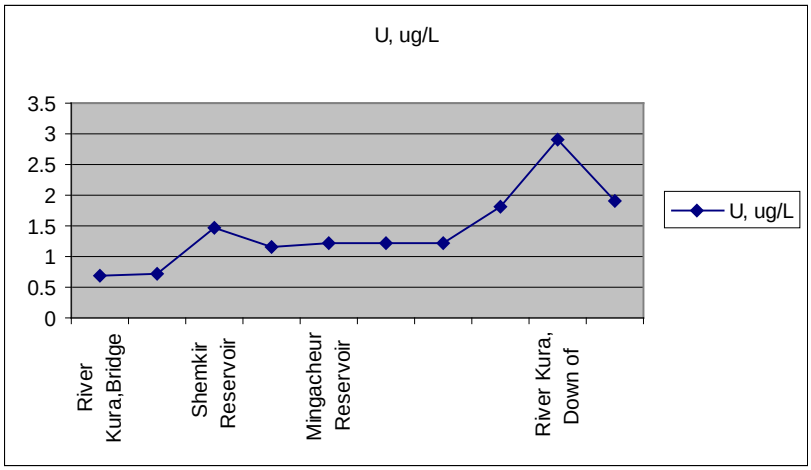

Fig.1 Spatial distribution of uranium along River Kura

In the work also are measured the concentrations of uranium and thorium a few point of the basin at the Kura-Araz (Khrami and Alican rivers, lakes Duzdag and Jandar)

The EPA and WHO set a Maximum Contaminant Level for uranium of 30 micrograms per liter based on the chemical toxicity of uranium. The Canadian current guideline for uranium in drinking water is a Maximum Acceptable Concentration (MAC) of 20 µg/L. The Indian Atomic Energy Regulatory Board has set a limit for uranium in drinking water of 60 µg/L.

The concentration of uranium in measured water samples, were less than the limit of recommended by the World Health Organization (WHO) and US Environmental Protection Agency-30 µg/L

4. Conclusion

From the present observations it can be concluded that the concentration of uranium level vary considerably from natural source to source and place to place.

The range of uranium in the water samples from along River Kura varies from 0.697 to 7.035 ug L^{-1} with an average value of 1.812 ug L^{-1}. The measured thorium content in all water samples were less than 0.01 ug/L. The concentration of uranium in measured water samples, were less than the limit of recommended by the World Health Organization (WHO) and US Environmental Protection Agency-30 µg/L

The daily intake of uranium through drinking water in the region is much less than the tolerable intake limit.

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ОПРЕДЕЛЕНИЕ УРАНА И ТОРИЯ В ВОДНЫХ ПРОБАХ ВЗЯТЫХ ВДОЛЬ РЕКИ КУРА С ПРИМЕНЕНИЕМ МАСС-СПЕКТРОМЕТРА С ИНДУКТИВНО СВЯЗАННОЙ ПЛАЗМОЙ

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Резюме: Концентрации Урана и Тория в пробах взятых вдоль Реки Кура и в некоторых точках Бассейна Кура и Араза были определены с применением Масс-Спектрометра с Индуктивно связанной плазмой, фирмы Аджилент, серии 7700х. Концентрация Урана в взятых водных образцах находится в интервале 0.697-7.035 мкг/л, с среднем значением 1.812 мкг/л. А значение Тория на всех точках отбора пробы было меньше чем 0.01 мкг/л. Содержание урана во всех водных образцах было меньше чем пределное значение - 30 мкг/л, рекомендованное Всемирной Организацией здравоохранения (ВОЗ) и американским Управлением по охране окружающей среды.

Ключевые слова: Уран, Торий, Масс-спектрометр с индуктивно связанной плазмой, радионуклиды.

KÜR ÇAYI BOYUNCA GÖTÜRÜLMÜŞ SU NÜMUNƏLƏRİNDƏ, URAN VƏ TORİUMUN ICP-MS-lə TƏYİN EDİLMƏSİ

M.M. Əhmədov, F.Y. Hümbətov, V.S. Balayev, B.A. Suleymanov, K.S. Yusifova, Y. M.Əliyeva

Xülasə: Kur çayı boyunca və eləcədə Kur-Araz hövzəsində bir sıra nöqtələrdən götürülmüş su nümunələrində, Acilent firmasının istehsalı olan 7700x serial İnduktiv Əlaqəli Plazma-Kütlə Spektrometrini (İƏP-KS) tətbiq etməklə uran və toriumun konsentrasiyaları təyin edilmişdir. Götürülən su nümunələrində uranın konsentrasiyası 0.697–7.035 ug/L intervalında olmaqla, orta qiyməti 1.812 ug/L-dır. Toriumun konsentrasiyası butun nöqtələrdə 0.01 ug/L-dən kiçik olduğu müəyyən edilmişdir. Bütün su nümunələrində uranın miqdarı Ümum Dünya Sağlamlıq Təçkilatının və Amerika Birləşmiş Ştatlarının Ətraf Mühit Agentliyinin uran üçün qıbul etdiyi limitdən kiçikdir.

Açar sözlər: Uran, Torium, İnduktiv Əlaqəli Plazma-Kütlə Spektrometri (İƏP-KS), radionuklidlər.