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Uranium and Thorium Determination in Water Samples Taken along River Kura

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Abstract: The uranium and thorium concentrations 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} in water take along River Kura. The values of thorium on all sampling point less than 0.01 µg/L. The measured uranium content in water samples has been found to be less than the limit of 30 ug/L recommended by the WHO (World Health Organization) and US Environmental Protection Agency.

Key words: Water quality management, radionuclides, ICP-MS, Kura-Araks rives, Azerbaijan.

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 radionuclides 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 × 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} percent and are found in rocks and minerals such as granite, metamorphic rocks lignite, 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

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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].

Azerbaijan is a country of small rivers. There are more than 8,300 rivers in its area. Only 21 of them have 100 km long in the country area. All rivers refer to Caspian pool. The rivers of Samur-Devchi and Lenkoran plains directly flow into Caspian Sea and the rest by Kur and Araz streams. Existing hydrographic network was divided unequally. The largest density is in the hilly areas. The smallest network density is in Djeyranchol, Gobustan, Apsheron, Southeast Shirvan and in Kur-Araz lowland.

The river water is polluted by impact of human factors and in the result of drainage of salty underground waters in plain areas the salinity is increasing, the chemical structure becomes complicated and the water type changes. These cases are observed in Shirvan. in the streams of Kur flown from Mil-Karabagh lowlands as well as in Kur itself and also in Araz River.

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. In Georgia water of the Kur is used for agriculture, in Armenia for agriculture and industry, in Azerbaijan it is used as drinking water supply, agriculture and industry. Azerbaijan receives heavily polluted water from its neighbors resulting in serious problems in health of population, because the Kur is a source of drinkable water. The Kura also pollutes the Caspian Sea, increasing degree of its pollution. Azerbaijan, situated along the lower stretches of Kura–Aras, may be particularly exposed to pollution from countries located further up along the rivers [6-8].

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) [9]. 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).

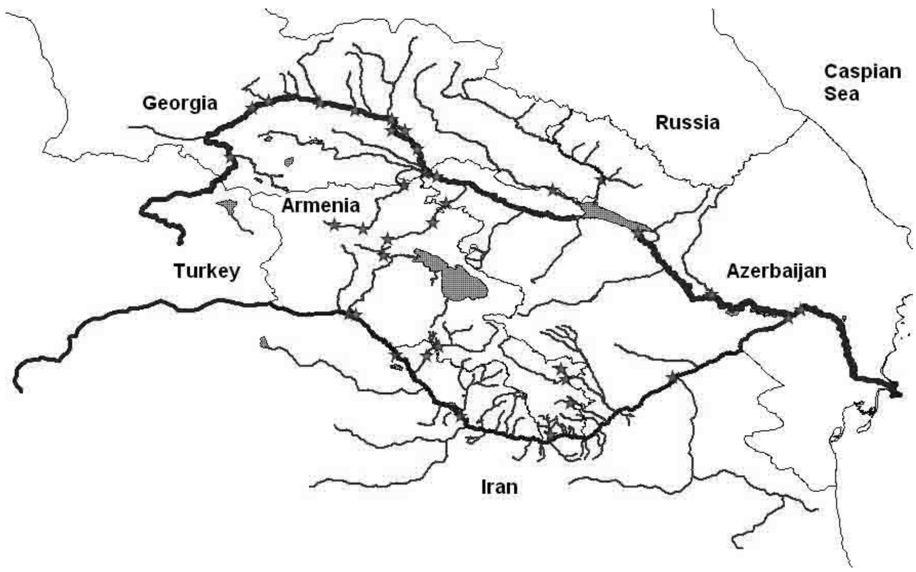

Fig. 1 Kura-Araks watershed.

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% HNO_3 in /1% HNO_3 correspondingly. The evaluation of the analytical curves linearity was done based on injections of the standard solutions prepared in HNO_3 1% at the concentration 0.25, 0.5, 1, 5 and 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:

RF power: 1550 W;
S/C tempr: 2 degC;
Plasma gas flow: 15 L/min;
Discriminator: 4.5 mV;
Carrier gas flow: 1.05 L/min;
Pulse HV: 1,149 V;
Nebulizer pump: 0.1 rps;
Analog HV: 1,697 V.
Smpl depth: 8 mm;
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 HNO_3 for 24 h and rinsed with ultra pure water before being used. Milli-Q ultra pure water (resistivity 18.2 MΩ·cm), was

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

Table 2 The calculated radioactivity of Thorium and Uranium for measured samples.

NN	Sampling points	Th232 (mBq/g)	U (mBq/g)	NN	Sampling points	Th232 (mBq/g)	U (mBq/g)
1	Elican River	< 4.07E-5	1.75E-02	9	Jandargol Reservoir	< 4.07E-5	1.75E-02
2	Varvara Reservoir	< 4.07E-5	1.51E-02	10	River Kura, Bridge Poylu	< 4.07E-5	8.67E-03
3	River Kura, Bridge	< 4.07E-5	1.50E-02	11	River Kura, Till of Aras River	< 4.07E-5	2.26E-02
4	Mingacheur Reservoir	< 4.07E-5	1.51E-02	12	River Aras, Novruzlu village bridge, post	< 4.07E-5	8.75E-02
5	Yenikend Reservoir	< 4.07E-5	1.44E-02	13	River Kura, Down of Aras Rive, bridge	< 4.07E-5	3.63E-02
6	Shemkir Reservoir	< 4.07E-5	1.84E-02	14	Duzdag Lake	< 4.07E-5	2.83E-02
7	River Kura, Girzan village	< 4.07E-5	8.91E-03	15	River Kura, Banka settlement	< 4.07E-5	2.38E-02
8	River Khrami, Red Bridge	< 4.07E-5	8.82E-03				

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

The values of uranium and thorium in samples are presented in Table 1. The values of thorium on all sampling point less than 0.01 μg/L. The values of uranium in samples ranges from 0.697 μg/L in River Kura Bridge Poylu to 7.035 μg/L in River Aras Novruzlu village bridge with an average value of 1.812 μg/L . 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 MAC (Maximum acceptable concentration) of 20 μg/L. The Indian Atomic Energy Regulatory Board has set a limit for uranium in drinking water of 60 μg/L.

The measured uranium content in water samples has been found to be less than the limit of 30 μg/L recommended by the World Health Organization (WHO) and US Environmental Protection Agency [10].

4. Conclusions

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 $ug \cdot L^{-1}$ with an average value of 1.812 $ug \cdot L^{-1}$. The measured thorium content in all water samples are less than

0.01 ug/L. However, the uranium concentration in all the water samples is well below the recommended limit of 30 $\mu g \cdot L^{-1}$. The daily intake of uranium through drinking water in the region is much less than the tolerable intake limit. The annual effective dose from drinking water samples of these areas is in the range of 0.33-37.78 μSv, which is safe from the health hazard point of view.

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