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URANIUM AND THORIUM DETERMINATION IN WATER SAMPLES TAKEN FROM RIVERS OF AZERBAIJAN REPUBLIC

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Abstract: Concentrations of Th and U, and physicochemical parameters such as DO, TDS, Conductivity, pH, Temperature in water samples were measured and statistically analyzed. Concentrations of uranium and thorium in water samples collected from different rivers of Azerbaijan Republic has been measured using inductively coupled plasma mass spectrometry. The uranium concentration varies in the range between 0.017–3.263 ug L^{-1} with a mean value of 0.385 ug L^{-1} in analyzed water samples. Thorium concentration is less than 0.01μg/L in all sampling points (except two stations). The measured uranium content in all water samples has been found to be less than the limit of 30 ug/L recommended by the World Health Organization (WHO) and US Environmental Protection Agency.

Keywords: Uranium, Thorium, River water, 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 % 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. 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 in the exploration of the natural resources of this element. Of 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 hydro geochemical 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). B.S.Bajwa and et.al detected uranium concentration in 498 drinking water samples taken from four districts of SW-Punjab India has been found to vary between 0.5–579 $\mu g l^{-1}$ with an average of 73.5 $\mu g l^{-1}$ (9). The concentration of uranium in various rivers of India such as Yamuna (0.09–3.61 ppb) and Chambal (0.2–1.74 ppb) (10), Bhagirathi (2.11–3.96 ppb) and Alakanda (1.86 ppb) (11) have been studied earlier. Springs and streams in Himachal Pradesh, India had 0.07 to 4.65 ppb of uranium (12). The estimated worldwide averages for dissolved uranium in rivers range between 0.3-0.6 ppb (13) and reach to abnormal high values in some cases due to chemical weathering of uraniferous rocks such as in Platte River of the North American High Plains Region where uranium contents reach up to 31.7 ppb (14). Palmer and Edmond (15) determined the concentrations of dissolved uranium in forty major rivers from around the world with an average concentration of 0.31 ppb. They noted that this value could be biased by the very high levels observed in the Ganges-Brahmaputra and the Yellow River. Excluding these two river systems, the global average of uranium is reduced to 0.19 ppb. Compared to uranium, thorium is highly particle-reactive element and does not readily occur as a dissolved ion (Langmuir and Herman, (16).

In the present study, waters collected from different sources of Azerbaijan Republic were analyzed for uranium and thorium concentration determination. 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-Devechi 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. 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. The distribution of Uranium and Thorium concentration along River Kura and Aras studied in works (17,18).

In the present investigations, uranium and thorium concentration in water samples taken 24 different rivers located in the northwest and northwestern parts of the Republic of Azerbaijan has been measured using inductively coupled plasma mass spectrometry (ICP-MS). The Agilent 7700x Series ICP-MS applied to analysis of water samples.

2. Materials and methods

In this study, 25 river water samples were collected during April 2017 to August 2018 (Table 1.).

Table 1. The geographical coordinates of sampling stations

N:	Sampling point description	Geographical coordinate	
Stations	Rivers	N	E
St.1	Pirssaatçay	40.591560	48.697700
St.2	Ağsuçay	40.679813	48.497303
St.3	Girdmançay	40.622645	48.251261
St.4	Vəndamçay	40.954296	47.933565
St.5	Dəmiraparançay	41.017576	47.898107
St.6	Qaraçay	40.79079	47.621709
St.7	Tikanlıçay	41.009793	47.752516
St.8	Nəzərçay	40.940179	47.612026
St.9	Türyançay	40.773726	47.605466
St.10	Sincan çay	40.931651	47.580803
St.11	Daşağılçay	41.096443	47.362361
St.12	Küngüt çay	41.083058	47.294746
St.13	Əlicançay	40.864997	47.266148
St.14	Qaynar çay	41.255800	47.207083
St.15	Kiş cayı	41.145181	47.038964
St.16	Şin cayı	41.332504	47.103837
St.17	Əyri çay su anbarı	41.190865	46.974076
St.18	Hamamçay	41.467143	47.079202
St.19	Kümrükçay	41.363886	46.764973
St.20	Qaraçay	41.573836	46.764166
St.21	Talaçay	41.594565	46.555447
St.22	Katexçay	41.685084	46.573762
St.23	Katexçay,	41.585550	46.36064
St.24	Balakənçay	41.639130	46.36746
St.25	Mazımçay	41.658223	46.249608

The water samples were collected after 30 minutes of pumping to avoid stagnant and contaminated water. The white plastic containers were rinsed out 3-4 times with the water to be sampled. 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 rinsed with ultrapure water.

The samples were analyzed for U and Th using an Agilent model 7700x inductively coupled plasma -mass spectrometry. A portable pH meter (Lutron, PH-201) and a conductivity.

TDS meter (Shimandzu 1100) was used for the determination of pH and TDS, respectively. 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. 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. CRMs were purchased from the NRCC (National Research Council of Canada) and at the Absolute standard and were analysed to validate our procedure: SLRS-5 (river water) and SRM 1640 (naturel water) a respectively.

3. Results and discussion

A total of 25 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.

Results of physicochemical analysis of the water samples collected from 25 monitoring station are given as follows. Mainly concentrations of physicochemical parameters such as DO, TDS, Conductivity, pH, Temperature, Th and U were statistical analyzed (Table.1). The results showed that the DO concentration ranged from 7.49-10.2 mg L-1, the TDS concentrations varied from 78 to 603 mg L-1, the COND values ranged from 134 to 1044 *μSm/Cm*, pH varied from 7.41-8.63, and the temperature ranged from 8.4-22.4 C. The values of thorium on all sampling point (except St.1 and St.19) less than 0.01μg/L. The value of uranium in samples ranges from 0.017 μg/L in Katehchay River to 3.263 μg/L in Pirsaatchay River with an average value of 1.434 μg/L.

Table 2. The concentrations of the analyzed parameters in water samples

	pH	COND	TDS	DO	T	Th	U
		µsm/cm	*mg/L*	*mg/L*	*oC*	ug/L	ug/L
St.1	8.17	551	319	8.86	15.6	0.014	3.263
St.2	7.96	602	348	8.90	15.8	<0,01	1.210
St.3	8.24	597	345	9.42	14.2	<0.01	0.464
St.4	8,12	286	165	9.50	11.0	<0,01	0.099
St.5	8.28	377	218	9.74	8.4	<0,01	0.075
St.6	7.93	460	266	8.86	16.4	<0.01	0.227
St.7	7.95	398	230	9.95	8.8	<0,01	0.078
St.8	8.02	493	280	9.59	12.1	<0,01	0.187
St.9	7.96	485	279	9.23	15.4	<0,01	0.270
St.10	7.94	457	264	10.16	9.6	<0,01	0.165
St.11	7.96	321	186	9.59	10.3	<0,01	0.160
St.12	7.87	281	162	9.38	12.2	<0.01	0.131
St.13	7.78	856	495	7.84	22.4	<0,01	1.133
St.14	8.59	449	260	7.97	16.4	<0,01	0.194
St.15	8.13	471	272	8.20	19.9	<0.01	0.350
St.16	8.13	351	203	7.49	20.7	<0.01	0.136
St.17	8.06	496	286	8.97	20.2	<0.01	0.475
St.18	8.38	237	137	8.97	9.8	<0.01	0.042
St.19	7.96	1044	603	9.29	15.1	0.011	0.495
St.20	8.63	358	207	8.17	18.1	<0.01	0.109
St.21	8.26	274	158	8.28	22.1	<0.01	0.055
St.22	7.41	135	78	9.54	11.2	<0.01	0.017
St.23	7.93	251	144	8.22	17.4	<0.01	0.090
St.24	7.55	329	190	7.67	21.7	<0.01	0.086
St.25	7.52	216	124	8.68	15.9	<0.01	0.114
MİN	7.41	135	78	7.49	8.4	<0,01	0.017
MAX	8.63	1044	603	10.2	22.4	0.014	3.263
MEAN	8.03	431	249	8.90	15.23		0.385
St.Dev	1.63	199	115	0.744	4.38		0.672

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.

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 g/L. The Indian Atomic Energy Regulatory Board has set a limit for uranium in drinking water of 60µg/L.

Correlation analysis provides an effective way to reveal the relationships between multiple variables and thus has been helpful in understanding influencing factors as well as the sources of chemical components. And the analytical results are listed in Table 3.

Table 3. Pearson correlation matrix, between different parameters in the rivers water

	pH	TDS	DO	T	U
pH	1				
TDS	0.091	1			
DO	-0.14	-0.013	1		
T	0.004	0.225	-0.868	1	
U	0.057	0.437	-0.08	0.168	1

According to the results of correlation matrices, significant negative correlations existed between DO and Temperature (R=-0.868), there was moderate positive correlation between U and TDS (R=0.437); very weak positive correlation betveen U and pH and temperature. Very week negative correlation existed between DO and pH, DO and TDS; weak positive correlations appeared between TDS and temperature. The analysis results indicated that significant positive correlations not existed between parameters of water quality.

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AZƏRBAYCAN RESPUBLİKASI ÇAYLARINDAN GÖTÜRÜLMÜŞ SU NÜMUNƏLƏRİNDƏ URAN VƏ TORİUMUN TƏYİN EDİLMƏSİ

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Xülasə: Su nümunələrində Th və U konsentrasiyaları, HO, THQ, Keçiricilik, pH, Temperatur kimi fizikokimyəvi parametrlər ölçülmüş və statistik olarak analiz edilmişdir. Azərbaycan Respublikası ərazisindəki müxtəlif çaylardan götürülən su nümunələrində uran və torium konsentrasiyaları induktiv cütləşmiş plazma - kütlə spektrometri vasitəsilə ölçülmüşdür. Analiz edilən su nümunələrində uran konsentrasiyası ortalama qiymət 0.385 ug L^{-1} olmaqla 0.017–3.263 ug L^{-1} arasında olmuşdur. Torium konsentrasiyası bütün nümünəgötürmə nöqtələrində (iki stansiya istisna olmaqla) 0.01µg/L dən azdır. Bütün su nümunələrində ölçülən uran miqdarının Dünya Sağlamlıq Təşkilatı (DST) və ABŞ Ətraf Mühiti Mühafizə Agentliyinin məsləhət gördüyü limit qiyməti olan 30 ug/L dən az olduğu müəyyənləşdirilmişdir.

Açar sözlər: Uran, Torium, Çay suyu, Azərbaycan

ОПРЕДЕЛЕНИЕ УРАНА И ТОРИЯ В ОБРАЗЦАХ ВОДЫ ВЗЯТЫХ ИЗ РЕК АЗЕРБАЙДЖАНСКОЙ РЕСПУБЛИКИ

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Резюме: Измерялись и статистически анализировались концентрации Th и U и физико-химические параметры, такие как DO, TDS, проводимость, pH, температура в образцах воды. Концентрации урана и тория в образцах воды, собранных из разных рек Азербайджанской Республики, были измерены с использованием масс-спектрометрии с индуктивно связанной плазмой. Концентрация урана варьируется в диапазоне 0,017-3,263 мкг/л со средним значением 0,385 мкг/л в анализируемых образцах воды. Концентрация тория составляет менее 0,01 мкг/л во всех точках отбора проб (кроме двух станций). Было установлено, что измеренное содержание урана во всех образцах воды меньше предела 30 мкг/л, рекомендованного Всемирной Организацией Здравоохранения (ВОЗ) и Агентством по охране окружающей среды США.

Ключевые слова: Уран, Торий, Речная вода, Азербайджан