ЕҢБЕК ҚЫЗЫЛ ТУ ОРДЕНДІ
«Ә. Б. БЕКТҰРОВ АТЫНДАҒЫ
ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»
АКЦИОНЕРЛІК ҚОҒАМЫ

ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА

CHEMICAL JOURNAL of KAZAKHSTAN

АКЦИОНЕРНОЕ ОБЩЕСТВО
ОРДЕНА ТРУДОВОГО КРАСНОГО ЗНАМЕНИ
«ИНСТИТУТ ХИМИЧЕСКИХ НАУК
им. А. Б. БЕКТУРОВА»

4 (64)

ОКТЯБРЬ – ДЕКАБРЬ 2018 г.

ИЗДАЕТСЯ С ОКТЯБРЯ 2003 ГОДА

ВЫХОДИТ 4 РАЗА В ГОД

АЛМАТЫ
2018

UDC 504.5

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CONTENT OF URANIUM ISOTOPES IN COALS OF KAZAKHSTAN

Abstract. The content of natural isotopes of uranium (uranium-238 and uranium-234) is considered in the presenting paper. The samples of coals from three main coal deposits, located on the territory of Kazakhstan (Karazhyra, Shubarkol and Ekibastuz) were analyzed by alpha-spectrometric method after the corresponding chemical separation, which included separation of radionuclides by liquid-liquid extraction (30% solution of TBP in toluene) and preparation of counting sample by electrodeposition. The measurements were done at the high resolution alpha-spectrometer (Canberra, semiconductor PIPS detectors) and the Alpha Analyst program was used for processing spectra.

The content of total uranium increases in the following series: coal of Karazhyra deposit < coal of Shubarkol deposit < coal of Ekibastuz deposit.

The results showed that the most safety is coal from Karazhyra coal deposit (0.55±0.12 Bq/kg and 0.85±0.14 Bq/kg for uranium-238 and uranium-234, correspondently). The highest values of concentration of uranium isotopes were recorded for coals of Ekibastuz deposit, but even for it the content of uranium-238 is much lower than the average natural radionuclide activity concentrations in coal.

Keywords: coal, uranium isotopes, alpha-spectrometry, Karazhyra, Shubarkol, Ekibastuz.

Introduction. In recent years naturally occurring radioactive materials got increasing attention all over the world [1].Naturally occurring radionuclides may become concentrated in the residues, waste material and end products due to non-nuclear industrial activities such as burning fossil fuel, phosphates and fertilizers production, metals and rare earth elements mining, oil and gas production.

In primary energy consumption, the coal takes second place approximately 29% share after oil, which takes the first place about 33% share as of 2015 [2]. Kazakhstan contains Central Asia's largest recoverable coal reserves, 3.69% of the world total. The greater part (63%) of counted (i.e. measured) reserves consists of bituminous coal, found in Karaganda, Ekibastuz and Teniz-Korzhankol basins, Kushokinsk, Borly, Shubarkol and Karazhyra deposits, and elsewhere.

As a result of coal firing wastes such as fly ash, slag and flue gas are also produced [3]. Coal, residues and wastes produced by the combustion of coal contain naturally occurring radionuclidesof uranium and thorium series [1, 4]. The average natural radionuclide activity concentrations in coal are given as 20 Bq kg^{-1} for ^{238}U, ^{232}Th and decay products [3]. Uranium in coal is mainly associated with organic matters, and a lesser extent occurs in minerals [5].

In the process of coal combustion, the natural radionuclides can be partially released to the atmosphere [6], resulting to increas of human exposure.

After high-temperature combustion most radionuclides in coal end up in ash and slag, which are further reused to make building materials such as cinder bricks. These bricks release radon and its decay products. which lead to increase the public exposure [1]. Another application of coal fly ash is in road construction and asphalt's mixture [7], in order to increase subgrade support capacity of pavements [8]. The natural radionuclide activity concentrations of the coal combustion products are much higher than the average concentrations in the Earth’s crust. The average natural radionuclide activity concentrations for^{238}U, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{232}Th, ^{228}Th, and ^{228}Ra are 200, 240, 930, 1700, 70, 110, and 130 Bq kg^{-1} respectively [3]. In this direction, coal-based thermal power plants are considered as the most important source of technologically enriched natural radioactivity [9].

The amounts of natural radionuclides caused human exposure by different ways depend on a number of factors, including initial concentrations in coal[4]. The determination of initial concentration of uranium isotopes in coals of Kazakhstan is a goal of this investigation.

MATERIALS AND METHODS

Object description. The Karazhyra deposit is one of Kazakhstan’s higher grade coal deposits containing more than 1 billion tonnes of reserves with a large proportion being open pittable. The Karazhyra field was discovered in 1967, and locateon135 km south-west of Semey city towards the Zhana-Semey district of the East Kazakhstan region. Thedepositareais 21.4 km^2 and brand D coal is mined.

The Shubarkol deposit located in the Karaganda region, 350 km south-west of the city of Karaganda. The area of deposit is 70 km^2. Explored reserves of 1.5 bil-lion tons. Discovered in 1984, explored in 1984-1986. Brand D coal is mined.

The Ekibastuz coal deposit was discovered in the second half of the 19th century in Bayanaul area, Pavlodar region.The area of deposit is 155 km^2 with a length of 24 km and a maximum width of 8.5 km. Total geological reserves of coal is about 10 billion tons. According to industrial marking, they are classified as weakly baking (CC grade).

Determination of uranium isotopes. To pre-crushed coal samples about mass of 5 g U-232 tracer with precise activity was added. Samples were left for 24 hours. Uranium was extraction from the coal sample by 10% solution of sodium carbonate. After desorption process, the solution was filtered. Obtaining sample was boiled during 20 minutes for removing of carbon dioxide. 2 sm^3 of 1% $FeCl_3$ was added. After which iron hydroxide from the solution was precipitated by ammonium hydroxide until it reached pH = 8-9. Process of coagulation was carryed out. After coagulation, the precipitate was filtered and was dissolved in 50 ml of hot 7M HNO_3. The solution of nitric acid contains uranium isotopes.

Radiochemical separation by extraction was used for separation of uranium from other alpha-emitting radionuclides. 15 sm^3 of 30% solution of tributyl phosphate was added in a separation funnel to the previously prepared solution. The solution was shaken for 5 minutes. In this step, uranium compounds from the inorganic solution was extracted to organic phase. The separation of impurities was done by 15 ml of 7M HNO_3 (2 times) and 15 ml of 0.04M HF in 0.25 M HNO_3.

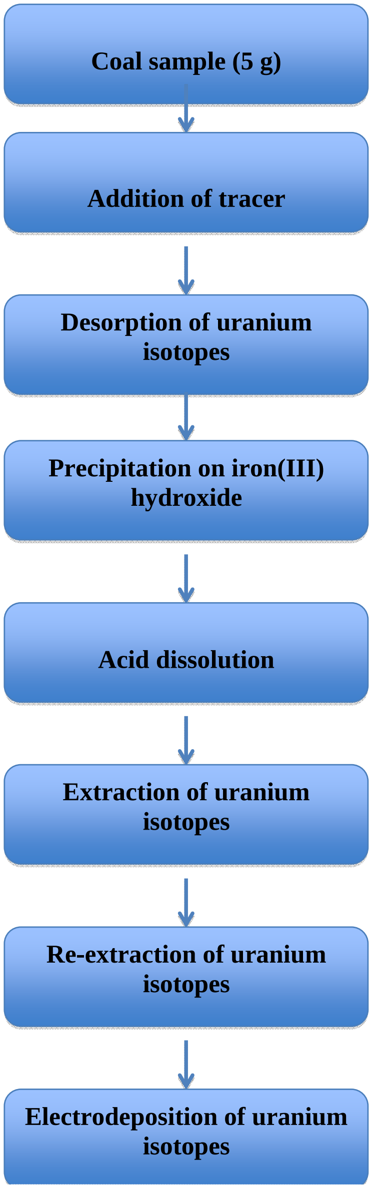

Figure 1 – Sequential circuit for determination of uranium isotopes

The last step was re-extraction of uranium from the organic to aqueous phase. 15 ml of bidistilled water was added in separation funnel and was shaken during one minute. This procedure was repeated three times.

The sample obtained after re-extraction was evaporated and beaker was treated by concentrated nitric acid three times in order to remove residues of organic substances.

Uranium isotopes were electrodeposited at stainless steel disc. The procedure consist of adding 4 ml of 0.5 M HNO_3, 4 ml of 1%Trilon B, 1 ml of 25 % NH_4Cl and 1 ml of saturated $(NH_4)_2C_2O_4$ to the beaker containing the dry residue after evaporation. The solution was put into electrodeposition cell and the pH was adjusted approximately to 8-9 by the adding ammonium hydroxide. Electrodeposition of uranium was conducted during 45 minutes with a current of 1-2 A [11, 12].

The applied radiochemical separation is represented at the figure 1.

Samples were measured by high resolution alpha-spectrometer (Canberra, semiconductor PIPS detectors) and the Alpha Analyst program was used for processing spectra.

RESULTS AND DISCUSSION

The results obtained by alpha-spectrometry method are presented in the charts (figures 2–5).

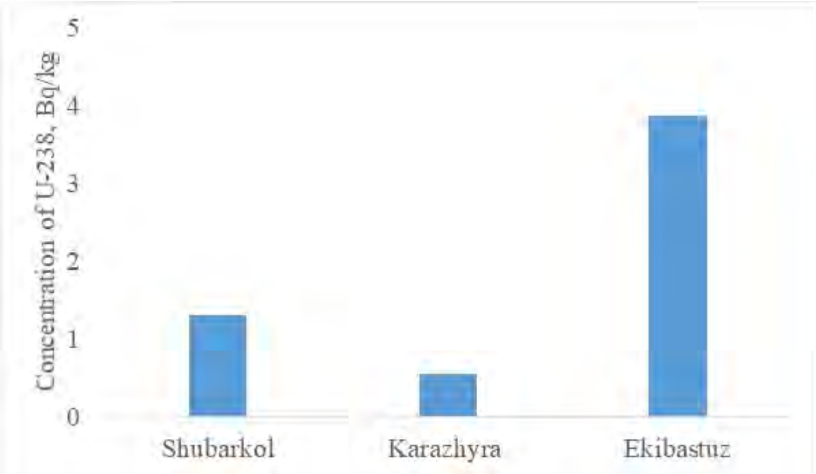

Figure 2 – The concentration of uranium-238 in coals

The lowest content (0.55±0.12 Bq/kg) of uranium-238 was in coal of Karazhyra deposit, as the highest was incoal of Ekibastuzdeposit and was equal to 3.9±0.4 Bq/kg, so even in it the content of uranium-238 was lower than the average natural radionuclide activity concentrations in coal [3].

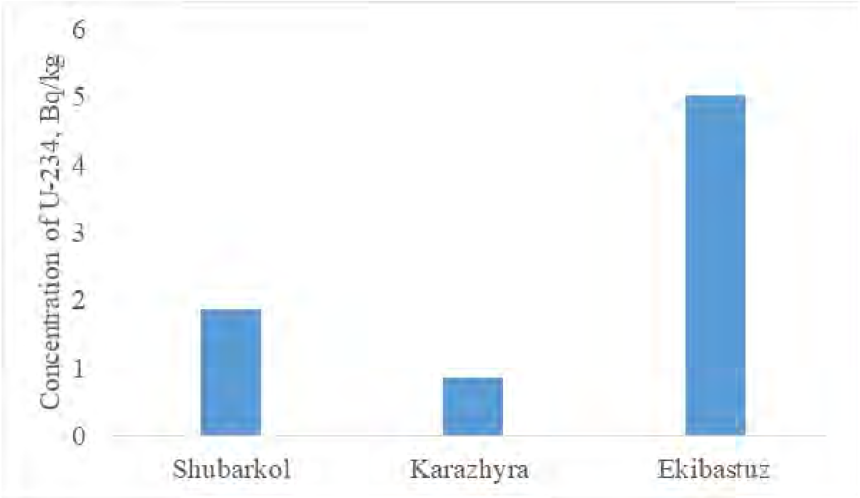

Figure 3 – The concentration of uranium-234 in coals

The content of uranium-234 was also higher in coal of Ekibastuzdeposit and was equal to 5.0±0.4Bq/kg, as the lowest value (0.85±0.14 Bq/kg) was found in coals of Karazhyra deposit.

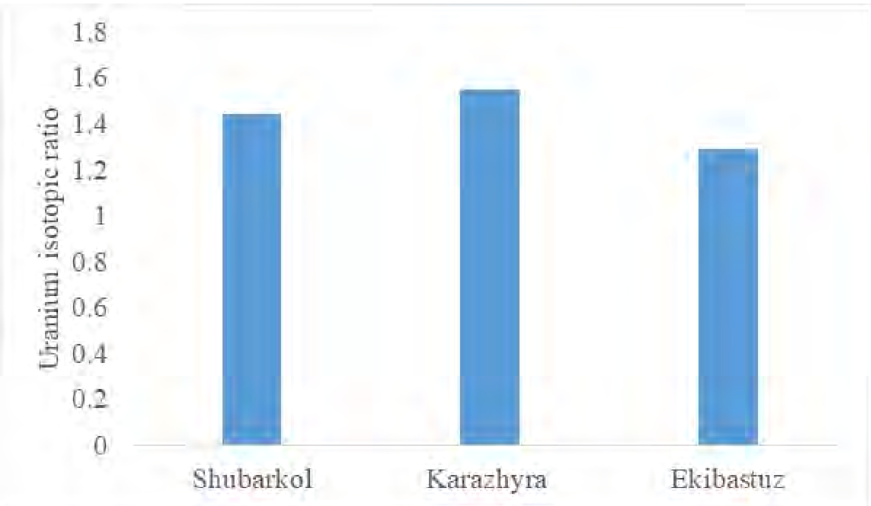

Figure 4 – The $^{234}U/^{238}U$ isotopic ratio in coals

The isotopic ratio $^{234}U/^{238}U$ was higher than equilibrium in all investigated samples.

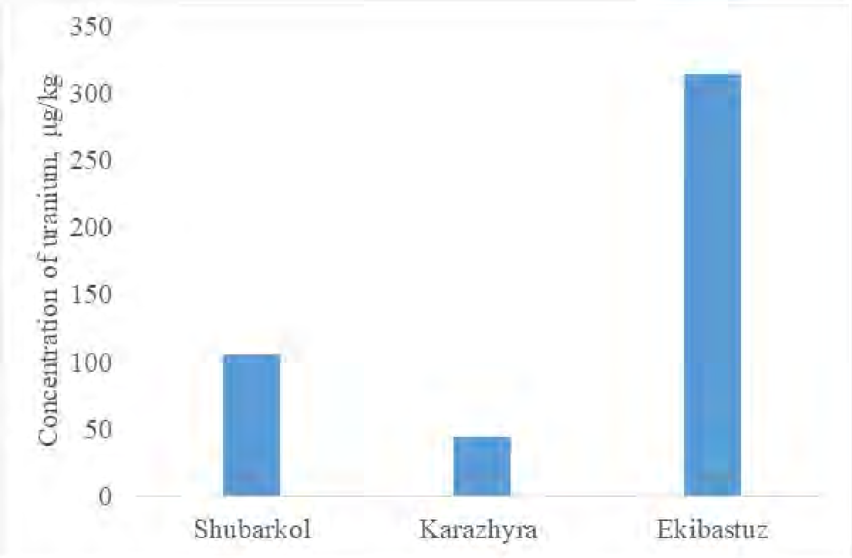

Figure 5 – Concentration of uranium in coals

The content of total uranium increases in the following series: coal of Karazhyra deposit (44±10 µg/kg) < coal of Shubarkol deposit (105±17 µg/kg) < coal of Ekibastuz deposit (314±28µg/kg).

The obtained results show that the most safety from radiological point of view is coal from Karazhyra coal deposit.

Conclusions. The obtained results showed that the most safety from radiological point of view was coal from Karazhyra deposit. Where the content of isotopes of uranium were the lowest and radiactivity equal about 0.55±0.12 Bq/kg and 0.85±0.14 Bq/kg for uranium-238 and uranium-234, correspondently.The content of total uranium compounds increase in the following swquences: coal of Karazhyra deposit (44±10 µg/kg) < coal of Shubarkol deposit (105±17 µg/kg) < coal of Ekibastuz deposit (314±28 µg/kg).

The highest values of concentration of uranium isotopes were recorded for coals of Ekibastuz deposit, but even for it the content of uranium-238 is much lower than the average natural radionuclide activity concentrations in coal [3].

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Резюме

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ҚАЗАҚСТАН КӨМІРІНДЕГІ УРАН ИЗОТОПТАРЫНЫҢ МӨЛШЕРІ

Ұсынылған мақалада уран изотоптарының (уран-238 және уран-234) мөлшерін анықтау қарастырылған. Қазақстандағы үш негізгі тас көмір кен орындарының (Қаражыра, Шұбаркөл және Екібастұз) көмір үлгілері сұйық-сұйықтық экстракциясы (30% ТБФ толуолда) және электрлі тұндыру әдісімен санақ үлгісін дайындау сияқты тиісті химиялық дайындықтан кейін, альфа-спектрометрия әдісімен талданылды. Өлшем мәліметтері жоғары ажыратымдылыққа ие альфа-спектрометрде (Canberra, жартылай өткізгіш PIPS детекторлары) алынды, спектрді өңдеу үшін Alpha Analyst бағдарламасы қолданылды.

Уранның жалпы мөлшері келесі ретте артады: Қаражыра кен орнының көмірі < Шұбаркөл кен орнының көмірі < Екібастұз кен орнының көмірі.

Зерттеулер Қаражыра кен орнының көмір үлгілері радиациялық тұрғыда ең қауіпсіз екендігін көрсетті (0,55±0,12 Бк/кг және 0,85±0,14 Бк/кг сәкесінше уран-238 және уран-234 үшін). Екібастұз кен орнынан алынған көмір үлгілерінде уран изотоптарының ең жоғары концентрациясы анықталды, алайда уран-238 изотопының мөлшері көмірдегі табиғи радионуклидтердің орташа концентрацияларынан әлдеқайда төмен.

Түйін сөздер: көмір, уран изотоптары, альфа-спектрометрия, Қаражыра, Шұбаркөл, Екібастұз.

Резюме

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СОДЕРЖАНИЕ ИЗОТОПОВ УРАНА
В УГЛЯХ КАЗАХСТАНА

Содержание изотопов урана (урана-238 и урана-234) в углях рассматривается в представленной статье. Образцы угля трех основных угольных месторождений, расположенных в Казахстане (месторождение Каражыра, Шубарколь и Экибастуз), были проанализированы с использованием альфа-спектрометрического метода после соответствующей химической подготовки, которая включала разделение радионуклидов жидкостно-жидкостной экстракцией (30%-ный раствор ТБФ в толуоле) и приготовление счетного образца методом электроосаждения. Измерения проводились на альфа-спектрометре высокого разрешения (Canberra, полупроводниковые PIPS-детекторы), для обработки спектров использовалась программа AlphaAnalyst.

Содержание общего урана увеличивается в следующем ряду: уголь с месторождения Каражыра < уголь с месторождения Шубарколь < уголь с месторождения Экибастуз.

Результаты показали, что наиболее безопасным является уголь месторождения Каражыра (0,55±0,12 Бк/кг и 0,85±0,14 Бк/кг для урана-238 и урана-234, соответственно). Самые высокие концентрации изотопов урана были зарегистрированы для угля с месторождения Экибастуз, но даже для него содержание урана-238 намного ниже, чем средние концентрации природных радионуклидов в угле.

Ключевые слова: уголь, изотопы урана, альфа-спектрометрия, Каражыра, Шубарколь, Экибастуз.