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DETERMINATION OF TRACES OF URANIUM AND THORIUM IN SOME EGYPTIAN ENVIRONMENTAL MATRICES BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

Uranium and thorium isotopes found in soil, rock, water, plant, air, etc., contribute to the exposure of the population to natural radiation. Uranium and thorium concentrations in some Egyptian environmental samples like Toshiki soil, Aswan iron-ore, El-Sukari and Atud gold vein deposits in Eastern desert and phosphate samples from El-Sibayia in the Nile Valley and El-Quseir in the Red Sea coast were determined using instrumental neutron activation analysis. The samples were irradiated with thermal neutrons flux of 7×10^{11} n/cm^2·s in Mainz TRIGA research reactor. The results showed that the phosphate rocks are rich natural sources of uranium and thorium among the other minerals forming the earth crust. Here, for comparison, the delayed neutron activation analysis was used to determine the uranium content in the same samples.

1. INTRODUCTION

^{238}U and ^{232}Th are naturally occurring long-lived radionuclides, which along with their daughter products are the radioactive sources that can affect man. Due to natural processes these are getting transferred to living beings through different pathways and need to be monitored to assess the possible hazards. Environmental studies are generally carried out in order to trace the pathway of radionuclides/radiotoxic elements to living beings. Environmental monitoring and meaningful interpretation of data from man-made pollution become more complicated without adequate knowledge about the natural abundance of radioactive elements in the environment. Uranium content in geological samples provides an adequate information necessary for geological considerations, and the analytical determination of uranium concentrations in such samples is of great im-

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portance for solving numerous problems in the field of geochemistry. The abundance of thorium is about four times that of uranium in the earth crust (TAYLOR [1]). The uranium content in soils is usually in the range from 1 to 8 ppm, while that of thorium is in the range from 5 to 50 ppm. In fact, the general distribution of uranium in soils is very similar to that in stream sediments (DURRANCE [2]).

There are several methods which are applicable to determination of uranium and thorium concentrations in geological samples. Each method has its advantages and disadvantages. Considering various sensitivities of analytical methods which can be used for the determination of uranium and thorium contents, instrumental neutron activation analysis (INAA) is of particular interest. This method is simple, fast, non-destructive and can be used for samples with relatively low contents of the elements investigated. The neutron activation analysis also allows overcoming many of the limitations encountered in other methods such as matrix effect, internal and external interference. In the present work, the INAA method has been used to determine the elemental concentrations of uranium via ^{238}U and thorium via ^{232}Th in soil, iron, gold and phosphate samples collected from different places in Upper Egypt. By neutron capture and successive β-decay, the activation converts ^{238}U and ^{232}Th into ^{239}Np and ^{233}Pa, respectively,

$$^{238}U\ (n, \gamma)\ ^{239}U \xrightarrow{\beta-} {}^{239}Np, \quad E_r = 106\ \text{keV},$$

$$^{232}Th\ (n, \gamma)\ ^{233}Th \xrightarrow{\beta-} {}^{233}Pa, \quad E_r = 312\ \text{keV}.$$

The characteristic γ-rays can be detected using γ-spectroscopy.

However, the world-wide increase in uranium exploration has encouraged the demand for uranium analysis; activation analysis has proved to be a suitable method. The present work concerned with determination of uranium and thorium concentrations in some environmental samples such as Toshki soil, Aswan iron-ore, Gold vein deposits and phosphate samples from Upper Egypt by INAA and DNAA.

2. EXPERIMENTAL

2.1. SAMPLES PREPARATION AND IRRADIATION

The samples under investigation have been collected from different locations in Upper Egypt as follows: 10 soil samples from Toshki area nearly 280 km from Aswan city, 10 gold vein deposits from El-Sukari and Atud in the Eastern Desert, 5 samples from each, 5 iron-ore samples collected from Aswan iron-ore northeast of the Aswan city and 10 phosphate samples collected from El-Sibayia in the Nile Valley and El-Quseir in the Red Sea coast.

The samples were finely ground into homogeneous material. They were crushed in such a way that their diameters were less than 125 μm and greater than 63 μm. The crushed samples were dried at 105 °C to constant weight. Polyethylene capsules filled with 100 mg of powdered samples and empty capsules treated as the standard reference material were irradiated with thermal neutrons at the University of Mainz, Triga research reactor (100 KW_{th}), for 6 hours with a flux of 7×10^{11} $n/cm^2 \cdot s$. The data were collected for various measurement and appropriate cooling times, i.e., 2 days for uranium and 14 days for thorium (Kch-report-Triga Mainz, 1989).

2.2. INSTRUMENTATION

The low-level gamma-ray spectrometer used in our experiments consists of a HPGe detector with its electronic circuit. The detector has the following specifications: energy resolution (FWHM) at 1.33 Mev Co-60 is 1.70 keV, Peak to Compton ratio Co-60 is 65.2, relative efficiency at 1.33 Mev Co-60 is 29.2 %, energy resolution (FWHM) at 1.22 MeV Co-57 is 686 eV, and operation bias voltage is +2000 dc. The detector is connected to the following components: preamplifier, amplifier, ADC converter and MCA. The measurements were performed and analysed using the Intergamma Software produced by Intertechnique Deutschland GmbH, Mainz, Germany. Elemental contents were determined relative to certified reference materials, which were irradiated and counted under the same conditions. The electronic dead time in all measurements was less than 10% and was automatically corrected by the Intergamma Software.

For the delayed neutron activation analysis measurements: polyethylene capsules filled with 100 mg of powdered samples were sent to the irradiation position near the reactor core by using a pneumatic transfer system. After irradiation time of 2 min the samples were automatically sent to the counting station, and after a decay time of 15–20 seconds they were counted for 1 min with ^3He proportional counters in a circular arrangement. The Mainz measuring system contains 15 ^3He tubes placed in a cylindrical configuration. The delayed neutrons are thermalized by paraffin and polyethylene and then detected with high efficiency. The detector assembly was coupled to an electronic counting system. After suitable electronic processing, pulses due to neutron interactions were measured in a counter/timer. The background was determined by irradiating and counting empty capsules. In our experiments, the background was 5 counts/min.

3. RESULTS AND DISCUSSION

3.1. URANIUM AND THORIUM CONCENTRATIONS IN TOSHKI SOIL SAMPLES

Table 1 shows the concentrations of uranium and thorium in different soil samples collected from different places in the Toshki area in Upper Egypt. The results

obtained reveal that the uranium concentration ranges between 1.0 and 1.6 ppm, while that of thorium between 6.2 and 8.2 ppm. The statistical error in the determination of the concentrations of both elements in soil lies between 20 and 30% for uranium and between 2 and 3% for thorium. The error for ^{238}U in the case of ordinary soil is thus rather high. More accurate results can be obtained in the case of soils having relatively high uranium contents. The extensive use of phosphate compounds or phosphate rocks as altering fertilizers could contribute to the increase in uranium and thorium levels. The results presented in this paper suggest that the phosphate fertilizers have not contributed significantly to the radioactivity levels of the region under study, because this is a new agricultural area where the use of fertilizers is not observed.

Table 1

Concentrations of uranium and thorium in Toshki soil samples (in ppm)

Sample number	Uranium	Statistical error (%)	Thorium	Statistical error (%)
1	1.4	± 9.7	8.2	± 2.7
2	1.0	± 11.5	6.2	± 2.5
3	1.1	± 11.3	8.1	± 2.6
4	1.2	± 10.8	6.6	± 2
5	1.3	± 10.4	7.9	± 2.6
6	1.4	± 10	7.9	± 2.6
7	1.5	± 9.4	7.6	± 2.5
8	1.6	± 9.0	7.0	± 2.4
9	1.6	± 9.0	7.1	± 2.5
10	1.6	± 8.9	7.1	± 2.5
Average value	**1.4**		**7.4**	

Interpretation of the results of soil surveys can be extremely difficult, depending upon the type of the terrain concerned. It should always be borne in mind that transport of elements takes place in soils. Under some circumstances, it is also possible for solid soil particles to be moved over considerable distances by the wind. These effects will vary from one soil to another depending on meteorological circumstances. The concentration of ^{238}U is significantly increased in the upper layers of the soil compared with the original values. The main reason for this, over and above the deposition of the fly ash, is the mixing of the original soil with the slag of the coal due to industrial, building activity and some household activities of the private population. The concentration ranges for uranium and thorium presented in our study are shown in table 2 and compared with the values reported for soils in other countries collected by ROBOTHAN et al. [5].

Table 2

Concentrations of uranium and thorium in soil samples from different countries (in ppm)

Country	Uranium		Thorium	
	Range	Mean	Range	Mean
U.S.A	0.3–10.7	3.7	2.2–21	7.6
Canada	0.72–2.0	1.22	4.2–14.1	8.0
Germany	0.42–11	–	0.4–15	8.0
Jamaica	0.7–14	–	0.9–25	–
Cuba	1.5–5.6	3.1	5-12.3	7.2
India	–	3.38	–	19.72
Egypt (this paper)	**1–1.6**	**1.4**	**6.2–8.2**	**7.4**

From table 2 it can be seen that the uranium concentration measured by us is similar to that in Canada soil and nearly consistent with the values obtained in U.S.A., Germany, Jamaica, Cuba and India. Our thorium results are in accordance with the results for the lower limits in U.S.A., Germany, Cuba and Jamaica soils.

3.2. URANIUM AND THORIUM IN ASWAN IRON-ORE DEPOSITS

The concentrations of uranium and thorium in iron-ore samples under investigation were determined as described above for the soil samples, i.e., via the activities of the neptunium and protactinium obtained after neutron capture and β-decay. These values are listed in table 3.

Table 3

Concentrations of uranium and thorium in Aswan iron-ore samples (in ppm)

Sample number	Uranium	Statistical error (%)	Thorium	Statistical error (%)
1	3.1	± 16.2	7.4	± 2.5
2	3.4	±24.7	7.5	±3.0
3	3.1	± 16.2	6.2	±2.4
4	3.3	± 18.5	7.5	±3.0
5	3.3	± 18.5	6.1	±2.0
Average value	**3.2**		**6.9**	

From the results in table 3 it can be seen that average concentrations of uranium and thorium in Aswan iron-ore samples are 3.2 and 6.9 ppm, respectively. The statistical error varies between 6 and 26% for uranium and between 2 and 3% for thorium.

3.3. URANIUM AND THORIUM IN GOLD VEIN DEPOSITS

Table 4 shows the uranium and thorium contents in gold vein deposits collected from El Sukari and Atud in Eastern Desert, Egypt.

Table 4

Concentrations of uranium and thorium in El Sukari and Atud gold deposits (in ppm)

Sample number	Place	Uranium	Statistical error (%)	Thorium	Statistical error (%)
1	El Sukari	0.5	± 9.7	3.4	± 2.3
2	El Sukari	0.5	± 9.7	3.5	± 2.4
3	El Sukari	0.5	± 9.7	3.4	± 2.3
4	El Sukari	0.5	± 9.7	3.6	± 2.8
5	El Sukari	0.5	± 9.7	3.5	± 2.4
6	Atud	0.3	± 8.7	2.4	± 1.5
7	Atud	0.3	± 8.5	2.4	± 1.5
8	Atud	0.4	± 9.0	2.5	± 1.8
9	Atud	0.3	± 8.5	2.5	± 1.8
10	Atud	0.4	± 9.4	2.5	± 1.8
Average	–	**0.4**	–	**2.9**	–

3.4. URANIUM AND THORIUM IN PHOSPHATE ROCKS

Because of an increasing use of phosphate in industry world-wide, it is interesting to investigate the radioactivity control of phosphate ores. In the present work, the concentration of uranium and thorium in two types of Egyptian phosphate ores containing different amounts of P_2O_5 has been investigated, the first from El-Sibaiya in the Nile Valley, and the second from El-Qusier at the Red Sea coast. Sedimentary and igneous phosphate ores are used as raw material for the production of phosphoric acid, and consequently as fertilizers for agricultural purposes. Depending on the technology used for producing fertilizers or phosphoric acid, the distribution of radioactive elements among the various products may be different. Sometimes fertilizers and the common by-product phosphogypsum are characterized by such high activities of natural radioactive elements that the resulting radiological impact should be considered carefully.

The concentration of isotopes from the ^{232}Th series in phosphate rocks of all types is similar to that observed normally in soil, whereas the concentrations of ^{238}U and its decay products tend to be higher in phosphate deposits of sedimentary origin. It is widely believed that the radioactivity associated with phosphate rocks of sedimentary origin is formed by the adsorption and co-precipitation of uranium

with calcium. Several investigators have indicated that the content of radionuclides in phosphate deposits increases with an increasing P_2O_5 (GUIMOND [6]). The primary potential environmental radiation problem associated with phosphate rock mining and processing concerns mining spoils and processing waste products. While these materials do not present direct radiation hazards, problems may be created by their use. Occupational exposures mainly occur during mining processing and transportation of phosphate rock, as well as during transportation and utilisation of phosphate fertilizers (UNSCEAR [7]).

The concentrations of uranium and thorium in phosphate samples from El-Sibaiya in the Nile Valley and El-Quseir in the Red Sea coast are recorded in units of ppm in table 5. The results show that the concentrations of uranium in El-Sibaiya phosphate deposits are higher than those in El-Quseir phosphate deposits. On the other hand, the concentrations of thorium in El-Quseir phosphate deposits are greater than those for El-Sibaiya phosphate deposits. The statistical counting errors ranged from 3 to 9% for uranium and from 2 to 12% for thorium.

Table 5

Concentrations of uranium and thorium in El-Sibaiya and El-Quseir phosphate samples (in ppm)

Sample number	Place	Uranium	Statistical error (%)	Thorium	Statistical error (%)
1	El-Sibaiya	46.3	± 8.2	2.6	± 3.0
2	El-Sibaiya	46.1	± 8.1	2.5	± 2.5
3	El-Sibaiya	47.0	± 8.7	2.7	± 3.5
4	El-Sibaiya	46.0	± 7.7	3.0	± 4.0
5	El-Sibaiya	45.3	± 9.7	3.0	± 5.0
6	El-Quseir	23.3	± 3.0	9.4	± 8.0
7	El-Quseir	27.0	± 4.5	12.0	± 11.5
8	El-Quseir	31.8	± 6.0	11.5	± 10.0
9	El-Quseir	31.3	± 5.5	10.7	± 8.0
10	El-Quseir	33.1	± 5.0	10.8	± 8.7

The activity concentrations of ^{238}U and ^{232}Th (in Bq/kg) in El-Sibaiya and El-Quseir phosphate and other phosphate deposits from different countries are given in table 6. It is seen that the Egyptian phosphate rocks are characterized by low radioactivity.

Based on the results presented in this section, we find that the activity concentrations of ^{238}U and ^{232}Th are within the world average value reported in the literature and given in table 6. This provides enough information, especially for naturally occurring radionuclides, to establish a baseline map in the areas under investigation.

Table 6

Activity of uranium and thorium in (Bq/kg) in phosphate rock from different countries

Country	^{238}Uranium	^{232}Thorium	Reference
Morocco	1700	20	GUIMOND [6]
U.S.S.R. (Kola)	40	80	GUIMOND [6]
U.S.A. (Florida)	1500	20	GUIMOND [6]
U.S.A. (Western)	1000	20	GUIMOND [6]
U.S.A. (North Florida)	281	–	ROSSLER et al. [8]
Jordan	–	2	OLSZEWSKA [9]
Tunisia	–	29	OLSZEWSKA [9]
Algeria	–	64	OLSZEWSKA [9]
Israel	–	11	OLSZEWSKA [9]
Sudan (Uro)	2598	2.5	SAM and HOLM [10]
Sudan (Kurum)	684	0.83	SAM and HOLM [10]
Tanzania (Arusha)	4641	717	MAKWEBA and HOLM [11]
Egypt (Abu-Tartur)	408	23.7	KHATER et al. [12]
Egypt (Abu-Zaabal)	523	37	HUSSEIN [13]
Egypt (El-Sibaiya)	538	25	**This work**
Egypt (El-Quseir)	358	38	**This work**

3.5. DETERMINATION OF URANIUM BY DELAYED NEUTRON ACTIVATION ANALYSIS (DNAA)

The concentrations of uranium in ppm determined by DNAA in the Toshki soil samples, Aswan iron-ore samples, and phosphate deposits from El-Sibaiya in the Nile Valley and El-Quseir at the Red Sea coast are given in tables 7 through 9 and compared with the results obtained by the INAA technique. The difference between both results for ^{238}U is found (^{238}U from DNAA systematically higher) as shown in the figure. This is probably caused by a high statistical error in the INAA method. On the other hand, γ-pile-up may lead to spurious events in DNAA. Two different standard reference materials were used for determining the uranium concentrations, i.e., uranylnitrate (UO_2 $(NO_3)_2$) containing 20 ng of ^{235}U in the case of DNAA and geostandard reference materials in the case of INAA. Using these two different standard reference materials may also affect the results.

Table 7

Uranium concentrations in Toshki soil samples by determined DNAA and INAA (in ppm)

Sample number	Place	Count/min	Statistical error (%)	^{235}U (ppm) by DNAA	^{238}U (ppm)	^{238}U (ppm) by INAA
1	Mahbat area	107	± 9.7	0.02	2.1	1.4
2	Toshki lower	75	± 11.5	0.01	1.5	1.0
3	Toshki spillway	78.5	± 11.3	0.01	1.6	1.1
4	Km30	85.6	± 10.8	0.01	1.8	1.2
5	Km35	92.7	± 10.4	0.01	1.8	1.3
6	Km40	99.8	± 10	0.01	2.0	1.4
7	Km45	112.7	± 9.4	0.02	2.2	1.5
8	Km50	123.4	± 9	0.02	2.4	1.6
9	Km58	122	± 9	0.02	2.4	1.6
10	Km63	124.8	± 8.9	0.02	2.5	1.6

Table 8

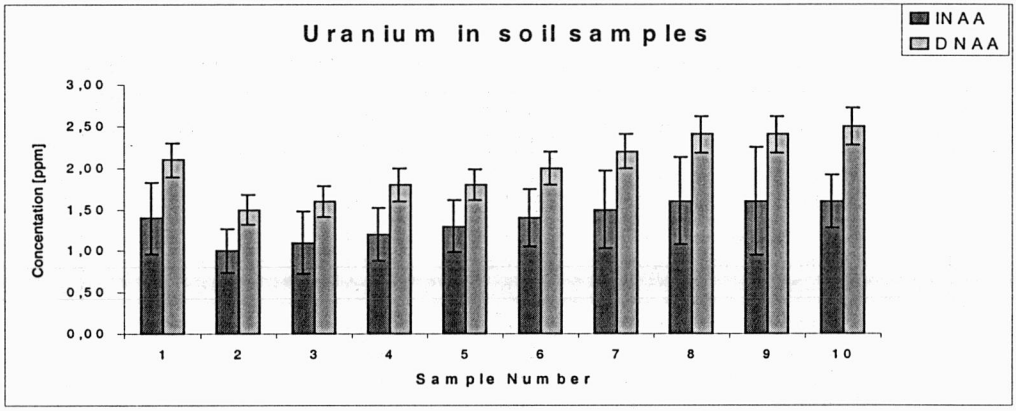
Uranium concentrations in Aswan iron ore samples determined by DNAA and INAA (in ppm)

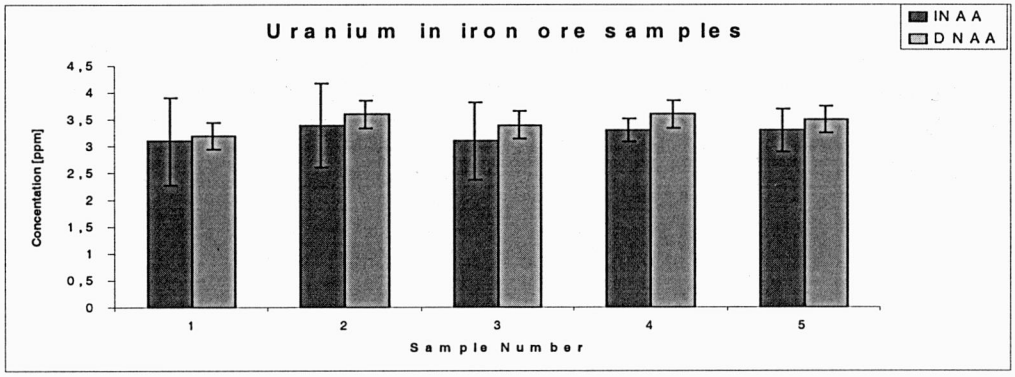
Sample number	Count/min	Statistical error (%)	^{235}U (ppm) by DNAA	^{238}U (ppm)	^{238}U (ppm) by INAA
1	170	± 7.8	0.02	3.2	3.1
2	192	± 7.3	0.03	3.6	3.4
3	178	± 7.6	0.02	3.4	3.1
4	190	± 7.4	0.03	3.6	3.3
5	185	± 7.3	0.03	3.5	3.3

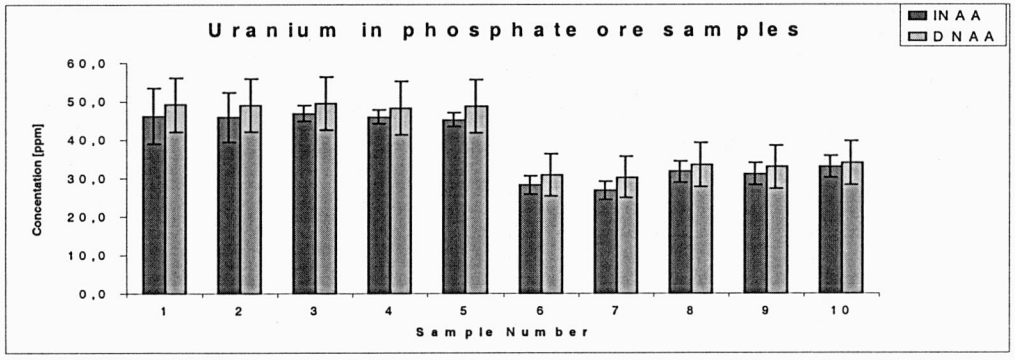
Table 9

Uranium concentrations in El-Sibaiya and El-Quseir phosphate deposits determined by DNAA and INAA (in ppm)

Sample number	Place	Count/min	Statistical error (%)	^{235}U (ppm) by DNAA	^{238}U (ppm)	^{238}U (ppm) by INAA
1	El-Sibaiya	2503	1.9	0.35	49.2	46.3
2	El-Sibaiya	2489	2.0	0.39	49.0	46.0
3	El-Sibaiya	2517	1.9	0.35	49.5	47.0
4	El-Sibaiya	2460	2.0	0.35	48.3	46.0
5	El-Sibaiya	2482	2.0	0.35	48.7	45.3
6	El-Quseir	1576	2.5	0.22	31.0	23.3
7	El-Quseir	1540	2.5	0.22	30.3	27.0
8	El-Quseir	1704	2.4	0.24	33.5	31.8
9	El-Quseir	1683	2.4	0.24	33.0	31.3
10	El-Quseir	1733	2.4	0.24	34.1	33.1







Comparison between uranium contents in soil, iron-ore and phosphate samples determined by INAA and DNAA

4. CONCLUSION

Neutron activation analysis is a powerful tool established for the determination of trace elements in a variety of matrices. The results obtained for ^{238}U concentrations by DNAA have been found to be systematically higher in comparison with those performed by INAA.The delayed neutron activation technique has several major advantages: samples can be analysed non-destructively and without the necessity of any sample preparation. It is sensitive and reliable and has low detection limits for ^{235}U. This technique can preferably be applied to the geochemical exploration of uranium deposits, in chemical control of uranium processing and in environmental mapping for uranium.

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REFERENCES

[1] TAYLOR S.R., Geochem. Cosmochem. Acta, 1973, 28, 273.

[2] DURRANCE E.M, *Radioactivity in geology principles and applications*, John Wiley and Sons, New York, 1986.

[3] EBERHARDT K., KRONENBERG A., *The research reactor TRIGA Mainz, A neutron source for versatile applications in research and education*, Kerntechnik, 2000, 65, 269.

[4] Kernchemie Report, *Tables for neutron activation analysis*, TRIGA, Mainz, 1989.

[5] ROBOTHAN H., LALOR G.C., MATTIS R., THOMPSON C., J. Radioanal. Chem., 1987, 116, 27–34.

[6] GUIMOND R.J, *Radium in fertilizers*, Technical Report No. 310, International Atomic Energy Agency (IAEA), Environmental behaviour of radium, 1990, 113–128.

[7] UNSCEAR, *Ionzing Radiation: Sources and Biological Effects*, United Nations Scientific Committee on the Effects of Atomic Radiation Report, 1988.

[8] ROSSLER C.E., SMITH Z.A., BLOCH W.E., PRINCE R.J., *Uranium and radium-226 in Florida phosphate materials*, Journal of Health Physics, 1979, 37, 269–277.

[9] OLSZEWSKA M., *Estimates of the occupational radiological hazard in phosphate fertilizers industry in Poland*, J. Radiation Protection Dosimetry, 1995, 58, 269–276.

[10] SAM A.K., HOLM E., *The natural radioactivity in phosphate deposits from Sudan*, The Science of the Total Environment, 1995 16, 173–178.

[11] MAKWEBA M.M., HOLM E., *The natural radioactivity of the rock phosphates, phosphatic products and their environmental implications*, The Science of the Total Environment, 1993, 133, 99–110.

[12] KHATER A.E., HIGGY R.H., PIMB M., *Radiological impacts of natural radioactivity in Abu-Tartur phosphate deposits-Egypt*, J. Environmental Radioactivity, 2001, 55, 255–267.

[13] HUSSEIN E.M., *Radioactivity of phosphate ore, superphosphate and phosphogypsum in Abu-Zaabal phosphate plant – Egypt*, J. Health Physics, 1994, 67, 280–383.

OZNACZENIE ŚLADOWYCH ILOŚCI URANU I TORU W KILKU EGIPSKICH SKAŁACH MACIERZYSTYCH METODĄ INSTRUMENTALNEJ ANALIZY AKTYWACYJNEJ NEUTRONOWEJ

Izotopy uranu i toru występujące w glebie, skałach, wodzie, roślinach i powietrzu mają udział w naturalnym napromieniowaniu populacji ludzkiej. Stężenia uranu i toru w próbkach gleby (Toshiki) rudy żelaza (Aswan), żyły złota (El-Sukari i Atud, pustynia we wschodnim Egipcie) i fosforanów (El-Sibayia w dolinie Nilu i El-Quseir na wybrzeżu Morza Czerwonego) zostały oznaczone metodą instrumentalnej analizy aktywacji neutronowej. Próbki były napromieniowywane strumieniem termicznych neutronów (7×10^{11}·n/cm^2·s) w reaktorze TRIGA. Otrzymane wyniki świadczą, że skały, których składnikiem są fosforany, stanowią bogate, naturalne źródło uranu i toru. W prezentowanej pracy dla porównania oznaczono zawartość uranu i toru w tych samych próbkach metodą opóźnionej analizy aktywacyjnej neutronowej.