RESEARCH ARTICLE

Analysis of Uranium Concentration, and $^{235}U/^{238}U$ Activity Ratio in Low Grade uranium Ore material by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Gamma Ray Spectrometry Technique

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Manuscript details:

Received: 02.11.2016
Accepted: 24.12.2016
Published : 27.01.2017

Editor: Dr. Arvind Chavhan

Cite this article as:
Nassef MH and Khater AM (2016) Analysis of Uranium Concentration, and $^{235}U/^{238}U$ Activity Ratio in Low Grade uranium Ore material by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Gamma Ray Spectrometry Technique, *International J. of Life Sciences*, 4 (4): 461-466.

Acknowledgement:
The authors would like to thank Prof. Dr Laila Attia Guirguis , and Adham Karam Mansour from Nuclear Material Authority-Egypt, for their cooperation and sample collection. Also thanks to prof. Dr Gad El hafnawi from Tanta University for his cooperation

ABSTRACT

In this study, uranium concentrations (ppm) and the natural activity ratios ($^{235}U/^{238}U$) in 6 representative samples of uranium ore samples were analyzed. The samples were collected from Gattar II ore site, which is located at the Red Sea northeastern desert of Egypt. The samples were measured using HPGe gamma ray detector (non-destructive technique) based on the measurement of the emitted gamma rays of uranium by using the photo peaks 163.33 keV for ^{235}U to avoid the overlapping with 186 keV of ^{226}Ra, and the 1001.03 keV photo peak of ^{234m}Pa daughter for ^{238}U concentration respectively. The uranium concentrations of the same analyzed samples were determined using ICP-MS (destructive technique) for comparison. Sharp correlation (R^2 =0.9881) was found between uranium concentration measured by non-destructive gamma ray spectrometry and that measured by destructive ICP-MS for the same analyzed samples.

Keywords: *Uranium Ore, $^{235}U/^{238}U$ Activity Ratio, Gamma ray* Spectrometry, *ICP-MS*

INTRODUCTION

The natural isotope of uranium includes ^{234}U, ^{235}U, and ^{238}U in which the ^{238}U isotope is the most abundant isotope by weight (99.28%), ^{235}U (0.72%) and ^{234}U (0.0055%). While on a mass basis there is far more activity concentration of ^{238}U than ^{235}U in a natural sample, different authors mentioned that, the activity ratio is approximately 21:1 (Powell et al., 2007; Beir, 1988). The majority of natural radioactivity of uranium (97.8%) is due to the uranium isotopes ^{238}U (48.9%) and ^{234}U (48.9%). The parent isotope of the uranium series is ^{238}U (of which ^{234}U is a decay product) while ^{235}U is the parent isotope of the actinide series.

The distribution of these radionuclide's in the environment are based on their biogeochemistry, half-life, and the nature of their surroundings (CSQG, 2007). There were different techniques (physical/ chemical) available for the determination of uranium concentration in uranium ore samples. It is useful to determine the content of uranium in every stage of prospecting and/or exploration processes of uranium-bearing minerals. One of the most useful property of uranium is its radioactivity (Sarangi,2000). It has been observed that granitic rocks contain higher amounts of thorium, uranium, and light rare earth elements (REEs) compared to other igneous rocks such as basalt and andesitic (Sarata et al., 2011). For measurement of ^{238}U by gamma-ray spectrometry, it is recommended to satisfy that any one of the daughters of ^{238}U should exist in equilibrium condition with ^{238}U. This condition is satisfied by one of the first three very short-lived daughters of ^{238}U, namely ^{234}Th (24.1d), ^{234m}Pa (1.17m) and ^{234}Pa (6.78h) compared with ^{238}U so that radioactive secular equilibrium is quickly achieved. The 63.3 keV gamma emission (4.5%) is a cleaner peak of ^{234}Th for uranium analysis by using high-purity Germanium. However, the 63.3 keV peak includes contributions from the 63.9 keV (0.255%) emission from ^{232}Th, the 63.9 keV (0.023%) emission from ^{231}Th and the 62.9 keV (0.018%) emission from ^{234}Th. Of these, the 63.9 keV peak of ^{231}Th, which is a daughter of ^{235}U, is a potential significant contribution only for samples highly enriched in ^{235}U. But the contribution of 63.9 keV (^{231}Th) in the natural uranium sample may be ignored since the concentration of ^{235}U in a natural sample is very low, i.e. 0.71% of the uranium concentrations can be measured accurately by use of the 1001 keV gamma ray emission line from ^{234m}Pa without any self-absorption correction. The 1001 keV Peak does not include any contribution from any other gamma emissions, and does not have any interference with other peaks in the region of interest. In surveying of literature, several recent gamma-ray measurements of the absolute emission probability of the 1001 keV peak of ^{234m}Pa have resulted giving a newly recommended value of 0.835%, and this new value provides a consistent basis for measurement of ^{234m}Pa in the samples (Yucel, et al., 1998; Yucel et al., 2003; Anilkumar et al., 2007). It is known that, uranium deposits with concentrations of about 1000 ppm (0.1%) U and greater of uranium may be considered "ore", that is, they may be economic to mine, In uranium ore deposits, 20 000 ppm (2.0 %) U is considered to be high grade while 1000 ppm (0.1%) U and 100 ppm (0.01%) U are considered low and very low grades, respectively (SENES, 2008; Susan et al., 2009; Sergani et al., 2003; Steve, 2011). The average grade of world's economic uranium deposits ranging from 0.02% (South Africa to 0.12% (U.S.A.) (Brinck, 1974). Gable Gattar uranium prospect is located 35 km to the west of Hurghada city in Egypt on the Red Sea coast. The area is located between latitudes 27° 12 30 and 27° 21 59 and Longitudes 33° 12 30 and 33° 25 00 E. Gabal Gattar area has a rugged mountainous nature, and it prospect about 27000 tons ore of inferred uranium resources have been identified will an ore grade ranging between 0.19-0.24% U_3O_8. In this prospect rocks hosting, the uranium mineralization is mainly represented by the Precambrian Calc-Alkaline granites referred to in Egypt as the younger granites. Distribution of this mineralization is mainly controlled by the shear structures cutting across the granitic masses (El-Shershaby, 2002, Abdel et al., 2010; Roz, 1994, OECD, 2009). In this study, high-resolution gamma-ray spectrometry (non destructive technique) and Inductively coupled plasma mass spectrometry ICP-MS (destructive technique) were used together to determine uranium concentration in 6 samples of uranium ore source material samples collected from Gattar area in Egypt and to verify the natural isotopic ratio of $^{235}U/^{238}U$.

MATERIALS AND METHODS

2.1 Description of the standard uranium ore sample

The IAEA-RGU-1 reference material is a uranium ore sample prepared by the International Atomic Energy Agency (IAEA). The RGU sample has the same matrix like our collected samples. The recommended uranium concentration in the IAEA-RGU sample is 400 ppm with uranium concentration of 0.04 Wt%. It is designed for testing the calibrations of gamma-ray spectrometers used for the determination of U in the studied samples. The IAEA-RGU reference material sample was used to compute the activity of the analyzed samples by comparison after calculation of the activity concentration of ^{238}U, and ^{235}U. The recommended concentration of uranium in the RGU sample is 400±8 µg/g with a certified activity of 4940 Bq/kg and a range between 4910-4970 Bq/kg (IAEA, 1987; Newman et al., 2008; Chaudry et al., 2002).

2.2 Gamma –energy lines of interest

The activities of each radionuclide were calculated through the comparison with the same energy line of the IAEA reference uranium ore sample (RGU-1). The standard uranium ore RGU sample was packed and sealed in a cylindrical container in the same geometry as that prepared for the collected samples. The self-attenuation of gamma-photons was included in our calculation. The gamma-energies lines used for activity calculation are 163.3 keV and 1001 keV for ^{235}U and ^{238}U respectively. The prominent gamma-energy lines and their corresponding yields are shown in Table 1.

Table 1. Prominent gamma-energy lines and their corresponding yields.

Nuclide	Energy keV	% B.I.,
^{235}U	163.3	5.08
^{234}Pa (^{238}U)	1001.03	0.845

2.3 Sample preparation for gamma spectrometry analysis

Six samples of uranium source materials (uranophane samples of Gattar rocks) were collected. All samples were crushed to a fine powder form and placed in Marrinelli cylindrical containers of 100 cc. To avoid any possibility of secular equilibrium with its gamma emitting decay products, the samples were tightly sealed. The specific activity of ^{238}U, ^{235}U were measured using n-type HPGe detector Model CANBERRA CR 40150, HV power supply Model TENNELEC 950A TC, Energy range 29-2615 keV and 40% efficiency. The system coupled with multi-channel analyzer and computer software for gamma-ray spectral analysis. The system resolution is 1.9 keV for 1332 keV gamma-rays of ^{60}Co. The detector is shielded from any background radiations coming from the surroundings with 7.5 cm lead shield. The lead shield, lined inside with grated absorbers of copper (1-2 mm) and cadmium (2 mm). The latter include a spectroscopy amplifier, an analog to digital converter (ADC) and a 8192 multichannel analyzer (MCA) with counting capacity of 228 counts per channel. The system was energy calibrated by different gamma emitters. These included Cesium-137 (661.66 keV), Cobalt-60 (1173.23 keV,1332.5 keV), Potassium-40 (1460.8 keV). In addition, Radium-226 is used for the efficiency calibration. The computer program MAESTRO was used for the analysis of closely spaced peaks in the measured spectrum. In order to get a better counting statistics, all the samples are counted for about 65000 seconds.

Table 2. Experimental conditions used in the ICP-MS measurements

Instrument	ELAN6100 (Perkin Elmer-Sciex)
Filter type:	Quadruple rods
Nebulizer :	cross-flow type
Spray chamber:	Scott-type
Sample uptake/ mL.min^{-1}:	1.8
Wash solution:	1% HNO_3
RF frequency/ MHz:	40
RF power/ W:	1250
Plasma gas flow rate:	15
Auxiliary gas flow rate:	1.0
Carrier gas flow rate:	0.95
Lens voltage:	adjusted daily
Detector:	26-segment dynode operating in both pulse and analogue modes
Instrument tuning:	
Data acquisition mode:	Performed using a 10 µgL^{-1} solution of Be, Mg,
Number of point per peak:	Cu, Pb, and U
Number of scan weeps:	Peak hopping
Dwell time per point:	100
	100 times
	50 ms

2.4 Sample preparation for ICP-MS analysis

In order to determine the radionuclide's concentration of uranium by ICP-MS, all the collected samples were crushed and sieved. The samples were then analyzed in ALS-Chemex Laboratories (Vancouver, Canada) using PerkinElmer ELAN 9000 ICP-MS. The next step is to dissolve the sample aliquot with aqua regia solution and finally filtrated. A multi-channel peristaltic pump (Minipuls-3), a GemTip cross-flow nebulizer and a Perkin Elmer Type II spray chamber made of Ryton, drained by the peristaltic pump, were used for sample introduction. This instrument was further equipped with a Perkin Elmer corrosion-resistant torch with standard alumina injector and a Channeltron. Continuous dynode electron multiplier was operated in the pulse counting mode. Experimental conditions used in the measurements are summarized in Table 2.

RESULTS AND DISCUSSION

3.1 Results of uranium concentration using gamma ray spectrometry (HPGe detector)

It was found that the results of the gamma spectrometric analysis of the analyzed samples show uranium concentrations exhibited a big variation as shown in Table 3. The uranium concentration ranged from 731.2 ppm to 4641.1ppm with an average value of 1928.3 ppm. The slight variation in the concentrations of uranium in the analyzed samples indicates that the environment of the area is not homogenous in its deposition state. The highest concentration was found in sample Gattar 1 (4641.1 ppm) with uranium concentration of 0.464 Wt%. Our data values matched with pervious work carried out in the same area (4354.9 ppm) by using Laser Induced Breakdown Spectroscopy (LIBS) technique (Sergani et al. 2003-10).

3.2 Results of Uranium Concentration using ICP-MS

For ICP-MS results, the concentration of uranium ranged from 726.0 ppm to 4620 ppm with an average value of 1982.7 ppm. The average uranium concentration value has 0.198 Wt%. In order to observe a correlation between the measured concentrations of uranium using both techniques, a graph was plotted as shown in Figure1. The results show good correlation coefficient ($R^2 = 0.9881$) which indicates good linear correlation between uranium measured by gamma spectrometry and uranium measured by mass spectrometry. The ratio between both techniques around 1. Therefore, both analytical techniques are suitable to measure the concentration of uranium in any matrices. However, ICP-MS technique requires small sample weight, rapid and precise technique and is preferred especially in verification methods.

3.3 Results of Activity Ratio Calculations

From Table 4, it is clear that the activity ratio of ^{235}U to ^{238}U ranged from 0.042 to 0.056 with an average value of 0.047, which is identical to the recommended reference value (0.047) in natural uranium (Powell et al.,2007). The calculated percentage bias not more than 19.1%. The value of the ratio $^{235}U/^{238}U$ is important in the analyzed samples due to its applications of age dating of natural materials. However, it seems that gamma spectrometry is not the choice to precisely determine that ratio.

Table 3. Uranium concentration (ppm) in the analyzed samples measured by ICP-MS and Gamma ray spectrometry techniques for comparison

Sample Code	Uranium concentration (ppm) measured by (ICP-MS)	Uranium concentration measured by (HPGe)		% Bias
		Bq/kg	ppm	
Gattar1	4620.0	57549.64	4641.1	0.46
Gattar2	977.0	10957.88	883.7	9.55
Gattar3	2030.0	26450.44	2133.1	5.08
Gattar4	853.0	10595.8	854.5	0.18
Gattar5	726.0	9066.88	731.2	0.72
Gattar6	2690.0	28843.64	2326.1	13.5

1 ppm of uranium = 12.4 Bq/kg.

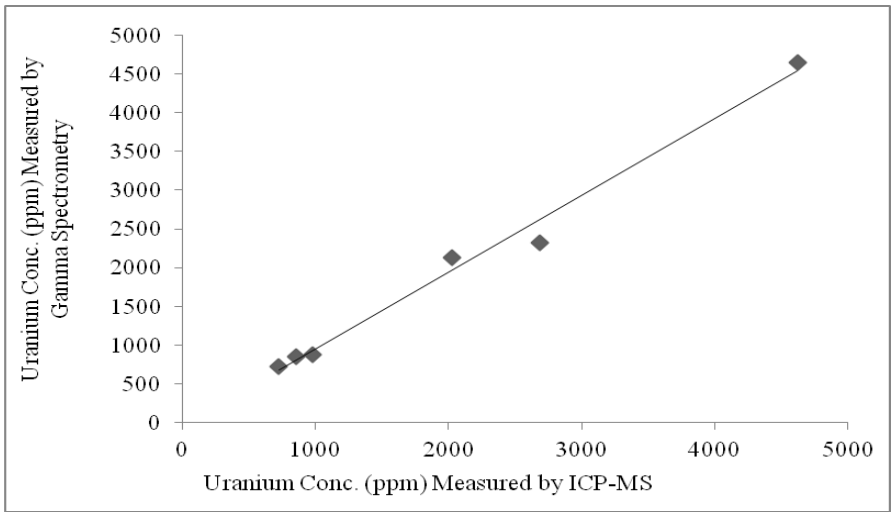

Fig. (1) Correlation between uranium concentration measured by ICP-MS and gamma ray spectrometry.

Table 4: Uranium concentration (ppm) at 1001 keV, 163 keV energy lines and the natural activity ration measured by Gamma ray Spectrometry.

Sample ID	*Uranium Concentration (ppm)*		*Activity Ratio $^{235}U/^{238}U$*		
	^{238}U (1001 keV)	*^{235}U (163 keV)*	*Natural**	*Calculated*	*% Bias*
Gattar1	*4641.1*	*33.13*	*0.047*	*0.046*	*2.1*
Gattar2	*883.70*	*7.68*		*0.056*	*19.1*
Gattar3	*2133.*	*15.61*		*0.047*	*0*
Gattar4	*857.5*	*468.3*		*0.044*	*6.4*
Gattar5	*731.2*	*4.69*		*0.042*	*10.6*
Gattar6	*2326.1*	*16.3*		*0.045*	*4.3*

**Activity ratio " Natural" $^{235}U/^{238}U$ has an activity ratio of 0.047 (Robin, K.H., 2008).*

Table 5: The uranium concentration (ppm) in different uranium ore samples from various locations in the world including this study.

Country/Type of uranium ore	Average value of Uranium concentration (ppm)
France/vein Type	32802
Czech Republic/vein type	30330
D.R of Congo /vein type	75765
U.S.A. /vein type	81579
Canda/Qtz, ped, Cong type	1270
U.S.A. /Sand Stone type	120000
Canda pol. placer type	46500
Egypt/Sheer zone in Calc-alkaline granite and inter-mountain basin **(This study)**	**1928**

Table 5 show the average value of uranium concentration (ppm) in different uranium ore with different type of ore from various locations in the world including this study Chaudry et al., 2002). The recent exploration activities in Egypt-2009 represent the first step in a long-term future plan aiming at diversifying and maximizing Egypt uranium resources, urgently required to support its national program of peaceful uses of nuclear energy needed to secure its energy resources for development projects. In Gabal Gattar prospect, about 27 000 tons ore of inferred uranium resources have been identified will an ore grade ranging between 0.19-0.24%U_3O_8 (IAEA, 2009).

CONCLUSION

Based on the destructive and non-destructive assay techniques, it can be concluded that the investigated samples contain uranium with high concentration up to 4620 ppm. This means that the granite of Gattar site classified as low-grade uranium deposit of economic concern. The analytical results show a good agreement between both techniques. The activity ratio ($^{235}U/^{238}U$) was found to be in the range from 0.042 to 0.056 with a mean value of 0.047which is identical to the

recommended reference value 0.047which is identical to the reference recommended value (0.047). ICP-MS is the better choice for uranium determination because this technique has more precise in measuring uranium concentration and the calculated activity ration of $^{235}U/^{238}U$ than gamma ray spectrometry. In the frame of Egyptian plan of NPP establishment at EL-Dabaa Site, efforts are to be considered in the field of uranium ore mining in the studied area as one of the strategic resources for uranium fuel fabrication within the ratified SG agreement between Egypt and IAEA.

Conflicts of interest: The authors stated that no conflicts of interest.

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