Measurement of Uranium and Thorium Series in Fertilizer Samples in Iraq Using Gamma Spectrometry Technique

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Abstract:

The present work deals with identifying and determining the concentration of natural occurring radionuclides, ^{238}U and ^{232}Th series in fertilizers used in Iraq. A total of 20 samples collected from markets and farms. The gamma-ray spectrometer (HPGe) detector was used for measuring gamma ray spectra. The ranges of radioactivity levels of ^{214}Pb, ^{214}Bi, ^{212}Pb, ^{208}Tl and ^{228}Ac are 402.53 – 17.09, 343.11– 2.50, 151.50 – 1.26, 67.62 – 1.12 and 42.84 – 3.53 $Bqkg^{-1}$, respectively. The mean activities of ^{238}U and ^{232}Th series in fertilizers are 69.39 and 14.31 $Bqkg^{-1}$ respectively. The obtained data are compared with available reported data from other countries in literature. The concentrations of ^{238}U series and ^{232}Th series in fertilizer are lower than the limit adopted in UNSCEAR (2000) reports, and within the limits of those used worldwide.

Key words: gamma-ray spectrometer, ^{238}U, ^{232}Th, fertilizers.

Physics classification : QC770-798

Introduction:

The earth's crust basically contains of naturally occurring radionuclides such as uranium and thorium. In soils, one of the sources of radioactivity other than those of natural origin is mainly due to the extensive use of fertilizers which are rich in phosphates used for agricultural purposes [1], [2]. The radionuclides are found in all the elements in the environment. They are present in varying amounts in the air, water, vegetables, animals, soil, rocks and the human body itself [3], [4]. The specific levels for the radioactivity of various soils are related to the nature of the parent rock [5], [6]. The agricultural practices have led to the depletion of the natural elements in soils. Therefore, phosphate fertilizers are used in huge amounts everywhere in the world and are essential for agricultural crops [7]. The natural resource of phosphorus in agriculture comes from phosphate rock. It is found in two types of rocks: sedimentary formations rock deposits which provide about 80-85% of the raw material for manufacturing phosphate fertilizers in the world, and the igneous rock which supplies the remaining 15 - 20% of rock phosphate to the fertilizers industry [8]. Several types of phosphate fertilizers are produced, and these are combined for the purpose of application in the field. The natural radionuclides of ^{238}U, ^{232}Th and decay series are found in the fertilizer samples. The concentration of natural radionuclides in phosphate fertilizers varies significantly from one country to another based on the origin of the components [9], [10]. Rocks of Morocco and United States of America have been assessed to measure the concentration of ^{238}U which was found to be 1700.0 Bq kg^{-1} and 1500.0 Bq kg^{-1}, respectively. Naturally, the sedimentary of the rocks contains an average 0.015% of U_3O_8 [11]. Guimond and Hardin [12] have reported that phosphate rocks generally have high concentration of ^{238}U. The main fertilizers used in Iraq are urea, ammonium sulphate, calcium ammonium nitrate, phosphate rock, single super phosphates, ammonium phosphate, potassium sulphate and NPK, NP and PK compound

fertilizers. Animal manure is also a complete fertilizer but is low in nutrients. Manures vary in nutrient content according to the animal source and what the animal has been eating. Commonly available manures include, cow, chicken and sheep. Several publications have been concerned about the radioactivity of phosphate fertilizers throughout the world [13]. The objective of the present study is to determine the radioactivity associated with U and Th contents of the fertilizer samples using gamma ray spectrometry (HPGe).

Materials and methods:

Sample collection and preparation:

A total of 20 representive fertilizer samples used in Iraq were obtained from farms and various companies dealing with agrochemicals. The fertilizer samples were prepared for measurement of the natural radioactivity of ^{238}U and ^{232}Th series, based on IAEA protocol using high purity germanium detector [14]. The samples were transferred into polyethylene bags and tightly sealed. The samples were crushed to obtain powder. Thereafter, the powder was heated at 110 ^{o}C in the oven for 24 h to remove moisture. All the samples were sieved using 2 mm mesh size, one kilogram was taken from each fertilizer and kept in containers. The samples then were labeled as type, time and date for each sample. All the fertilizer samples were stored in containers for at least two month to confirm the radioactive equilibrium between ^{238}U, ^{232}Th and their short-lived progenies [15], [16].

Instrumentation and calibration:

High-resolution spectroscopic system was used to measure the natural radioactivity of fertilizer samples. A high purity germanium coaxial detector (HPGe) system model no. GEM-F7040P4 was used which has a relative efficiency of 40% at 1.33 MeV for ^{60}Co. The detector has resolution 1.9 keV at 1.33 MeV of ^{60}Co. Spectral data from the detector was accumulated and analyzed by using computer software MAESTRO-32 model (A65-B32) provided by ORTEC as shown in Figure 1. The sources, ^{137}Cs, ^{60}Co, ^{133}Ba and ^{152}Eu from the International Energy

Agency IAEA, set no. 34 were used to calibrate the high purity germanium detector HPGe at a distance of ten centimeters between the detector and sources. The main details of the standard source are given in Table 1. The absolute efficiency calibration was achieved by mixed standard gamma sources (Ref. no. 34, IAEA) as shown in Table 1. The absolute efficiency was calculated by using the formula given below [17].

$$\varepsilon = \frac{C_n}{I_\gamma LT A_\circ e^{-\lambda t}} \quad (1)$$

where ε is the absolute efficiency for each gamma-ray energy E, C_n is the net area under the full energy peak of the gamma-ray energy, I_γ is the gamma-ray emission probability at energy E, LT is the live time for counting (sec) and $A_\circ e^{-\lambda t}$ is the activity (Bq) of the standard sources.

Figure (1): High purity germanium detector (HPGe) setup

Table (1): The mixed standard gamma sources (IAEA) used to determine the energy calibration and the absolute efficiency of the HPGe detector

Radionuclide	Energy (keV)	Activity (kBq)	Intensity (%)
^{137}Cs	661.6	371.6	85.10
^{60}Co	1173.24, 1332.50	387.0	99.97, 99.98
^{133}Ba	276.4, 356, 853	359.1	7.16, 62.1, 18.33
^{152}Eu	121, 344, 778, 1112, 1408	383.3	28, 26, 13, 13, 21

Radiometric Analysis:

Radiometric measurements were performed for 28,800 sec to measure the qualitative and quantitative determination of ^{238}U and ^{232}Th series in the fertilizer samples. The activities of ^{238}U and ^{232}Th series were measured through their daughters as given in Table 2. The activity (A_s) of the radionuclides was calculated using Equation 2 as given by [18].

$$A_s = \frac{C_n}{\varepsilon \times I_\gamma \times LT \times m} \quad (2)$$

where A_s is the specific activity in Bq kg^{-1}, C_n is the net count rate under peak per second and subtract the background under this peak, ε is the absolute efficiency for each gamma-ray energy E, I_γ is the gamma-ray emission probability at each energy, LT is the life time for counting (sec) and m is the mass of the samples (kg).

Table (2): Gamma-ray energy used to measure the activity of the radionuclides [14]

Parent Nuclide	Daughter Nuclide	γ-Ray Energy (keV)	Abundance (I_γ) %
^{238}U	^{214}Pb	351.9	35.8
	^{214}Bi	1120.3	14.9
^{232}Th	^{212}Pb	238.6	45
	^{208}Tl	583.1	30
	^{228}Ac	911.1	29

Results and discussion:

The concentrations of ^{238}U and ^{232}Th series are measured in different fertilizer samples used in Iraq are shown in Table 3. The radioactivity of ^{214}Pb ranged from 17.09 $Bqkg^{-1}$ in NPK to 402.53 $Bqkg^{-1}$ in Phosphorus, while the concentration of ^{214}Bi ranged from 2.50 $Bqkg^{-1}$ in Fish bone to 343.11 $Bqkg^{-1}$ in Phosphorus. The Phosphorus fertilizer contained higher contents of ^{238}U series than other fertilizers. The activity of ^{212}Pb ranged from 1.26 $Bqkg^{-1}$ in Organic fertilizers to 151.50 $Bqkg^{-1}$ in Fish bone, while the concentration of ^{208}Tl found from 1.12 $Bqkg^{-1}$ in NPK to 67.62 $Bqkg^{-1}$ in Fish bone $Bqkg^{-1}$, however, the concentration of ^{282}Ac ranged from 3.53 $Bqkg^{-1}$ in SSP to 42.84 $Bqkg^{-1}$ in Fish bone. The Fish bone fertilizers contained higher contents of ^{232}Th series than other fertilizers. The concentration of ^{214}Pb and ^{214}Bi were found in Organic fertilizers lower than in Phosphorus, SSP, RF, and TSP, while the concentration higher than in NPK and Urea. The activity of ^{212}Pb, ^{208}Tl and ^{228}Ac were found in Fish bone fertilizers higher than in Phosphorus, Korea fertilizers, Urea, Malaysian fertilizers, Organic, TSP, NPK, SSP and RF. The mean concentration of ^{214}Pb and ^{214}Bi are higher than the mean concentration of ^{212}Pb, ^{208}Tl and ^{228}Ac. Table.4 shows a comparison between the concentrations in fertilizer samples used in Iraq with other review of the worldwide data on natural concentration in fertilizers. The mean concentration of ^{238}U series were found lower than the concentration in Italy, Pakistan, India, Egypt and Nigeria, while the concentration higher than in Saudi Arabia. The mean concentration of ^{232}Th series were found higher than the concentration in Pakistan, India and Nigeria, while the concentration lower than in Saudi Arabia, Italy and Egypt. The present results showed the concentration of fertilizer samples lower than the concentration was reported by UNSCEAR. The highest concentration of ^{238}U series were found in phosphorus. This is in agreement with relevant previous studies that noted the concentration of uranium follows the concentration of P_2O_5 in

various fertilizers. There is a direct relationship between uranium and P_2O_5 content of fertilizers [19]. In general, the large amount of fertilizer has affected on soil, because of it increased of the radionuclides concentration. On the other hand, the application of these fertilizers causes an accumulation of radioactivity in soils that can be transferred to plants and it is harmful for the health of farmers and consumers of the products.

Conclusions:

The natural radioactivity of ^{238}U and ^{232}Th series has been measured in fertilizers used in Iraq. The mean concentration of ^{238}U and ^{232}Th series in fertilizers are 69.39 and 14.31 $Bqkg^{-1}$ respectively. The concentrations of ^{238}U series and ^{232}Th series in fertilizer are lower than the limit reported by UNSCEAR. On the other hand, the health of the entire population might be affected due to the use of phosphate fertilizers for agricultural purposes. Phosphate fertilizers pose a great danger on human health because its content has higher concentrations of uranium. These results widely supported the use of organic fertilizers in agriculture. The obtained data could be useful as baseline data for radiation exposure in fertilizers and their impact on human health.

Table 3: The concentrations of ^{238}U and ^{232}Th series in fertilizer samples collected from marketing

Fertilizer Samples	^{238}Useries ($Bqkg^{-1}$)		^{232}Th series ($Bqkg^{-1}$)		
	^{214}Pb	^{214}Bi	^{212}Pb	^{208}Tl	^{228}Ac
NPK	17.09	22.51	6.42	1.12	7.74
Organic	18.95	24.84	1.26	9.55	10.62
Malaysian Fertilizers	-	4.69	-	10.83	4.68
Urea	-	7.24	-	10.54	5.12
Korea Fertilizers	-	7.86	-	9.79	5.18
Fish bone	-	2.50	151.5	67.62	42.84
Phosphorus	402.53	343.11	6.04	24.67	26.60
Triple Supper Phosphate (TSP)	44.88	58.66	6.92	6.04	6.86
Rock Phosphate (RF)	80.87	109.08	2.49	3.64	6.59
Single Superphosphate (SSP)	130.25	111.94	1.68	2.42	3.53
Mean	**69.45**	**69.24**	**17.63**	**15.31**	**11.98**

Table 4: A comparison of the concentrations of ^{238}U and ^{232}Th series of fertilizer samples with the values reported for other countries

Country	^{238}U series ($Bqkg^{-1}$)	^{232}Th series ($Bqkg^{-1}$)	References
Italy	120.00	3.50	[20]
Pakistan	526.00	50.00	[21]
India	120.00	65.00	[22]
Egypt	410.00	7.90	[23]
Saudi Arabia	64.90	6.01	[24]
Nigeria	557.90	16.10	[13]
Mean	**69.39**	**14.31**	**Present Study**

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قياس وليدات اليورانيوم والثوريوم في نماذج الاسمده في العراق باستخدام تقنية طيف كاما

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الخلاصة:

حساب تركيز نويدات سلسلة اليورانيوم والثوريوم في الاسمدة المستخدمة في العراق. عشرون نموذج جمعت من الاسواق والمزارع. كاشف الجرمانيوي النقاوة (HPGe) استخدم لقياس طيف اشعة كاما. مدى تركيز الرصاص-214, البزموث- 214, والرصاص-212, والثاليوم -208 و الاكتنيوم-228 تراوح بين – 402.53 17.09, 2.50 -343.11, 1.12 – 67.62, 1.26 – 151.50 و 3.53 – 42.84 بكرل/ كغم على التوالي. معدل تركيز عناصر سلسلة اليورنيوم – 238 والثاليوم – 232 في الاسمده كان 69.39 بكرل/ كغم و 14.31 بكرل /كغم على التوالي. قورنت النتائج المستحصل عليها مع ما منشور عالميا في البحوث ووجد ان تركيز عناصر سلسلة اليورانيوم -238 والثوريوم -232 في الاسمدة اقل من القيمه المحددة والمنشورة في مجلس العلمي للامم المتحدة باثار الاشعاع النووي, ووجد ايضا ان تراكيز العناصر المشعة ضمن الحدود المسموح بها في الاستخدامات.

الكلمات المفتاحية: طيف اشعة كاما, اليورانيوم, الثوريوم, الاسمدة.

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