

Determination of the Concentration of ^{40}K of Mudstone in Northern Iraq by Using Gamma Ray Spectroscopy and Flame Photometry Technique

Hala D. Kharrufa
Department of Science
College of Basic Education
University of Mosul

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ABSTRACT

The study of natural radionuclide materials is important to assess the health hazards on human being and one of these materials is ^{40}K which is present in soil and different types of stones. This study is performed to assess the ^{40}K concentration in mudstones in the north of Iraq by (flame photometry and γ -ray spectroscopy) and to compare between these two techniques in measuring its level. So the activity of potassium was measured by these methods, and their results were compared with the results of other studies. The results show that the concentration of ^{40}K ranges from 284.3 Bq/kg to 2481.2 Bq/kg using γ -ray spectroscopy and 511.7 Bq/kg to 3623.6 Bq/kg using flame photometer technique and these results were comparable with the upper level of the world mean specific concentration of ^{40}K and cause no health hazard. The results obtained by the two methods were also, compared using T-test and P-value and they show no statistical significant difference.

Keywords: Mudstone, radioactive potassium, gamma ray spectroscopy, flame photometer, northern iraq.

^{40}K

40-

40-

/ 2481.2 - / 284.3 40 -
/ 3623.6 - / 511.7

INTRODUCTION

All studies on radiation levels and radionuclide distribution in the environment provide vital radiological baseline information. Such information is essential in understanding human exposure from natural and man-made sources of radiation and necessary in establishing rules and regulations relating to radiation protection as shown by (Harb *et al.*, 2008). Gamma radiation emitted from naturally occurring radioisotopes, such as ^{40}K which exists at trace levels in all ground formations represents the main external source of irradiation to the human body. Since ^{40}K not belong to the radionuclide chains ^{238}U and ^{232}Th so it's study regarded as an essential determination of the background natural radiation (Ukla, 2004). More specifically, natural environmental radioactivity and the associated external exposure due to gamma radiation depend primarily on the geological and geographical conditions, and appear at different levels in the soils of each region in the world and there is an increased interest in measuring radionuclide concentration in the environment due to their health hazards and environmental pollution as found by (Tzortzis *et al.*, 2004).

Potassium is considered as one of the main metallic elements in nature. It is widely spread in the earth crust. The radioactive isotope of potassium is ^{40}K , having a half-life of 1.28×10^9 years. It forms 0.017% of the total natural potassium (Hasan and Mheemeed, 2008). In fact, about (13.8%) of ^{40}K is responsible for the main contributions to the dose from natural radiation as found by (Wally *et al.*, 2001) and ^{40}K like all radionuclide elements can cause cancer in which the main source of exposure was inhalation followed by ingestion.

Different minerals with different concentrations are present in soil, clay and mudstone and the amount of potassium in soil differs according to the area, and from the geotechnical point of view the soil clay is the most active mineral component of soil due to its high specific surface area. In soils, clay is defined in a physical sense as any mineral particle less than two microns in effective diameter (Soils, 1977). Mudstone (also called mud rock) is a fine grained sedimentary rock whose original constituents were clays or mud. (Blatt and Tracy 1996).

The transformation of rock into soil is designated as soil formation. The rock may be, limestone, shale, sand, loess, peat, etc. To avoid too liberal an interpretation of the term "rock," soil scientists prefer to use the expression "parent" material or "soil" material to describe the formation of soil from rock (Jenny, 1994); So mudstones can be compared with soil due to the high similarity between them (Fityus and Smith, 2004), while mudstone properties may vary from soil and rock depending on its detailed lithology and its state of weathering.

Many researchers have been actively involved in the field of environmental radioactivity and radiation levels in the last few decades (Al-Farrash *et al.*, 1997; El-Sayd *et al.*, 1997; Sroor *et al.*, 2001). The studies of radionuclide ^{40}K was performed for different materials like soil (Hasan and Mheemeed, 2008), limestone (Najam *et al.*, 2011), marbles and granites (Wally *et al.*, 2001).

This study is performed to determine the ^{40}K concentration (using γ - ray spectroscopy and flame photometry) in mudstone in different areas in northern Iraq which indirectly reflect the natural health hazard, especially if we consider the wide use of mudstone particularly in rural areas; and to compare between the two methods of measuring ^{40}K .

MATERIALS AND METHODS

Eleven rock samples (mudstone) were collected from different locations in northern Iraq as shown in the map below:



Fig. 1: Location of selected samples

The potassium concentration was measured by two methods; γ -ray spectroscopy which was performed in the Nuclear Research Laboratory – Department of Physics- College of Science- Mosul University, and flame photometry which was performed in the Research Laboratory – Department of Science, College of Basic Education, Mosul University.

1- γ -ray spectroscopy

A sample of 100gm are taken from different areas. These samples were crushed manually to form a homogenous powder. Weighted samples were placed in glass containers of 500 cm³ volume then the radioactivity measured by γ -ray spectroscopy, employing a Scintillation detector NaI(Tl) (Oak Ridge, TN 37830. USA.) of diameter 3.8 cm and thickness 2.5 cm. The detector was interfaced to a PC-Computer with a program installed for this purpose to make it equivalent to a multi-channel analyzer.

The system also contains a usual electronic components of preamplifier, amplifier and power supply. The detector has resolution (FWHM) of 33.3 keV for the 1332.5 keV γ -ray line of ⁶⁰Co. The γ -ray spectrometer energy calibration was performed using ¹³⁷Cs and ⁶⁰Co point source in a lead protected box. Typical 7200 sec spectra were registered 1460 KeV from ⁴⁰K ($T_{1/2} = 1.28 \times 10^9$ years). The absolute efficiency of the detector for each γ -ray energy was then calculated from the formula (Sroor *et al.*, 2001):

$$E_{ff} = \frac{C}{A \cdot T} \quad \dots\dots\dots(1)$$

$$A = \frac{0.693}{T_{1/2}} \times \frac{W_i \cdot N_A}{A_i} \quad \dots\dots\dots(2)$$

Where E_{ff} is the absolute photo peak efficiency, C is the net count for the standard or sample, A is the activity of the radionuclide used in (Bq), T is the measurements time, $T_{1/2}$ is the half life of calculated isotope, W_i is the weight of the calculated isotope, N_A is the Avogadro's number, A_i is the weight number of calculated isotope, and I is the absolute intensity of the γ -transition. After the determination of the absolute efficiency, we can use the same eq(1) to calculate the activity of any sample at any selected energy, then the weight of ⁴⁰K isotope can be calculated in order to estimate their concentrations from the formula :

$$C \text{ (ppm)} = \frac{W_i(g)}{W_s(g)} \times 10^6 \quad \dots\dots\dots(3)$$

Where W_s is the weight of the sample. In order to determine the background due to the naturally occurring radionuclide in the environment around the detector, any empty container of the same (500 cm³) volume was counted. Measurement time for both samples and background was 7200 sec. The background spectra were used to correct the net γ -ray peak for the studied isotope. ⁴⁰K isotope concentration is usually expressed in terms of part per million (i.e) microgram per gram and in terms of specific activity Bq/kg, (1 μ g/gm = 258.46 Bq/kg for ⁴⁰K) it was calculated from the following formula:

$$\text{Specific activity} = \frac{A}{W_s} \quad \dots\dots\dots(4)$$

Where A is the weight number of ⁴⁰K.

2- Flame photometry

A photoelectric flame photometer is a device used in inorganic chemical analysis to determine the concentration of certain metal ions like potassium. Principally, it is a controlled flame test with the intensity of the flame color quantified by photoelectric circuitry. The intensity of the color depends on the energy absorbed by the atoms that was sufficient to vaporize them. The sample is introduced to the flame at a constant rate. Filters select which colors the photometer detects and exclude the influence of other ions. Before measurement, the device requires calibration with a series of standard solutions of the ions, so the solutions and standards are prepared from 0.5 M aqueous solution of ammonium acetate/acetic acid by taking 38.55g ammonium acetate and dissolving it in 29 ml of glacial acetic acid and the volume completed to 1 liter with distilled water. This solution was used as blank and to dilute standards and samples. The standard potassium solutions are prepared by weighing 1.907 g of potassium chloride in about 50-ml ammonium acetate / acetic acid solution and regarded as standard solution. A soil of 1 gm was transferred to a plastic bottle containing acetate / acetic acid solution and shaken using an automatic shaker for 30 minutes, allowed to settle for several minutes and filtered before aspiration of the blank and standards, then measured by the flame photometer and enter the values when prompted. Finally, the potassium content of the soil extract by spraying the solution was determined, without further dilution, by the flame photometer and reading result on the display (<http://www.jenway>, 2006). ^{40}K concentration can be found as (AUS-TUTE, 2012)

$$^{40}\text{K} \text{ (ppm)} = \frac{W(\text{g})}{V(\text{ml})} \times 10^{-6} \quad \dots\dots\dots(5)$$

^{40}K concentration calculated from the well –known formula (Georges, Audi 2003).

$$^{40}\text{K}(\text{ppm}) = K(\text{ppm}) \times 0.00017 \quad \dots\dots\dots(6)$$

RESULTS AND DISCUSSION

The concentration and activity of potassium are measured by flame photometer and γ -ray spectroscopy. On review of the results from the 11 regions in the north of Iraq as shown in Table (1), it is obvious that the potassium activity with γ -ray spectroscopy varies between 284.3 Bq/kg in sample 8 and 2481.2 Bq/kg in sample 9, while when the mudstone samples were examined by flame photometer the ^{40}K activity varies between 511.7 Bq/kg in sample 8 and 3623.6Bq/kg in sample 9.

Table 1: The concentration and specific activity of ^{40}K of studied samples in different locations with γ -ray spectroscopy and flame photometry while delta refers to the ratio between the two methods

Sample no.	Location	γ -ray spectroscopy		Flame photometry		* $\Delta = C_F/C_\gamma$
		activity	Conc.	activity	Conc.	
		Bq/kg	C_γ (ppm)	Bq/kg	C_F (ppm)	
1	Al-jeelah	620.3	2.4	930.4	3.6	1.5
2	Bashiqah	387.6	1.5	1243.1	4.81	3.2
3	Hamam Al-alel	749.5	2.9	801.2	3.1	1.06
4	Al-shirqat	757.2	2.9	790.8	3.06	1.05
5	Talkayf	485.3	1.8	630.6	2.44	1.3
6	Duhok	832.4	3.2	622.8	2.41	0.75
7	Talafar	1296.9	5.0	1933.2	7.48	1.49
8	Mindan	284.3	1.1	511.7	1.98	1.8
9	Zummar	2481.2	9.6	3623.6	14.02	1.4
10	Al-Namrod	310.1	1.2	666.8	2.58	2.1
11	Al-Ba'aj	827.0	3.2	1062.2	4.11	1.2

* Δ represents the ratio between the ^{40}K concentration which is measured by flame photometry and γ -ray spectroscopy.

These results show that the ^{40}K concentration which was measured by γ -ray spectroscopy and flame photometry were comparable, and the mean ratio between the two techniques was 1.53 ± 0.67 which was close to all samples except samples (2 and 6) in which the ratio in sample 2 was 3.2 and in sample 6 was 0.75 and this difference may occur due to the difference in the concentration, time and method of the storage of the chemical materials used in flame photometry.

The statistical analysis of these results using T-test and P-value shows that there is no statistical difference between the two methods as shown in Table (2) which means that both methods are reliable. In statistical hypothesis testing, the P-value is the probability of obtaining a test statistic at least as extreme as the one that was actually observed, assuming that the null hypothesis is true. One often "rejects the null hypothesis" when the P-value is less than the significance level α , which is often 0.05 or 0.01. When the null hypothesis is rejected, the result is said to be statistically significant.

Table 2: The comparison between the two methods using T-test and P-value

Mean γ -ray spectroscopy	SD	Mean flame photometry	SD	Number	T-test	P-value
3.1636 ppm	2.4138	4.5082 ppm	3.5107	11	1.0467	0.3077
821.073 Bq/kg	623.055	1165.127 Bq/kg	907.386	11	1.0367	0.3122

These results when compared with (Hasan and Mheemeed, 2008) results (there are 6 common areas) two of them are comparable while there are significant differences in the remaining four areas (double in one and half in the three) as shown in Table (3).

Table 3: Comparison between the activity of (Hasan and Mheemeed, 2008) and this study

Sample no.	Common Location	γ -ray spectroscopy (Bq/kg)	(Hasan and Mheemeed, 2008) (Bq/kg)
2	Bashiqah	387.6	793.45
3	Hamam Al-alel	749.5	388.63
5	Tall kayf	485.3	1009.36
7	TalAfar	1296.9	1014.76
8	Mindan	284.3	536.26
10	Al-Namrod	310.1	383

This can be probably explained if we know that (Hasan and Mheemeed, 2008) study includes soil and as we mention it was expected that the ^{40}K activity is lower than mudstone and they use γ -ray spectroscopy in their study.

(Najam *et al.*, 2011) study which was accomplished in northern Iraq and done on lime stones showed a narrower range of activity ranged between (290.5 Bq/kg – 637.1Bq/kg) but their study was done in different areas while the ^{40}K activity in Halabja city – Iraq / Sulaimania where (309.3 Bq/Kg) (Abdulla, 2009).

Most of the researches were involved soil not mudstones, but this study determines the concentration of potassium in the parent material of soil (mudstones), and as we mention the potassium activity and concentration are much higher than it was concentrated during the formation of mudstones.

If the ^{40}K activity in mudstones is compared with other types of stones (Granite and Marble) the average results will vary from (4.95 to 1335.18 Bq/kg) in different samples from Egypt as found by (Wally *et al.*, 2001) in which ^{40}K activity (the average from 12 samples was 127.1Bq/Kg), while the concentration of natural radioactivity in green Indian marble is lower than the concentration in the Egyptian marble and it is obvious that these results have greater range than ours. Also we have to mention that marble is a non-foliated metamorphic rock composed of recrystallized carbonate minerals, most commonly calcite or dolomite and

the geologists use the term "marble" to refer to metamorphosed limestone; however stonemasons use the term more broadly to encompass un metamorphosed limestone (Kearey and Philip, 2001).

The world mean specific concentration of ^{40}K (activity per unit soil mass) is 370 Bq/kg, varying from 100 to 700 Bq/kg (Mcaulay and Moran, 1988), while the average activity in this study was 821 Bq/kg which was comparable with the upper level of the world mean value.

Nevertheless, Table (4) shows that the mean of our results was comparable with south Bangladesh, very close with Japan and less than Egypt (soil from farm), Nile island soil, and this can be explained if we consider the factors responsible for soil formation in particularly climate factor and probably the similarity between Iraq and Bangladesh as both was riverine country (Bangladesh has 800 rivers) including tributaries flow through the country constituting a waterway of total length around 24,140 km, most of the country's land is formed through silt brought by the rivers (<http://en.wikipedia>, 1981); also in Japan there are more than 15 first class rivers which are characterized by their relatively short lengths and considerably steep gradients due to the narrow and mountainous topography of the country. The concentration of potassium in the remaining countries was lower than the results of this study which excepts being very low in Vietnam and Nigeria.

Table 4: Comparison of natural radioactivity levels in soil samples under investigation with those in other countries

Location	Activity(Bq/kg)	Reference
Vietnam (South-est)	34.6	Huy and Luyen (2006)
Nigeria	34.8	Arogunjo <i>et al.</i> , (2004)
Cyprus	104.6	Tzortzis <i>et al.</i> , (2004)
South India	117.5	Narayanq <i>et al.</i> , (2001)
Jordan (Amman Aqaba Highway)	138-601	Al-Jundi <i>et al.</i> , (2003)
Saudi Arabia Taif	162.8	El-aydarous (2007)
Syrian	270	UNSCEAR (2000)
Turky (Istanbul)	342	Karahan and Byulken (2000)
Denmark	460	UNSCEAR (2000)
Canada (Sackatchewan)	480	Kiss <i>et al.</i> , (1988)
Mexico(Zacatecas and Guandalupe)	530	Mireles <i>et al.</i> , (2003)
Pakistan(Lahore)	561.6	Akhtar <i>et al.</i> , (2005)
Spain	578	Quindós <i>et al.</i> , (1994)
Brazil (Rio Grande do Norte)	704	Malanca <i>et al.</i> , (1996)
Japan	794	Chen <i>et al.</i> , (1993)
Northern Iraq	821	This study (2012)
Bangladesh(Southern districts)	833	Chowdhury <i>et al.</i> , (2006)
Egypt (Farm soil)	1233	Ahmed and El-Arabi (2005)
Nile island's soil	1636	Ahmed and El-Arabi (2005)

CONCLUSION

From the results obtained, it can be concluded that the level of ^{40}K is reasonable in mudstone and falling in the range of other countries worldwide and comparable with soil and other types of stones. It is apparent that the difference in the levels of radiation activity is due to the differences in the geological and geographical nature of these regions. The mean concentration of ^{40}K in all samples is comparable with the upper world average limits. Potassium level was measured by two methods and there was no statistical significant difference between the them.

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