DETERMINATION OF NATURAL RADIOACTIVITY LEVELS IN Oil SLUDGE SAMPLES USING γ-RAY SPECTROSCOPY

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الملخص

تضمنت هذه الورقة دراسة تعيين تراكيز الفاعليات الإشعاعية الناتجة عن انحلالات سلاسل اليورانيوم والثوريوم وكذلك نويدة البوتاسيوم_40 في عينات الوحل المصاحبة لعمليات استخراج النفط وذلك باستخدام منظومة مطيافية أشعة جاما التي أساسها كاشف الجرمانيوم عالي النقاوة (HPGe). تراوحت تراكيز ^{226}Ra ما بين 9.7 إلى 180 Bq/kg بينما تفاوتت بين 7.87 إلى 895 Bq/kg لـ ^{232}Th أما 40K فكانت التراكيز ما بين 121 إلى 304 Bq/kg. كما تم حساب كميات أخرى مشتقة من هذه التراكيز كمكافئ الريديوم (Bq/kg) ومعدل الجرعة الممتصة(nGy/hr) وكذلك ومعدل الجرعة الفعَالة (μSv/hr) ومؤشر الخطورة الخارجي والذي تعدى القيمة المفترضة (1≤) في بعض العينات.

ABSTRACT

Activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in sludge generated during oil extraction and production operations were determined using a gamma spectroscopy system based on high purity germanium (HPGe) detector. Concentrations ranged from 9.7 to 1180 Bq kg^{-1} for ^{226}Ra, 7.87 to 895 Bq kg^{-1} for ^{232}Th and 121 to 304 Bq kg^{-1} for ^{40}K. The calculated radium-equivalent $(R_a)_{eq}$ activities ranged from 3.0 to 373 Bq kg^{-1} which are slightly higher in sample" X14 " than the permitted value (370 Bq/kg) . The evaluated absorbed dose rates were between 1.44 to 1.3 x10^3 (nGy/hr), while the deduced values for the effective dose rates and the external hazard index were between 1.77 to 1.36x10^3 μSv/yr and 0.072 to 5.36 respectively. The magnitude of these results demonstrates the need of screening oil residues for their radionuclide content in order to decide about their final disposal.

KEYWORDS: Activity concentrations; Gamma spectroscopy system; NORM; Dose rate; Hazard index.

INTRODUCTION

The radioactive elements: ^{238}U ($T_{1/2}$ = [4.468 ± 0.003] ×10^9 years), ^{232}Th ($T_{1/2}$ = [1.405 ± 0.006] ×10^{10} years) and ^{40}K ($T_{1/2}$ = [1.277 ± 0.008] ×10^9 years) are present in rocks that have condensed with the earth 4500 million years ago. These nuclei and their daughters decay either by alpha (α), beta (β) or gamma (γ) emission, until a stable lighter nucleus is reached. Contemporary studies on natural radioactivity have established that the presence of the uranium and thorium series and potassium-40 in various material constitute potential exposure to the global population. In the ^{238}U decay series, radon (^{222}Rn) is the only radionuclide found in the gaseous state and it can therefore emanate naturally from soil. The γ-emitting decay products of ^{222}Rn are lead (^{214}Pb) and bismuth (^{214}Bi), which are found in radioactive secular equilibrium with radium (^{226}Ra) only if sealed to stop radon from escaping [1].

Statistics indicate that these radionuclides are also found in crude oil, gas product, produced water, sludge and scale deposits in the surface and/or surface production facilities in the oil and gas industries. Naturally occurring radioactive materials (NORM) are problems

failings the Libya oil and gas industry today as many other oil producer countries many tons of NORM scale and sludge materials are remain on production sites awaiting for disposal.

NORM waste typically is created during an industrial, mining or manufacturing process that concentrates the naturally occurring radioisotopes to a level above background. The main radionuclides concentrated in scales and sludge during the processing of crude oil and natural gas are ^{226}Ra and ^{228}Ra. Radium-226 is the material of major interest of its solubility in water. Uranium and thorium are not very soluble and may not be leached. Measurements of natural radioactive nuclides in crude oil and other materials have been reported in a number of studies worldwide [2]. A number of techniques have been used to assess natural radionuclides in different environmental media. The commonly used methods include direct gamma spectroscopy, alpha spectrometry, liquid scintillation counting. The primary aim of this work is to determine the activity concentration of the natural radionuclides ^{238}U, ^{232}Th, and ^{40}K using gamma spectrometry based on a high pure germanium (HPGe) detector.

MATERIALS AND METHODS
Sample preperation

In this study all samples were collected from the south eastern part of Libya. The samples were dried, screened, weighted and then packed and stored. To optimize the detection efficiency in measuring environmental samples, a large quantity of the sample must be as close to the detector crystal as possible [3]. In order to achieve this Marenelli beakers were used. The Marenelli beaker used in this study is a liter polypropylene beaker with a 90 mm annular bottom (Figure 1).

Figure 1: A picture of the Marenelli beaker used in this study.

By using the Marenelli beaker the sample effectively surrounds the detector so that the counting efficiency is greater than would be the case if the sample were in any other type of container "close geometry radioactivity measurements".When γ-ray spectrometry is used for the measurement of natural radioactivity, the samples must be properly sealed for about four weeks to obtain radioactive secular equilibrium between ^{222}Rn (radioactive noble gas), its decay products (^{214}Pb and ^{214}Bi) and radium (^{226}Ra), from the ^{238}U decay series. In the ^{232}Th decay

series the radon isotope (^{220}Rn) poses no serious problem because of its short half-life of 55 seconds and in the ^{40}K decay series no equilibrium is needed.

EXPERIMENTAL PROCEDURE:

HPGe detector system

The detector used in the **N**uclear **R**adiation **L**aboratory (NRL) at the Department of Nuclear Engineering is a HPGe with a built-in preamplifier (Figure 2). To attenuate cosmic and other outside radiation, a lead castle of approximately 10 cm thick, with a copper lining on the inside to absorb any lead X-rays that are produced.

Figure 2: A photograph of the HPGe detector with accompanying lead castle used by the NRL.

Energy Calibration

The calibration was performed using full-energy peaks from a standard mixed, one liter Marenelli beaker source contains gamma emitters cover the energy range from 0.06 to 1.84 MeV. Using known gamma energies with their corresponding counts, the relationship between energy and channel number was established. The linear equation derived from the linear relationship is represented in following equation:

Energy (keV) = 1.305x (Channel) - 3.674   (1)

Equation (1) was used to obtain the relationship between energy and counts and hence spectra used in identification of radionuclides present in background and the samples.

Detector efficiency determination

The detector efficiency is dependent on the geometry, density and chemical composition of the sample and can be calculated using the formula [4]:

$$\varepsilon = \frac{C}{LT * Br * A}$$ (2)

Where
 ε = absolute photo peak efficiency,
 C = net counts in photo peak, after appropriate background subtraction,
 LT = live time, the time during which the system is available for processing a pulse,
 A = activity the source.

Br = branching ratio.

The net counts, C, for a particular photo peak from the spectrum is determined by manually setting a region of interest (ROI) around the peak of interest and the Gamma Vision software then uses an algorithm to automatically calculate the gross and net counts (i.e. those above the background in the sample spectrum) associated with the ROI. The obtained efficiency curve for the detector using in this study is presented in Figure (3).
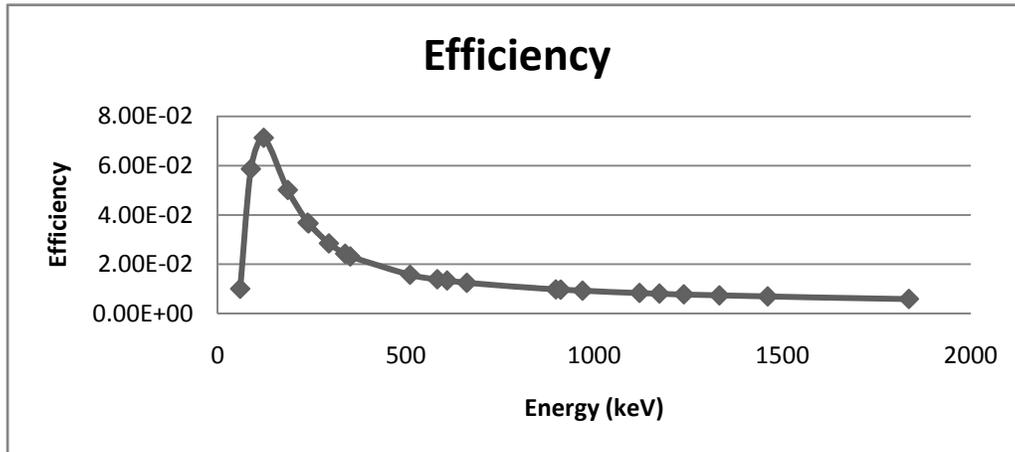
Figure 3: The absolute pho topeak efficiency calibration curve obtained from standard sources.

RESULTS AND DISCUSSION

Background spectrum

The measurement of environmental background is most significant when working with low level samples in order to determine the minimum detectable activity of the counting system [5]. The spectrum of the background radiation collected from in-active clear sand before sample counting is shown in Figure (4).

Radionuclides in Sludge Samples

In this study, 16 samples from different locations were collected and used for assessment of the level of radioactivity. The spectra were collected in the same geometry as background spectrum for 24 hours. Figure (5) presents gamma spectra for X2 sample.

Detection Limit and Minimum Detectable Activity (MDA):

It is essential to understand the detection limit when working with low-level samples such as environmental samples. The detection limit is calculated to estimate the detection capability of the measuring system. By calculating the detection limit, one can be able to claim with a certain level of confidence that the radionuclide presents in the sample can be detected by the system or not. The detection limit is defined as the counts that can be seen within fixed certainty. Generally, *LD* is defined by the following equation [5]:

$$\text{MDA} = \frac{N_d}{\varepsilon P_\gamma T} \tag{3}$$

Where $N_d = L_c + 2.706$, $L_c = 4.653\,\sigma_{NB}$, σ_{N_B} the standard deviation of the background and T is the sample counting time.

The formula used to calculate MDA to ensure that the distribution of the number of net counts lies above critical level within 95% confidence interval. From the results, it is clear that MDA is gamma energy dependent. The obtained results show that the minimum detectable activity values range between 0.0699 to 1.47 Bq. This range of values was used as a basis to decide the activity of radionuclide if the activity concentrations found in samples are below or above detectable limit throughout this study.

Activity Concentrations

The activity concentrations of radionuclides from ^{238}U, ^{232}Th series and ^{40}K present in the sample of mass m, was calculated using the following equation [6]:

$$A = \frac{C}{LT * Br * \varepsilon * m} \tag{4}$$

Tables (1) represents the activity concentrations of daughter radionuclides in the ^{238}U and ^{232}Th decay chains used in average activity concentration calculations of each series as well as the activity concentration for ^{40}K for four samples. The average activity concentrations are summarized in Table (2).

Radium Equivalent Activity

The expulsion of γ-rays from a mixture of ^{238}U, ^{232}Th, and ^{40}K in the sample is known as Radium Equivalent Dose (Ra$_{eq}$).The following equation was used to evaluate the hazard from gamma radiation in Bq/kg to humans from the samples [7].

$$Ra_{eq} = A_U + (A_K \times 0.077) + (A_{Th} \times 1.43). \tag{5}$$

Where A_U, A_K and A_{Th} are the specific activities of ^{226}Ra, ^{40}K and ^{232}Th in (Bq/kg)

Gamma Dose Rate

The gamma dose rate (D) in nGy/hr caused by naturally occurring radioactive materials in air at 1 m above the ground surface can be estimated using the following formula [8].

$$D = 0.461A_{Ra} + 0.623A_{Th} + 0.0414A_K \tag{6}$$

The results of Radium Equivalent Activity as well as the absorbed dose rate are presented in Table (2). From the table one can note that the lowest values were recorded for E2, N3 and W4 samples, while the highest values were obtained from X2, X5 and X14 samples.
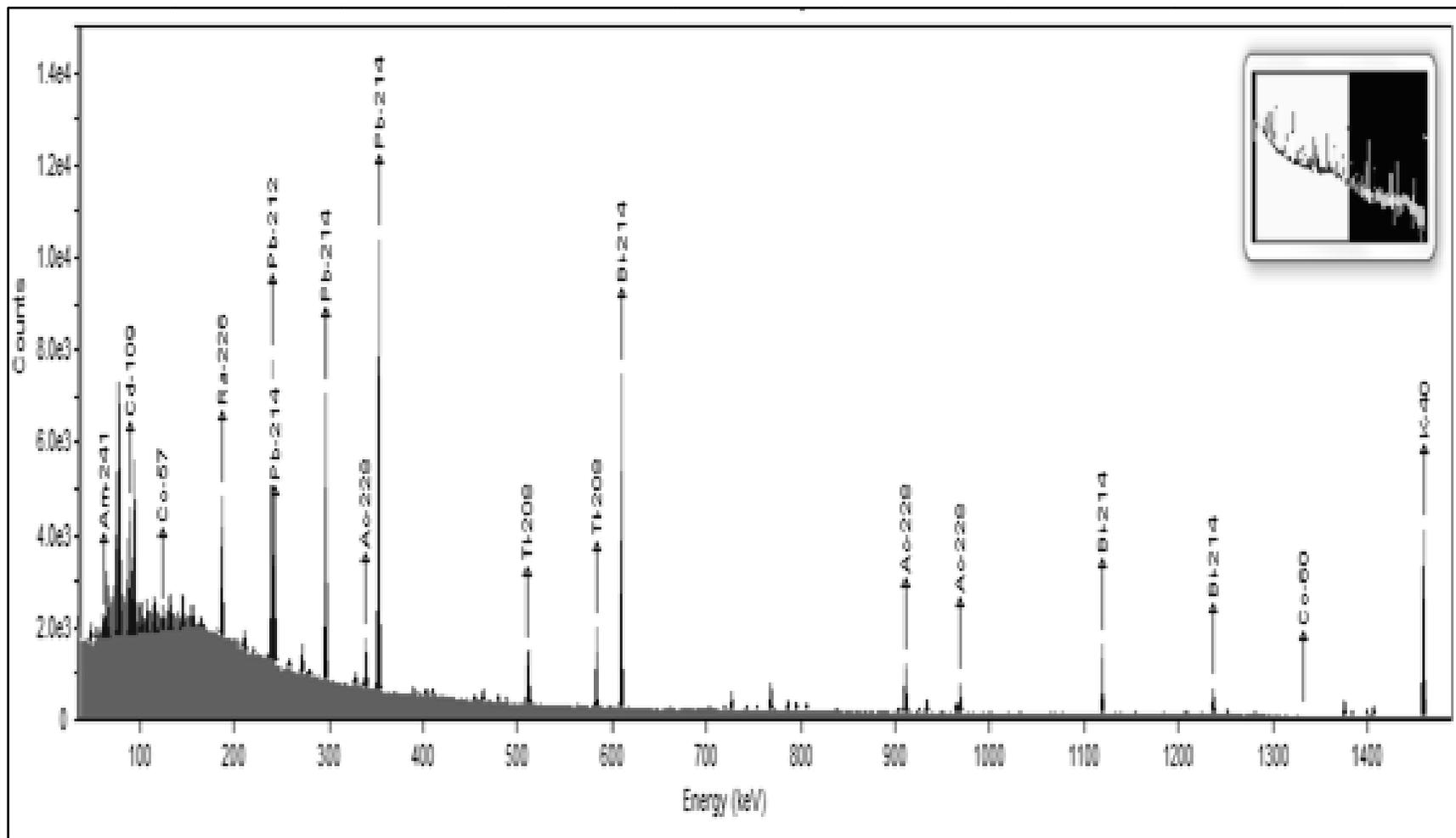
Figure 4: The background spectrum measured with clean sand sample collected for 24 hours.
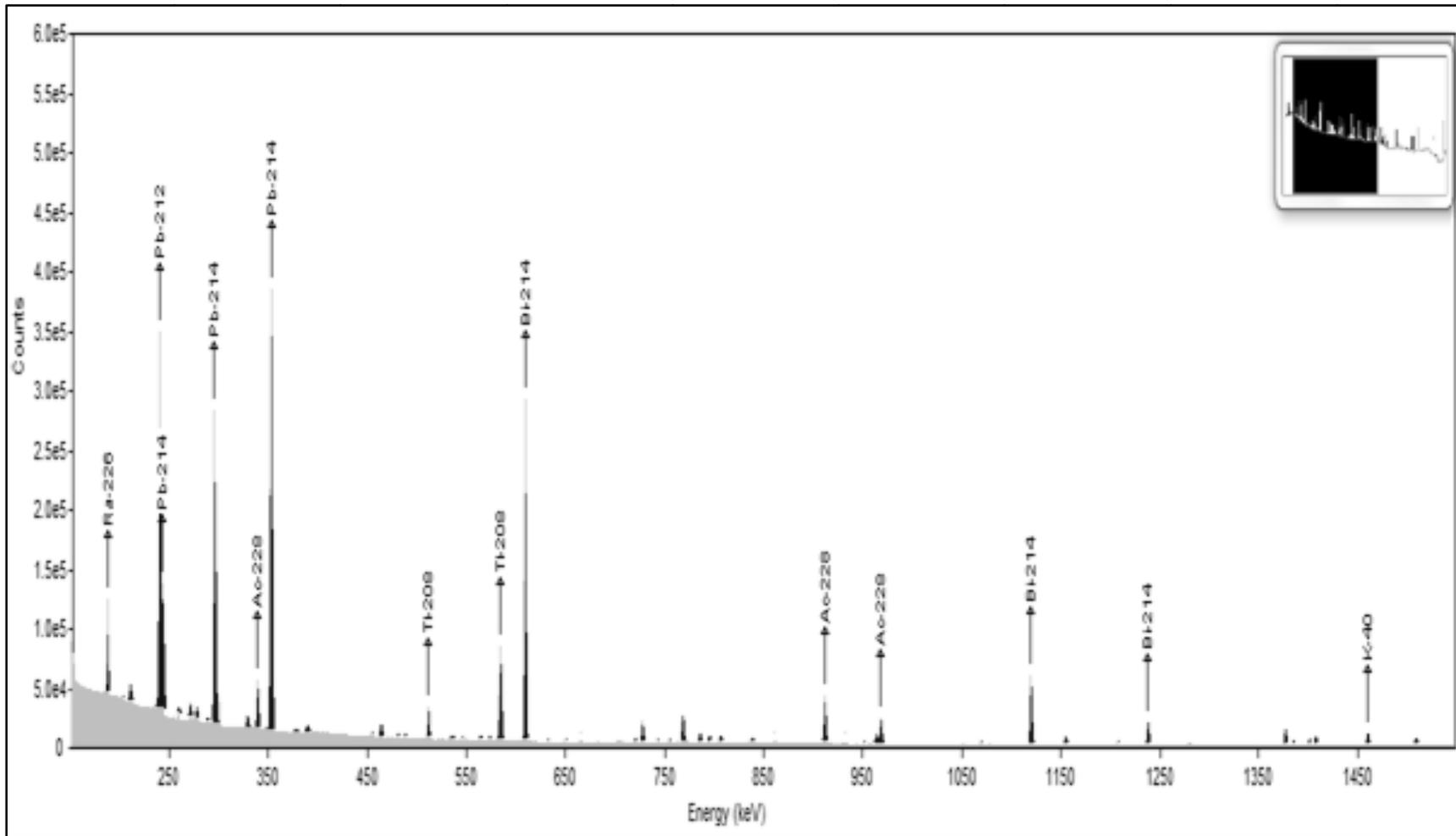
Figure 5: Gamma-ray spectrum of Sample X2

Table 1: Activity concentrations for decay products of ^{238}U, ^{232}Th and K^{40} for four samples.

Series	Radionuclide	Energy	Specific Activity samples (Bq/kg)							
			E2		S1		W4		X14	
			Ac	±Ac	Ac	±Ac	Ac	±Ac	Ac	±Ac
U-238	Ra-226	185.99	1.53E+01	2.80E-01	1.91E+02	3.49E+00	1.58E+01	2.89E-01	1.33E+03	2.42E+01
	Pb-214	241.92	7.12E+00	1.53E-01	1.17E+02	2.51E+00	9.49E+00	2.03E-01	1.04E+03	2.23E+01
	Pb-214	295.22	9.34E+00	1.95E-02	1.50E+02	3.12E-01	1.14E+01	2.38E-02	1.20E+03	2.50E+00
	Pb-214	351.99	1.04E+01	1.97E-02	1.50E+02	2.84E-01	1.23E+01	2.32E-02	1.23E+03	2.33E+00
	Bi-214	609.32	9.18E+00	3.19E-02	1.32E+02	4.58E-01	1.23E+01	4.28E-02	1.11E+03	3.85E+00
	Bi-214	1120.28	9.95E+00	1.99E-02	1.55E+02	3.08E-01	1.08E+01	2.16E-02	1.27E+03	2.53E+00
	Bi-214	1238.11	1.06E+01	5.38E-02	1.54E+02	7.82E-01	1.44E+01	7.32E-02	1.22E+03	6.21E+00
	Avg.		9.73E+00	3.91E-02	1.44E+02	5.75E-01	1.20E+01	4.86E-02	1.18E+03	4.72E+00
Th-232	Pb-212	238.63	7.93E+00	9.25E-03	1.05E+02	1.22E-01	9.99E+00	1.17E-02	6.87E+02	7.98E-01
	Ac-228	338.4	8.25E+00	4.69E-04	1.62E+02	4.96E-03	1.08E+01	6.13E-04	9.55E+02	2.55E-02
	Tl-208	510.72	3.27E+00	3.24E-04	4.17E+01	2.36E-03	3.81E+00	3.96E-04	3.16E+02	1.45E-02
	Tl-208	583.14	3.12E+00	2.59E-03	3.98E+01	3.25E-02	3.25E+00	2.71E-03	2.74E+02	2.23E-01
	Ac-228	911.07	8.76E+00	1.21E-02	1.64E+02	2.26E-01	1.12E+01	1.55E-02	9.89E+02	1.36E+00
	Ac-228	968.9	8.99E+00	1.54E-02	1.90E+02	3.27E-01	1.03E+01	1.77E-02	9.80E+02	1.68E+00
	Avg.		7.87E+00	1.30E-03	1.51E+02	1.88E-02	1.02E+01	1.60E-03	8.95E+02	1.10E-01
K-40		1460.75	1.21E+02	8.10E-04	1.72E+02	1.34E-03	1.53E+02	1.04E-03	2.42E+02	1.16E-03

Table 2: Gamma Dose Rate (nGy/h) and Radium Equivalent Activity from all samples.

Sample	Ac (Bq/kg)								Dose rate (nG/hr)	
	Ra-226		Th-232		K-40		Ra$_{eq}$			
	Ac	±Ac	Ac	±Ac	Ac	±Ac	Ac	±Ac	D	±D
E2	9.73E+00	3.91E-02	7.87E+00	1.30E-03	1.21E+02	8.10E-04	3.03E+01	4.11E-02	1.44E+01	1.81E-02
S1	1.44E+02	5.75E-01	1.51E+02	1.88E-02	1.72E+02	1.34E-03	3.73E+02	6.02E-01	1.68E+02	2.65E-01
W4	1.20E+01	4.86E-02	1.02E+01	1.60E-03	1.53E+02	1.04E-03	3.83E+01	5.10E-02	1.82E+01	2.24E-02
N3	1.04E+01	4.13E-02	8.06E+00	1.45E-03	1.51E+02	1.10E-03	3.36E+01	4.35E-02	1.61E+01	1.91E-02
X2	5.41E+02	2.09E+00	1.69E+02	2.50E-02	1.78E+02	9.64E-04	7.96E+02	2.13E+00	3.62E+02	9.65E-01
X3	2.39E+02	9.40E-01	2.31E+02	3.18E-02	1.90E+02	9.81E-04	5.83E+02	9.86E-01	2.62E+02	4.34E-01
X5	2.67E+02	1.08E+00	2.76E+02	3.16E-02	1.81E+02	9.86E-04	6.77E+02	1.12E+00	3.03E+02	4.97E-01
X7	2.73E+02	1.09E+00	2.31E+02	2.97E-02	1.73E+02	1.28E-03	6.16E+02	1.13E+00	2.77E+02	5.02E-01
X8	2.70E+02	1.04E+00	2.41E+02	3.20E-02	1.59E+02	6.92E-04	6.26E+02	1.08E+00	4.75E+02	4.79E-01
X9	8.32E+01	3.30E-01	8.30E+01	1.09E-02	3.04E+02	1.94E-03	2.25E+02	3.46E-01	2.85E+02	1.52E-01
X10	1.21E+02	4.92E-01	1.34E+02	1.67E-02	1.58E+02	1.31E-03	3.25E+02	5.16E-01	2.81E+02	2.27E-01
X12	1.38E+02	5.45E-01	1.51E+02	2.05E-02	1.93E+02	1.36E-03	3.68E+02	5.74E-01	3.25E+02	2.51E-01
X13	1.91E+02	7.42E-01	5.96E+01	8.67E-03	1.63E+02	1.06E-03	2.89E+02	7.54E-01	2.61E+02	3.42E-01
X14	1.18E+03	4.72E+00	8.95E+02	1.10E-01	2.42E+02	1.16E-03	2.48E+03	4.88E+00	1.70E+03	2.18E+00
X15	1.88E+02	7.19E-01	1.18E+02	2.13E-02	2.14E+02	1.10E-03	3.73E+02	7.50E-01	3.38E+02	3.32E-01
X16	5.21E+02	2.03E+00	5.35E+02	6.38E-02	2.09E+02	1.14E-03	1.30E+03	2.12E+00	9.32E+02	9.38E-01

The Annual Effective Dose Rate:

The annual effective dose equivalent (AEDR) in μSv/y was calculated using equation (7) [8] and the results are listed in Table (3).

$$\text{AEDR } (\mu Sv/y) = D \ (nGy/h) \times 8760(h/y) \times 0.2 \times 0.7(Sv/Gy) \times 10^{-3} \tag{7}$$

Table 3: The Annual Effective Dose Rate for 16 Samples.

Sample	AEDR (μSv/y)	±AEDR (μSv/y)	Sample	AEDR (μSv/y)	±AEDR (μSv/y)
E2	1.77E+01	2.22E-02	X8	3.45E+02	5.87E-01
S1	2.05E+02	3.26E-01	X9	1.26E+02	1.87E-01
W4	2.23E+01	2.75E-02	X10	1.79E+02	2.79E-01
N3	1.97E+01	2.34E-02	X12	2.03E+02	3.08E-01
X2	4.44E+02	1.18E+00	X13	1.62E+02	4.19E-01
X3	3.21E+02	5.32E-01	X14	1.36E+03	2.67E+00
X5	3.72E+02	6.09E-01	X15	2.07E+02	4.07E-01
X7	3.39E+02	6.15E-01	X16	7.14E+02	1.15E+00

External Hazard Index

Humans are exposing to gamma radiation from natural Radionuclides surrounding them. The external hazard index, H_{ex}; is deduced by the following equation:

$$H_{ex} = \frac{C_K}{4810} + \frac{C_{Th}}{259} + \frac{C_{Ra}}{370} \leq 1 \tag{8}$$

This expression indicates that the value of this index must be less than unity for the radiation hazard to be insignificant. Thus, the maximum values of H_{ex} equal to unity correspond to the upper limit of Ra_{eq} being 370 Bq/kg [9]. Table (4) shows the external hazard index calculated for each sample. External hazard index was found in some cases to be higher than the recommended value (≤ 1).

Table 4: External Hazard Index from 16 Samples.

Sample #	E2	S1	W4	N3	X2	X3	X5	X7
Hex	7.23E-02	1.01E+00	1.04E-01	9.07E-02	2.15E+00	1.58E+00	1.83E+00	1.66E+00
±Hex	1.06E-04	1.56E-03	1.31E-04	1.12E-04	5.66E-03	2.54E-03	2.91E-03	2.94E-03
Sample #	X8	X9	X10	X12	X13	X14	X15	X16
Hex	1.54E+00	5.42E-01	8.06E-01	1.01E+00	4.49E-01	5.36E+00	1.09E+00	3.13E+00
±Hex	6.76E-04	1.88E-04	3.06E-04	4.58E-04	2.18E-04	2.20E-03	6.85E-04	1.21E-03

DISCUSSION AND CONCLUSSION

The energy calibration curve shows the linear relationship between the channel and gamma-ray energy. The linear equation was used to obtain the relationship between channel number and energy which was then used in the entire process of peak identification.

As shown in Figure (1), the absolute efficiency of the detector varies with the gamma energy. At low energies, the absolute efficiency increases with increasing energy of gamma rays. This is due to the fact that at low energies photoelectric interaction is the dominant process. In high energy region, a significant amount of gamma rays can pass the detector without interaction. This implies that the probability of detecting radionuclides decreases as photon energy increases.

The radionuclides found in the samples spectra come from natural occurring radioactive materials (NORM). Almost all the radionuclides are the progeny of 232Th and 238U decay chains namely ^{228}Ac, ^{212}Pb, ^{214}Pb, ^{226}Ra, ^{208}Tl and ^{214}Bi. The collected gamma spectra for samples X2, E2 and W2 (Figures 5-7) demonstrate the presence of these natural radionuclides.

The specific activities of sixteen samples show a great variation (Table 2).The differences are due to the different composition and density of the samples. In initial stages of extraction, oil from reservoir is usually water-free, however, the more the oil is extracted the water present in the reservoir will begin to co-produce with the oil. High activity concentrations were found from sample X2, X4 and X14, while the lowest were registered by sample E2.

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