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NAA for Trace Elemental Analysis of Sludge Samples from Different Oil Sites in the Egyptian Eastern Desert

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Abstract: Determination of the radioactive isotopes concentrations in the petroleum waste of sludge and sand is an essential issue not only to refineries, industrial processing, waste disposal and transports but also, to human health and the environment. As these radioactive isotopes are radiation risky, therefore they should be assessed and controlled. Moreover, they might contain heavy and toxic elements which cause hazardous pollution. This paper will focus on the evaluation of the concentrations of metals, heavy and toxic elements in sludge samples from different petroleum companies' sites located in the eastern Egyptian desert. Five sludge oil samples were elementally analyzed by Neutron Activation Analysis (NAA) technique. The samples were irradiate using the irradiation box inside the Egyptian second research reactor (ETRR-2) (rabbit irradiation system) for 4 hours and then counted after 14 days using HPGe detector. 18 isotopes named (Ca, Sc, Cr, Fe, Co, Zn, Br, Rb, Sr, Ag, Sb, Cs, Ba, Eu, Yb, Lu, Hf, and Ta) were detected with different concentrations in the samples under investigation. The isotopes of Ca, Fe, Sr, and Ba had high concentrations compared with other isotopes in the samples. The toxic element of barium with high concentration and other trace elements with low concentrations were detected in the samples. High concentration of Fe trace elements above the standard level was detected in all samples. The outcomes of the study imply that more monitoring is needed for the petroleum waste in these locations to minimize the environmental pollution and to minimize the radiation risk for the workers.

Keywords: INAA, Sludge, TE-NORM, Irradiation, Oil trace elements.

1 Introduction

The measurement of trace elements in crude oil is a crucial issue not only for the petroleum research but also for the practical use of the oil afterword. As the final product of the oil is strongly affected by the trace amount of copper, vanadium, arsenic, and other metals in the crude oil [1]. The copper as one example has a poison effect in many refinery catalyst processes during the crude oil preparation [2]. From the practical use of product point of view, oil with less environmental pollution is critical, as the high sulfur contents in the oil cause prospect danger to the air due to the formation of sulfur dioxide after burning. It is essential to identify and know the concentration of the trace isotopes in the crude oils for the petroleum processing and utilization. It is believed that know the elemental compositions of the petroleum is mandatory not only is to recognize the harmful elements but also desired to assess the quality and identify the country of its origin [3]. Moreover, the existence/ absence, and concentration of the isotopes in the crude oil is an indicator of its marine and vegetable origin.

The oil-sludge is one of the petroleum wastes which consists of oil, water, sand, clay, corrosion products, flakes of paint, bacteria growth and fines derived from scale and salts which are generally formed during production, operation, storage, and refining of oil via digging machines, oil-water separator, storage tanks, desalted oil systems and transferring pipelines [4-6]. The accumulating of petroleum sludge in the bottom of tanks and on the inner wall of pipes makes the oil capacity and potential operation of oil to be lower over time, besides, creates a thick layer of an insoluble mixture of toxin isotopes, the radioactivity of heavy sediments and non-combustion solids. Efforts and techniques are potentially done to reuse the sludge via extracting valuable fuel oil, consequently, decrease the

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overall processing cost and to discard it by using safety ways [5-6]. The analysis of oil-sludge can be classified into three categories. The first one is called elemental analysis, which concerns the determination of the primary, minor and trace elements of sludge. The second category is the microbiological analysis, which studies microbes and bacteria within it, while, the third one is the mineralogical analysis, which handles with sand and clay in its residue [4]. In this study, the elemental analysis technique will be used to determine the trace elements of five sludge samples collected from different petroleum sites in the eastern Egyptian desert, see figure 1.

Various analytical techniques are well developed and used for counting of trace elements in petroleum. The considerably used techniques are requiring pre-concentration of the oil. Herein, the techniques are arranged from oldest to recent. Starting from 1968, the Colorimetric analysis [7], atomic absorption spectroscopy [8], polarography [9], neutron activation analysis (NAA) which has been used to measure trace elements in petroleum samples by different authors [10-13], and optical emission spectroscopy [14]. Due to its capability of detecting minimal quantities of elements, NAA techniques are widely used and investigated. The next paragraphs briefly present the main types of the NAA techniques.

The NAA technique can be classified into three categories sub-methods based on the energy of the activation neutrons: thermal, epithermal and fast neutrons. The Thermal-NAA, which depends on using the advantages of a high-activation cross-section of the thermal neutrons with more than 70 of

The natural elements through the (n,γ) reactions [15].

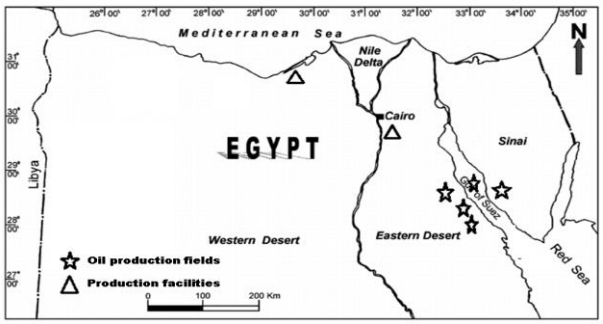

Fig. 1. Locations of the oil production fields and facilities in the eastern Egyptian desert.

Epithermal-NAA, which employ the non-thermal neutrons

to activate the elements and used to investigate the isotopes like U, Ti, In, Au, Ta, Ag, Br, Co, I and Sb [16]. Fast-NAA, sometimes called 14 MeV neutron activation analysis, in this method the fast neutrons from nuclear research reactor or an isotope neutron source are utilizing, and it has good advantages to detect of metal contaminations in the soil [17], example of these isotopes are Ag, Al, Au, Si, P, F, Cu, Mg, Mn, Fe, Zn, As, and Sn.

Another two different NAA techniques which are depending on the way in which the radionuclides are analyzed are RNAA and INAA. The Radiochemical-NAA technique is used in case of matrix activity is masking the induced radionuclides of trace elements, and the resulting radioactive sample is chemically decomposed [18-19]. Therefore, chemical separation techniques, (liquid extraction [20], ion exchange [21], precipitation [22], electrolysis [23], and chromatography [24]), are applied on the radionuclides for isolation into a single or several fractions. These fractions are free of interfering radio

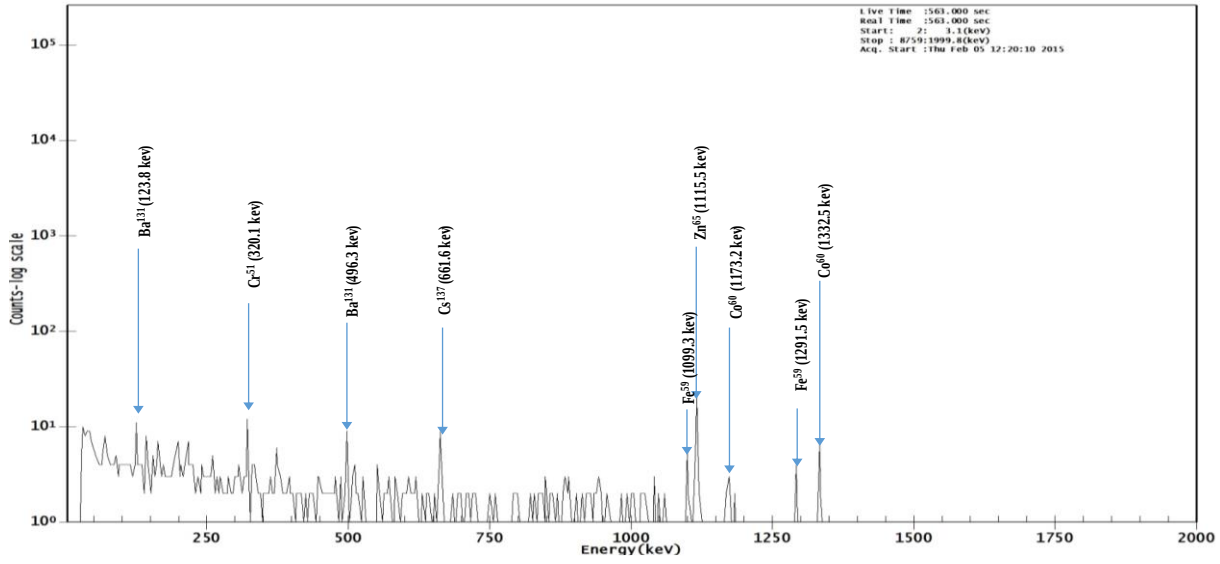

Fig. 2. Gamma spectrum of blank

activities each one or relatively few radionuclides. Instrumental-NAA, it is not like the RNAA method, the decomposition of the radioactive samples is not applied in this method. However, it is based on the difference of the decay rates via using high-resolution detectors to measure the decay rates at different intervals [25-27]. INAA method is widely used with most elements in a variety of samples and materials to find out the first and trace quantities.

Another NAA techniques which need for particular irradiation, or counting and data treatment like IVNAA, and CNAA, are merely explained herein. In Vivo-NAA, which concern the determination of the element concentrations like C, Ca, K, Na, O, and P, moreover, it can be used to trace element content in the human body [28]. Prompt Gamma-ray-NAA, which used to measure the concentrations of very short-lived isotopes (half-life <10 s) [29].

The object of this work is to evaluate the concentrations of metals, radioactive, heavy and toxic elements in sludge oil samples collected from five different locations in the eastern Egyptian desert. The evaluation will be conducted using the NAA technique and the HPGe detector as a non-destructive technique to determine the trace elements of sludge oil samples. Thermal neutrons irradiated the samples for 4 hours from the Egyptian second training research reactor (ETRR-2), and then the samples were counted using a high-resolution gamma-ray spectrometer after 14 days of irritation. The paper is arranged as next. In section II, the mathematical background and calculation technique used to determine the element concentrations and the uncertainty are presented, followed by experimental conditions in section III. In section IV, the results and discussion are depicted, and finally, the paper conclusions are mentioned in section V.

2 Concentration Calculations

To perform a quantitative calculation of mass concentrations of the isotopes in the sludge samples using NAA, there are several methods well developed and applied. These methods include absolute, relative and comparator methods [30]. In this paper, only the absolute method will be explained and applied to determine the element concentrations, then the uncertainty of the determined masses is obtained based on the calculated mass.

In this method, the concentrations of the elements under analysis are determined after getting exact information about the irradiation parameters and nuclear with reasonable accuracy. The mass (m_x) of an element (x) can be expressed regarding the flux parameters and nuclear data in the form:

$$m_x = N_p \frac{\lambda}{S.D.C.\phi_{th}.\sigma_{eff}.\gamma_x.\varepsilon_p.} \frac{M_x}{W\,\theta_x\,N_{Av}} \quad (1)$$

where N_p is the net peak area under the gamma peak of interest, M is the atomic mass of the element, λ is the half-life time, S is the saturation factor$S = (1 - e^{\lambda t_{ir}})$, t_{ir} is the irradiation time. While D is the decay factor $D = e^{\lambda t_d}$ and

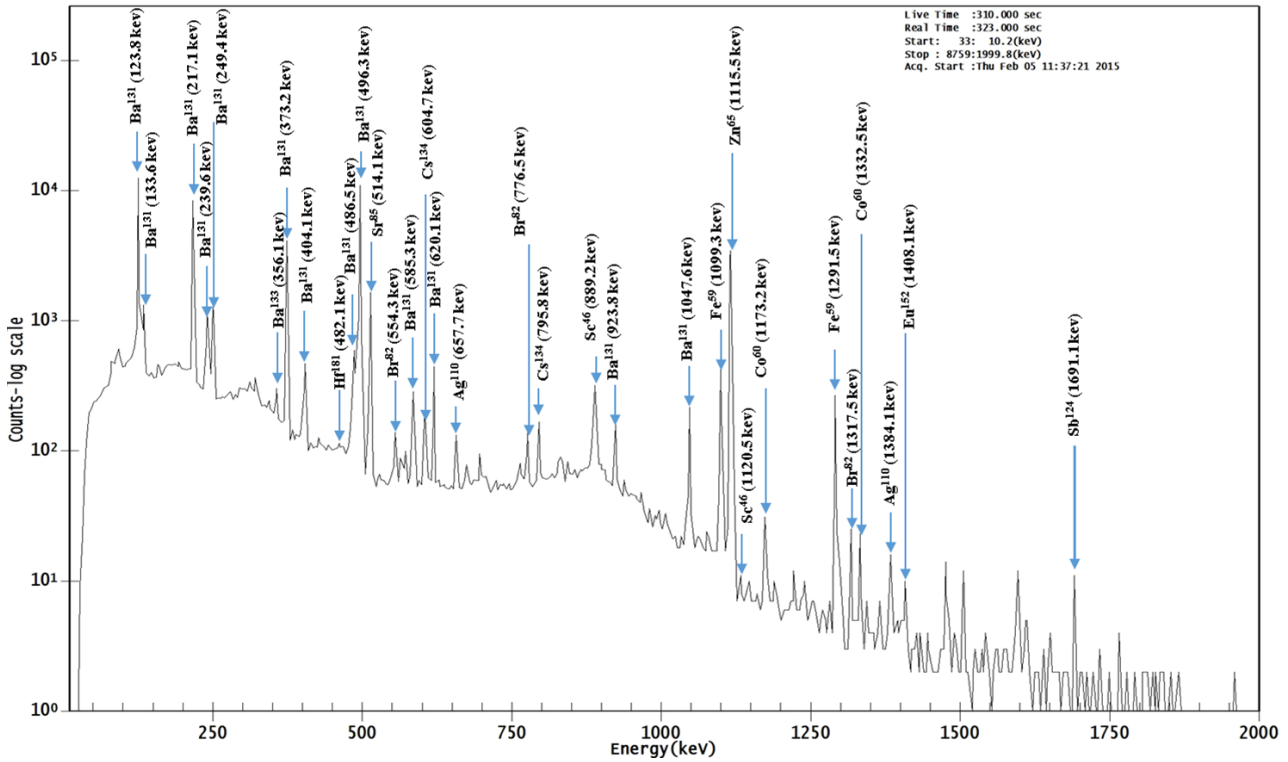

Fig. 3. γ– ray spectrum of neutron activated sludge oil sample (S-102) from Eastern desert in Egypt. Neutron integrated flux: 2.7×10^{14} n cm^{-2}, decay time is 14 days, count interval 300 sec.

t_d is the decay time. C is the correction factor for the decay during the counting period, $C = (1 - e^{\lambda t_m})/\lambda t_m$, and t_m is the counting time. ϕ_{th} is the thermal neutron flux, σ_{eff} is the effective cross-section, γ the yield of the analytical gamma line, ε_p is the photopeak efficiency, W is the sample weight, θ_x is the natural abundance of the target isotope, N_{av} is the Avogadro's number, more details of the methods are presented in [30]. The uncertainty of the mass can be determined from the absolute method using equation 2: [30]

$$\Delta m_x = m_x \sqrt{\left(\frac{\Delta N_p}{N_p}\right)^2 + \left(\frac{\Delta \gamma_x}{\gamma_x}\right)^2 + \left(\frac{\Delta \phi_x}{\phi_x}\right)^2 + \left(\frac{\Delta \varepsilon_x}{\varepsilon_x}\right)^2} \quad (2)$$

where ΔN_p, $\Delta\gamma_x$, $\Delta\phi_x$, and $\Delta\varepsilon_x$ are the uncertainty values of the net peak area under gamma peak, uncertainty of the yield of the analytical gamma line, the uncertainty of the measured thermal neutron flux, and the uncertainty of the photopeak efficiency, respectively.

3 Experimental

Pre-irradiation of the samples: the five samples were weighted and numbered (S-101~S-105). A 3 gm of the samples were washed with distilled water and nitric acid and then capsulated in polyethylene vials (1.4x0.6 cm^2). The vials were placed in Aluminum can (7x2.2 cm^2) which works as monitor flux to enhance the thermal ratio to epithermal neutron flux [31]. Then immediately the samples were measured to determine the background using through the technologically enhanced naturally occurring radioactive materials (TE-NORM) to see and compare the radioactivity of the samples before and after extended irradiation by thermal neutrons. The flux monitoring and golden sheets are associated with the samples during the

Table 1: Elements and there radioactive isotopes.

Elements	(n,γ) reaction product	σ_{th} barns	Half-life	Photon Energy keV
Ba	^{131}Ba	8.679	11.50 d	496.3, 123.8, 216.1
Ba	^{133}Ba	6.531	10.51 y	356.1, 302.9
Fe	^{59}Fe	1.149	44.50 d	1099.3, 1291.6, 192.2
Sc	^{46}Sc	27.166	83.79 d	889.2, 1120.5
Ca	^{47}Ca	0.7405	4.54 d	1297.1, 807.9, 498.2
Co	^{60}Co	37.184	5.27 y	1173.2, 1332.5
Cr	^{51}Cr	15.405	27.70 d	320.1
Hf	^{181}Hf	13.073	42.39 d	482.1, 133.1, 345.9
Zn	^{65}Zn	0.788	244.26 d	1115.5
Lu	^{177}Lu	2097.83	6.71 d	208.4, 321.3, 113.1
Rb	^{86}Rb	0.494	18.66	1076.6
Sr	^{85}Sr	0.822	64.84 d	514.1
Cs	^{134}Cs	29.054	2.062 y	569.3, 604.7, 795.8
Ag	^{110}Ag	90.266	249.79 d	657.7, 884.7, 937.5
Br	^{82}Br	2.365	35.30 h	554.3, 619.1, 776.5
Eu	^{152}Eu	9184.8	13.33 y	334.3, 121.8, 1408.1
Sb	^{122}Sb	5.773	2.72 d	564.1, 692.6
Sb	^{124}Sb	3.875	60.20 d	602.7, 722.8, 1691.1
Ta	^{182}Ta	21.126	114.43 d	1121.3, 1189.1, 1221.4
Yb	^{175}Yb	119.541	4.185 d	396.3, 282.5, 113.8

irradiation process to control and evaluate the neutron flux at irradiation position via a software program supplied to the reactor. The polyethylene capsules were sealed and neatly arranged in the irradiation capsules. Finally, the samples were transferred carefully to the irradiation site of the Egyptian second research reactor ETTR-2. The sludge-oil and flux monitoring samples were irradiated for 4 hours long with neutron flux of $2.7x10^{14}$ n/cm^{2}sec from the ETTR-2 operating at a power of 18 MW. After irradiation, the samples and flux monitoring were removed from the reactor for cooling and decay unwanted short-lived activates for 14 days. For counting the samples and flux monitors after the decay time, High Purity Germanium (HPGe) system was used. The detection system consists of Ortec co-axial p-type High Purity Germanium detector with a photopeak efficiency of 60%, 2 keV energy resolution for Co^{60} at FWHM. The detector was calibrated at energies of Co^{60} (2 lines at 1173.2 and 1332.5 keV), Cs^{137} (661.62 keV), and Ba^{133} (4 lines at 302.84, 356, 383.85 and 276.4 keV). Gamma vision software was used for energy and efficiency calibrations. Genie-2000 software was used for data acquisition and calculating the photopeak areas, live time, FWHM, uncertainties, and efficiency. The HPGe detector was shielded using a Canberra low background chamber model 747E consisting of lead. The samples were counted at 5 cm distance from the detector's top crystal to decrease the dead time percentage and enhance the detector efficiency.

4 Results and Discussion

Figure 2, shows the gamma-ray spectrum of the polyethylene capsule (blank) before the irradiation, while figure 3 shows the spectrum of the activated sludge sample, sample S-102 as an example. The background level is minimal compared to the activated signal, even with that, the background values were subtracted from the activated one. Table 1, presents the target elements, thermal nuclear reactions used in this work and corresponding cross sections, half-life time for the isotopes and photon energy for every element. The parameters of the experiment are used in equation 1 to determine the mass concentrations of the isotopes in the samples. In the experiment the irradiation time (t_{ir}=4 hours), the decay time (t_d=14 days), the counting time (t_m=300 sec), thermal neutron flux ($\phi_{th}=2.7\times10^{14}$ n cm^{-2}), and Avogadro's number ($N_{av}=6.02214\times10^{23}$ mol^{-1}). The energy and corresponding interaction cross sections are determined and then used in equation 1. The results of the calculated concentrations are presented together with the uncertainty of the element concentrations which calculated using equation 2 and given in Table 2.

It is important to mention that, the (n, γ) or (n, p) reactions which produced from the fast and epithermal neutrons were ignored in this study, assuming the purity of the thermal neutron flux. Also, due to the absence of the chemical treatments of the samples, a definite difference in the concentration of the element was observed. The measurement after 14 days after the irradiation process mainly assists in lowering the background radiation and increases the ability to explorer isotopes with a low concentration and avoids the interference from the low half-life time isotopes. [32].

From figure 3, and Table 2, 18 isotopes named Ca, Sc, Cr, Fe, Co, Zn, Br, Rb, Sr, Ag, Sb, Cs, Ba, Eu, Yb, Lu, Hf, and Ta, were detected clearly in the samples. It is naturally observed from the Table 2 that, Ba, Fe, Sc, Co, Eu, and Sb appear in all samples with relatively high concentrations for Ba, and Fe and small concentrations for the rest of the elements. Also, the analysis of the samples S-101, and S-104 showed the same compositions by observing the existence of Ca, Lu, Rb, Ta, and Yb the first element (Ca) with high concentrations and the rest with low level. While, the elements of Cr, Hf, and Cs appeared at low levels in samples under investigations compared with Sr concentration. It is noted that the elements Zn and Ag appeared with high and low concentrations respectively, in the samples S-102 and S-102, 103 and 105. The content Br appeared in only one sample S-102 with low concentrations. The toxic trace elements of Be, Hg, Tl, As, Pb, Ni, F, Pu, Th, and Am were not detected from the analysis of the samples. Moreover, the rare earth elements of La, Ce, Pr, Nd, Sm, Gd, and Dy were not detected from the samples under investigations.

Due to the negative environmental impact of the petroleum because of its toxic to all life forms, it is essential to determine whether the petroleum sites include toxic elements or not and in which concentrations exist. The analysis of the element concentrations revealed that some toxic trace elements are maintained in the sludge oil samples. The Barium element was observed with low concentration levels in samples S-101 and S-104 and high concentrations in the rest of the samples as seen from Table 2, which imply additional consideration to the toxic element in all these petroleum sites. While, Cobalt, Hafnium, and Chromium trace elements were observed with low concentrations in 5/5, 4/5 and 3/5 of the samples respectively. Moreover, Strontium and Caesium trace elements were discovered in 4/5 of the samples with high concentrations in the range of 7.9~263 μg/g for the first and low concentration in the range of 0.028~0.081 μg/g for the second element. The hazardous wastes of the toxic trace elements can introduce contaminations in both grounds- and surface water, degradation of the soil, affect the air quality and affect the public health not only the workers in the petroleum sites but also the oil users afterword.

Based on the results mentioned above, it is critical to monitor the waste petroleum samples to minimize the hazardous to the environmental pollution and human health of the workers in the petroleum sites.

For details analysis of the elements concentrations in the samples, it can be seen from Table 2 that, the concentration of Zn in samples S-103 and S-105 are 101 and 177 μg/g

Table 2: Elements concentrations and the uncertainty in the concentrations, ppm (μg/g) for sample S-102 using INAA

	S-101	S-102	S-103	S-104	S-105
Ba	7.124 ± 0.613	1123.35 ± 19.72	636.705 ± 12.154	4.655 ± 0.059	941.590 ± 19.528
Fe	591.453 ± 21.343	207.106 ± 7.749	488.644± 17.695	537.564 ± 19.467	683.574 ± 24.622
Sc	$(184 \pm 7)10^{-4}$	$(68 \pm 3)\ 10^{-4}$	$(73 \pm 4)\ 10^{-3}$	$(133 \pm 5)\ 10^{-3}$	$(100 \pm 6)\ 10^{-4}$
Ca	242.382 ± 39.360	N.D	N.D	459.835 ± 60.076	N.D
Co	$(1388 \pm 56)10^{-4}$	$(210 \pm 14)10^{-4}$	$(59 \pm 3)10^{-3}$	$(248 \pm 9)10^{-3}$	$(95 \pm 4)10^{-3}$
Cr	$(395 \pm 25)\ 10^{-3}$	N.D	N.D	$(754 \pm 44)\ 10^{-3}$	$(723 \pm 49)\ 10^{-4}$
Hf	$(95 \pm 4)10^{-3}$	$(31 \pm 3)10^{-3}$	$(27 \pm 3)10^{-3}$	$(119 \pm 5)10^{-3}$	N.D
Zn	N.D	78.811 ± 3.964	100.973 ± 5.073	N.D	176.707 ± 8.861
Lu	$(30 \pm 4)10^{-4}$	N.D	N.D	$(85 \pm 7)10^{-4}$	N.D
Rb	1.007 ± 0.086	N.D	N.D	$(645 \pm 76)10^{-4}$	N.D
Sr	7.965 ± 0.887	263.083 ± 13.441	100.344 ± 5.497	N.D	151.886 ± 8.113
Cs	N.D	$(81 \pm 4)10^{-3}$	$(470 \pm 46)\ )10^{-4}$	$(28 \pm 3)10^{-3}$	$(75 \pm 7)10^{-3}$
Ag	N.D	$(90 \pm 7)\ 10^{-4}$	$(50 \pm 6)\ 10^{-4}$	N.D	$(60 \pm 7)\ 10^{-4}$
Br	N.D	1.645 ± 0.088	N.D	N.D	N.D
Eu	$(20 \pm 3)10^{-4}$	$(26 \pm 3)10^{-4}$	$(30 \pm 4\ )10^{-4}$	$(130 \pm 6)10^{-4}$	$(30 \pm 5)10^{-4}$
Sb	$(202 \pm 26)10^{-4}$	$(404 \pm 46)10^{-4}$	$(914 \pm 52)10^{-4}$	N.D	$(329 \pm 14)10^{-4}$
Ta	$(160 \pm 16)10^{-4}$	N.D	N.D	$(298 \pm 23)10^{-4}$	N.D
Yb	$(123 \pm 14)10^{-4}$	N.D	N.D	$(242 \pm 23)10^{-4}$	N.D

for the petroleum refineries 7-80 μg/g in the API 1989 report [33], which is dangerous form the chemical pollution for the environment point of view. Moreover, all samples show a high concentration of Fe, which varies between 207 and 683 μg/g which it is quite high according to the API 1989 report for the metal concentration in oily sludge from refineries 60-200 μg/g [33-34], as a result, fast corrosion may take place for the metal tubes and pipes which are using for the digging and oil extraction. Therefore, regular monitoring for the Fe concentration is required in all the petroleum sites.

The concentrations of the rare earth trace elements of Eu was detected in 5/5 samples with the range of 0.02~0.13 μg/g, while, Yb and Lu were detected in low concentrations levels in 2/5 samples in the range between 0.02~0.12 μg/g and 0.003~0.008 μg/g respectively. Rb element was detected in the samples S-101, and S-104 with 1.0 μg/g and 0.64 μg/g respectively, which can react violently with the water and cause a fire, therefore more carefully treat of the sludge oil must be taken to the petroleum sites 1 and 4. Br element was detected in sample S-102 with a concentration of 1.65 μg/g, and it is well known that a significant amount of this element is toxic for the workers and harmful for the environment.

5 Conclusion

Five sludge oil samples were collected, irradiated by thermal neutron flux (2.7×10^{14} n cm^{-2}) from the Egyptian rabbit irradiation system at ETRR-2 reactor for 4 hours and then counted after 14 days using HPGe detector. 18 isotopes were detected in the five samples, which exhibits different concentrations: relatively high concentrations Ba, Fe, Ca, Sr and Zn. While the rest of the isotopes with low concentrations Sc, Co, Cr, Hf, Lu, Rb, Cs, Ag, Br, Eu, Sb, Ta, and Yb. The results presented in this work show there is

a significant difference in the element concentrations and minimal error due to the absence of any chemical treatments in the samples, and reveal the accuracy of the NAA method to determine the low concentration level of the trace elements in the samples. Six toxic trace elements were determined in the samples, Ba, Co, Hf, Cr, Sr, and Cs. Continuous monitoring of the petroleum sites is needed to monitor the hazardous of the toxic elements and save the environment and humankind.

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