Journal of Radioanalytical and Nuclear Chemistry
https://doi.org/10.1007/s10967-018-5702-y

Neutron moderation effects in phc containinated soil samples

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Received: 13 September 2017

Abstract

Prompt gamma ray analysis of soil samples contaminated with petroleum hydrocarbons(PHC) like benzene was carried out using 14 MeV neutron beams. Intensities of silicon, carbon, oxygen, and hydrogen gamma rays were measured for soil samples containing 2.20–10.4 wt% benzene. With increasing benzene concentration, the intensity of the C gamma rays increased while those of Si, H, and O gamma rays decreased. The reduction in Si, H, and O gamma ray intensities may be due to increasing neutron moderation effect in benzene-contaminated soil samples. The experimental intensities of gamma rays are in good agreement with the calculated intensities.The neutron moderation effects in benzene contaminated soil samples are about 26% weaker than those reported for soil samples containing moisture. From the slopes of silicon gamma ray intensity as a function of benzene concentration as well as moisture concentration, a simple scheme has been suggested to correct for the loss in carbon counts caused by neutron moderation from PHC and moisture in the soil samples.

Keywords C, Si, O, and H prompt gamma ray measurements · Benzene contaminated soil samples · 14 MeV neutron beams · Neutron moderation effect

Introduction

Prompt gamma neutron activation analysis (PGNAA) has been successfully developed for soil samples analysis to determine toxic elements and carbon [1–5]. Beside pesticide and common toxic organic matter, hydrocarbons from petroleum and pertroleum products are a specific and potential source of soil containimation. Generally, crude oil is a major contributor towards environmental hydrocarbon contamination because of its widespread use and its associated disposal operations and accidental oil spills [6]. Total petroleum hydrocarbons (TPH) are important environmental contaminants which are toxic to humans and environmental receptors. The light PHC can contaminate groundwater supplies, while heavy PHC persist in the environment and tend to degrade soil quality. Benzene is a form of processed light PHC containing 6 carbon molecules. This requires monitoring of PHC contaminants in soil and water [7]. Standard PHC detection methods, involving laboratory analysis of soil samples, are commonly used for the measurement of PHC contaminants in soil. The commonly used analytical method for assessing total petroleum hydrocarbons (TPH) in soil, EPA method 418.1, is usually based on extraction with 1,1,2-trichlorotrifluoroethane (Freon 113) and FTIR spectroscopy of the extracted solvent [8]. This method is widely used for initial site investigation, due to the relative low price per sample. Further analytical methods used to quantify TPH levels in contaminated soils, are infrared spectrometry (IR) and gas chromatography (GC) [9]. Nonetheless, sample collection and analysis is a tedious task [10]. Moreover, the samples are not always representative of the contamination conditions, and they tend to suffer significant degradation during transportation and handling [11].

Nuclear techniques, particularly 14 MeV Neutron Activation Analysis, are well suited for the rapid non-destructive analysis of bulk samples containing hydrocarbons [4]. In some cases, Neutron Activation Analysis might even be indispensable as compared to the other analytical techniques used in the areas of biomedical, environmental, and health-related studies [1–3, 12]. In addition, 14 MeV

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neutrons have been used to detect H, C, Si, and O concentrations in different organic bulk samples using the PGNAA technique [13, 14].

Previously soil sample containing 5.0–14.0 wt% moisture were analyzed using 14 MeV neutron inelastic scattering [14]. A reduction in Si (1.78 MeV) and oxygen (6.13 MeV) gamma rays intensities from soil sample was observed for an increase in sample moisture, while the intensity of H (2.22 MeV) gamma rays increased with moisture. The reduction in the Si and the O gamma rays intensity might be due to a loss of the fast neutron flux caused by the 14 MeV neutron moderation effects from moisture in soil samples. In order to compare neutron moderation effect from moisture in soil samples with neutron moderation effect from PHC (benzene) in contaminated soil samples, a PGNAA study has been carried out on PHC (benzene)-contaminated soil samples using the KFUPM PGNAA setup [14]. A comparison of both PGNAA studies i.e. moisture effects in soil samples and benzene-contaminated soil samples might be useful for PHC analysis of soil samples. This study will be described in the following sections.

Calculations from benzene-containing soil samples

Si, C, O, and H gamma rays intensities were calculated for benzene-containinated soil samples using the code MCNP4B2 [15] and the associated modelling of KFUPM PGNAA setup [14]. The calculation procedure is also described in [14]. The elemental composition of soil sample (in wt%) consists of: SiO_2: 88.01; Al_2O_3: 1.99; Fe_2O_3: 0.28; MgO:0.57; CaO: 3.18; Na_2O:0.44; K_2O:0.85; TiO_2: 0.27 [14]. Figure 1 shows the calculated intensities of the Si, O, C, and H prompt gamma rays for various benzene concentrations in the soil samples. With increasing benzene concentrations in the sample, intensities of the Si and the O gamma rays decrease due to increasing moderation of fast neutrons in the sample.

Figure 1 depicts the negative slopes for the intensity of the Si and the O gamma rays and a positive slope for the C gamma ray yield for various benzene concentrations. Although the hydrogen concentration in the sample increases with increasing benzene concentration, the thermal neutron flux in the sample due to thermalization of 14 MeV neutrons is constant. This results in a constant yield of the H gamma rays as a function of benzene concentration, as shown in Fig. 1. Figure 2 shows the effect of moisture on the intensity of the Si, O, and H gamma rays from soil samples containing 5.1–14.0 wt% moisture, as reported in [14].

The trends of the Si and the O gamma rays intensities with increasing benzene concentration observed in this study agree with the results of the moisture study. However, the intensity of the H gamma rays stays almost constant up to a moisture concentration of 8.0 wt%. Since benzene has 13% less hydrogen concentration than water, the intensity of the H gamma rays remains constant up to a benzene concentration of about 10.4 wt%, which is also in agreement with the results of the moisture study.

Gamma ray measurements from standards and benzene-contaminated soil samples

For the calibration of energies of the peaks recorded by the detection system, pulse height spectra were recorded from silica fume, benzene and water standards. The silica fume standard consists of silica fume powder filled in cylindrical plastic bottles of 9.00 cm inner radius and 14.00 cm height. Silica fume contains 43.2 wt% silicon [14]. Similarly, pure benzene standard and water standards were also filled in the cylindrical plastic bottles. Benzene standard contained 92.3 wt% carbon.

Benzene-contaiminated soil samples were prepared by mixing 0–10.4 wt% benzene with soil samples. 1863.8 g of dry soil [14] was mixed thoroughly with 2.2, 4.4, 6.5, 8.5 and 10.4 wt% benzene to prepare the benzene-contaminated soil samples.

The gamma ray spectra from the standards and the benzene contaminated soil samples were acquired using the 14 MeV neutron-based PGNAA setup described in the previous study [14] with 65 μA beam current of 110 keV deuteron beam. The gamma-ray spectra were acquired using a cylindrical 3 inches × 3 inches (height × diameter) $LaBr_3$:Ce detector with 3.3% energy resolution for 661 keV ^{137}Cs gamma rays. LaBr3:Ce detector is fast and its dead time due to intrinsic activity is negligibly small. Morever, the overall dead time of the experiments as measured by the data acquisition system was less than 0.5%. Typical counting times varied from 40 to 45 min for standards. The gamma ray spectra from dry soil and soil mixed with benzene were irradiated with fast neutron flux. Data from each sample was recorded for 20–30 min.

Figure 3 shows the gamma ray spectra from pure benzene (C_6H_6) and pure water (H_2O) samples superimposed upon each other. The C, Pb, and H gamma ray peaks are quite prominent, along with the O peak.

Figure 4 shows the superimposed gamma spectra of the silica fume and the water samples exhibiting the locations of the Si, H, and O peaks, respectively, for identification. Also shown in Fig. 4 is a lead peak from the shielding material.

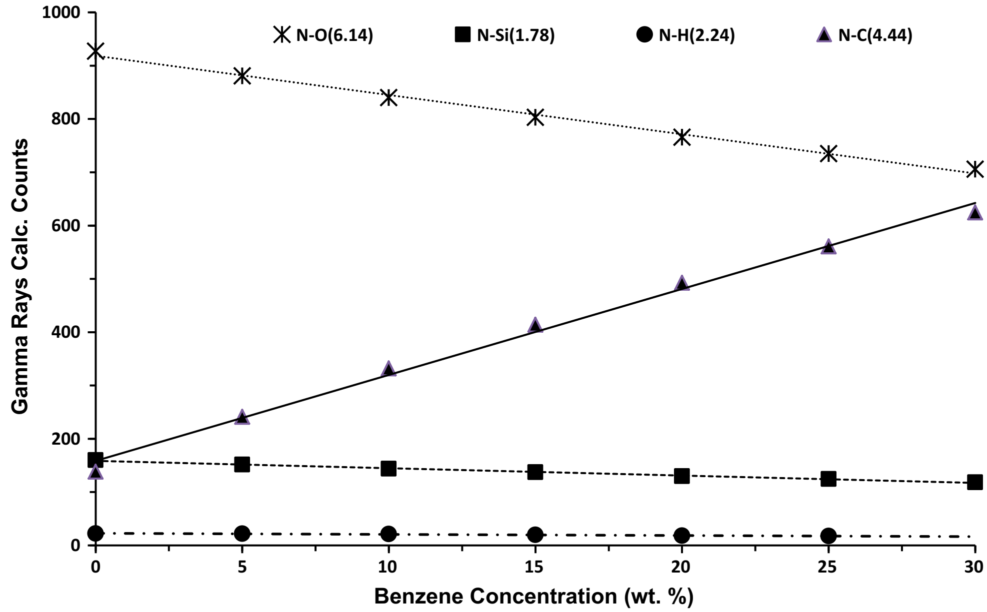


Fig. 1 Calculated intensities of Si, C, H, and O gamma rays for soil sample with various benzene concentrations

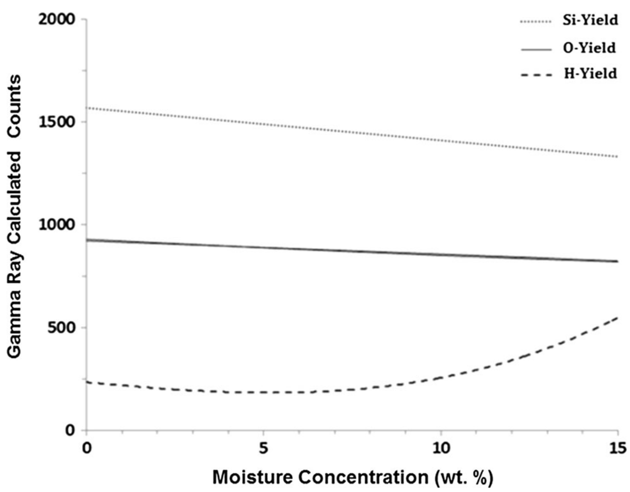


Fig. 2 Calculated intensities of the Si, H, and O gamma rays from soil sample as a function of moisture concentration [14]

Neutron moderation effect in benzene-contaminated soil samples

In order to show effect of benzene concentration on Si, O, C, and H gamma ray intensities, soil samples spectra containing 2.2, 4.4, 6.5, 8.5 and 10.4 wt% benzene have been plotted on an enlarged scale for these elements in Fig. 5a–d.

The intensity of the Si gamma rays in Fig. 5a decreases with increasing benzene concentration. This may be due to increasing neutron moderation effects in benzene- contaminated soil samples. The maximum intensity of the Si peak has been observed for the dry soil sample. The

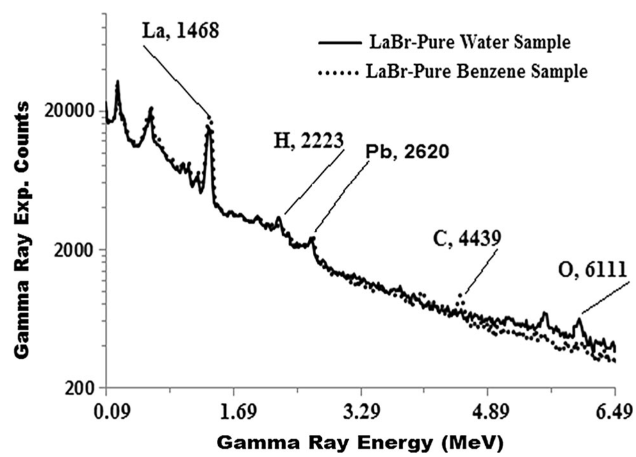


Fig. 3 Gamma ray spectra of pure benzene and pure water samples superimosed upon each other over

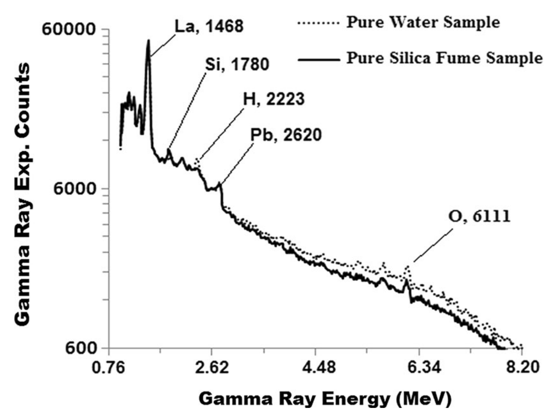
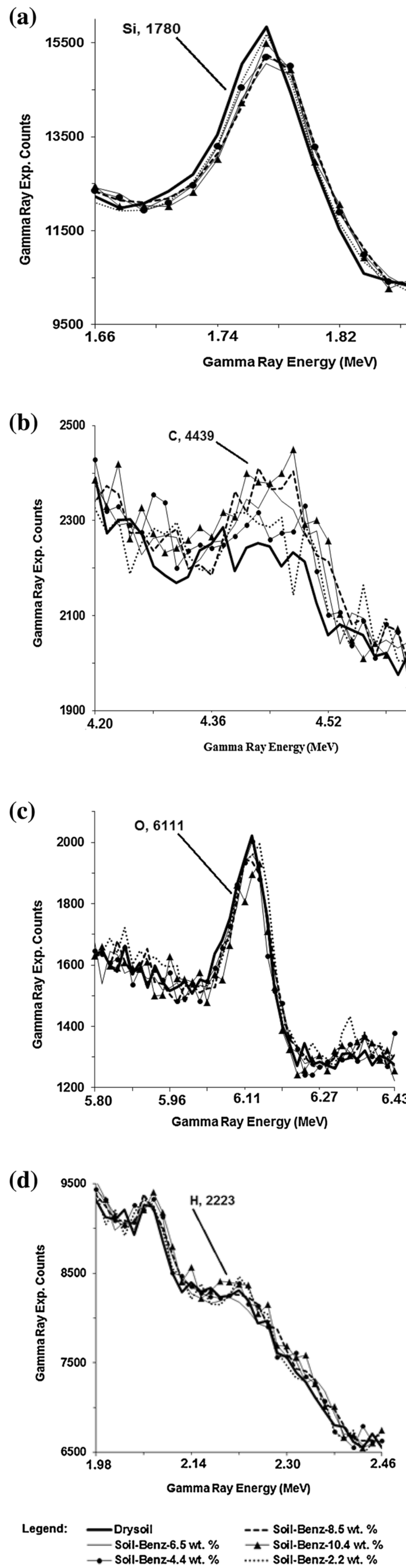


Fig. 4 Gamma ray spectra from the silica fume and the water samples superimosed upon each other



◀**Fig. 5** Gamma ray spectra from soil samples containing 2.2, 4.4, 6.5, 8.5 and 10.4 wt% benzene along with the spectrum from a dry soil sample showing gamma ray peaks on an enlarged scale in **a** silicon; **b** carbon **c** oxygen and **d** hydrogen

intensity of 4.44 MeV carbon peak, as shown in Fig. 5b, increases with increasing benzene concentration in the soil samples. The maximum count of carbon peak have been observed for the soil sample with 10.4 wt% benzene concentration. The decreasing intensity trend of gamma rays from soil samples with benzene concentration, which was observed for Si peak, has also been observed for 6.11 MeV oxygen gamma rays from the soil samples as shown in Fig. 5c.

This decrease may also be attributed due to increasing neutron moderation effects in benzene contaminated soil samples. The minimum counts of the O gamma rays has been observed for the soil sample with 10.4 wt% benzene concentration. The effect of increasing benzene concentration on the H gamma ray intensity, as shown in Fig. 5d is not pronounced.

The background was then subtracted from the Si, C, O, and H peaks of each sample spectrum by subtracting the dry soil sample spectra from each sample normalized to same counting time. The spectra were subtracted using excel data file, which were converted from output spectra of Multichannel Buffer Spectra generated by Scintivision Software of EG&EG-ORTEC. The counts under each peak were then integrated and normalized to the same neutron flux using the NE213 neutron monitor spectra [14]. The corrected net counts for the Si, C, O, and H peaks were finally plotted as a function of benzene concentration in the samples and are shown in Fig. 6.

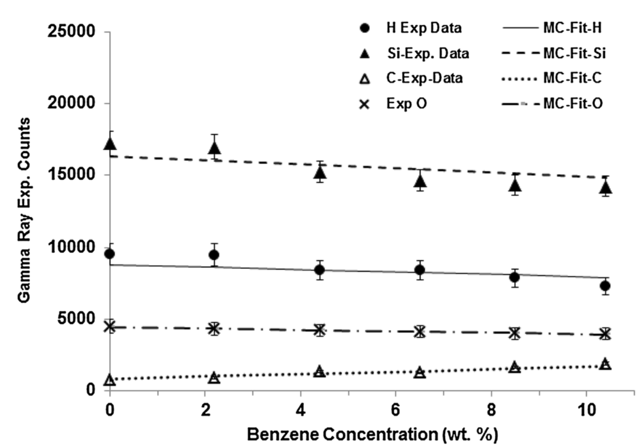


Fig. 6 Integrated counts of the Si, C, O, and H peaks from soil samples containing 0.0–10.4 wt% benzene concentration plotted as a function of benzene concentration. The lines fitted to the experimental data are the results of the simulations

The lines fitted to the experimental data show calculation results discussed in Sect. "Calculations from benzene-containing soil samples". The integrated counts of the C gamma rays increased while those of the Si, H and O gamma rays decreased with increasing benzene concentration. The measured slopes, i.e. change in counts per benzene concentration (wt%), of the Si, O, and H gamma rays intensity were − 142, − 91.0 and − 82.0 respectively. The O and H gamma ray slopes was 35 and 42% smaller than that of Si, respectively. Similarly, the measured slope of C gamma rays (in counts per benzene concentration (wt%) was + 84. The decrease in Si, O and H gamma ray intensity may be due to loss of 14 MeV neutron flux form scattering and moderation in benzene. Within the experimental uncertainties, the experimental results are in good agreement with the calculation results.

Finally, a comparison was carried out between neutron moderation effects in moisture-containing and benzene-containing soil samples to study difference in neutron moderation due to hydrogen contents in moisture and benzene. Figure 7 shows silicon gamma ray counts plotted as a function of moisture concentration (wt%) and benzene concentration (wt%) in soil samples. Both data sets have negative slope with moisture containing soil sample data having about 26% larger slope than that of benzene containing soil data. For the same concentration (wt%) of moisture and benzene in soil, hydrogen concentration is higher in moisture-containing soil than benzene-containing soil samples.

For example, a soil sample containing 10 wt% benzene and another soil sample containing 10 wt% moisture have 0.77 and 1.11 wt% hydrogen, respectively. Then silicon gamma ray counts dependence was calculated from moisture-containing as well as benzene containing soil samples as a function of hydrogen contents of the samples, as shown in Fig. 8. As expected, both curves have negative slope with moisture-containing soil sample data having 26% larger slope than that of benzene-containing soil data.

This larger slope may be due to higher hydrogen concentration in moisture than benzene. This difference in slope can be taken as a guide to correct for moderation effect in soil due to benzene and moisture in prompt gamma analysis of soil samples.

The measured carbon peak counts may be corrected for loss of fast flux from benzene and moisture in the soil using the slopes of silicon peak counts in benzene- and moisture-containing soil samples in the simplified scheme given below. Benzene concentration is infered through a measurement of the carbon concentration in the soil containing moisture and benzene. We call this yield Y_C. Knowing the variation of the Silicon counts as a function of benzene concentration on one hand, and as a function of moisture concentration on the other, the corrected yield from the carbon peak may then be approximated by the following equation

$$Y_C^{cor} = Y_C\left(1 - \frac{\Delta Y_{Si}}{\Delta Con_{Benz}} - \frac{\Delta Y_{Si}}{\Delta Con_{Moist}}\right),$$

where $\frac{\Delta Y_{Si}}{\Delta Con_{Benz}}$ is the slope of the silicon counts as a function of benzene concentration, and $\frac{\Delta Y_{Si}}{\Delta Con_{Moist}}$ is the slope of the silicon counts as a function of moiture concentration.

This study has provided useful results on prompt gamma analysis of benzene-contaminated soil samples. The data obtained herein can be used in the study of soil samples contaminated with petroleum hydrocarbons (PHC).

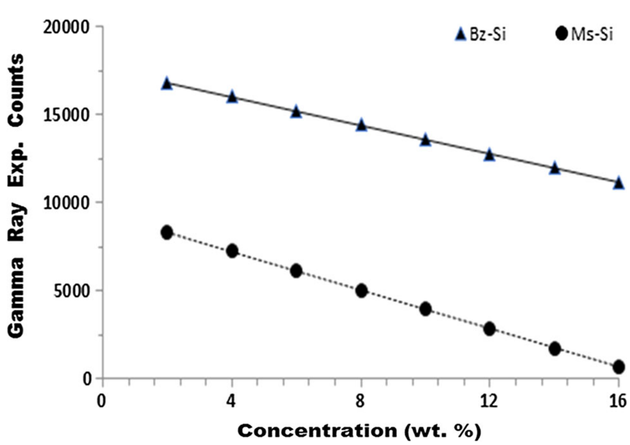


Fig. 7 Si gamma ray integrated counts plotted as a function of concentration (wt%) of moisture and benzene in soil samples

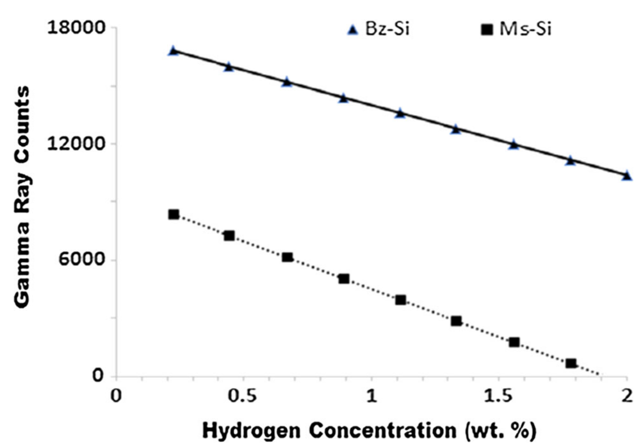


Fig. 8 Si gamma ray integrated counts plotted as a function of hydrogen contents (wt%) in moisture- and benzene-containing soil samples

Conclusions

Neutron moderation effects have been studied in the intensity measurements of the Si, C, O, and H gamma rays from benzene-containing soil samples with 2.2, 4.4, 6.5, 8.5 and 10.4 wt% benzene. Increasing benzene contents to the soil samples resulted in a an inrease in moderation of 14 MeV neutron flux. This caused a reduction in the intensities of the Si, H, and O gamma rays. Maximum reduction was observed for silicon gamma rays. A comparison of results of prompt gamma analysis of moisture containing and benzene-containg soil samples, showed 26% more neutron moderation effects for benzene-contaminated soil samples. From the slopes of silicon gamma ray intensity as a function of benzene concentration as well as moisture concentration, a simple scheme has been suggested to correct for the loss in carbon counts caused by neutron moderation from PHC and moisture in the soil sample.

The experimental results agree with the results of Monte Carlo calculations. This study has provided useful results on neutron moderation effects in benzene-contaminated soil samples.

Acknowledgements This study has been funded through the National Science, Technology and Innovation Plan (NSTIP), project # 12-ENV2367-04. The support provided by the Department of Physics, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia, is also acknowledged.

References

1. Kenneth Shultis J, Khan F, Letellierand B, Fawa Richard E (2001) Determining soil contamination profiles from intensities of capture-gamma rays using above-surface neutron sources. Appl Radiat Isot 54:565–583
2. Falahat S, Köble T, Schumann O, Waring C, Watt G (2012) Development of a surface scanning soil analysis instrument. Appl Radiat Isot 70:1107–1109
3. Szentmiklósi L, Zs Kasztovszky, Belgya T, Zs Révay, Kis Z, Maróti B, Gméling K, Szilágyi V (2016) Fifteen years of success: user access programs at the Budapest prompt-gamma activation analysis laboratory. J Radioanal Nucl Chem 309(1):71–77
4. Wielopolski L, Chatterjee A, Mitra S, Lal R (2011) In situ determination of Soil carbon pool by inelastic neutron scattering: comparison with dry combustion. Geoderma 160:394–399
5. Abha S, Singh CS (2012). In: Dr. Laura Romero-Zerón (ed) Hydrocarbon pollution: effects on living organisms, remediation of contaminated environments, and effects of heavy metals co-contamination on bioremediation. InTech Publisher. ISBN: 978-953-51-0629-6
6. Amadi A, Abbey SD, Nma A (1996) Chronic effects of oil spill on soil properties and micro flora of a rainforest ecosystem in Nigeria. Water Air Soil Pollut 86:1–11. https://doi.org/10.1007/BF00279142
7. Dabbs WC (1996) Oil production and environmental damage (http://www1.american.edu/ted/projects/tedcross/xoilpr15.htm#r2)
8. Schwartz G, Ben-Dor E, Eshel G (2012) Quantitative analysis of total petroleum hydrocarbons in soils: comparison between reflectance spectroscopy and solvent extraction by 3 certified laboratories. Appl Environ Soil Sci. https://doi.org/10.1155/2012/751956
9. Paíga P, Mendes L, Albergaria JT, Delerue-Mato CM (2012) Determination of total petroleum hydrocarbons in soil from different locations using infrared spectrophotometry and gas chromatography. Chem Pap 66(8):711–721
10. Kirka JL, Klironomosb JN, Leea H, Trevorsa JT (2005) The effects of perennial ryegrass and alfalfa on microbial abundance and diversity in petroleum contaminated soil. Environ Pollut 133:455–465
11. Mailaa MP, Cloeteb TE (2005) The use of biological activities to monitor the removal of fuel contaminants-perspective for monitoring hydrocarbon contamination: a review. Int Biodeterior Biodegradation 55:1–8
12. IAEA Report # IAEA-TECDOC-1121: Industrial and environmental applications of nuclear analytical techniques (1999)
13. Naqvi AA, Fares A, Al-Matouq FZ, Khiari AA, Isab M Raashid, Rehman Khateeb-ur (2013) Hydrogen, carbon and oxygen determination in proxy material samples using a LaBr 3: ce detector. Appl Radiat Isot 78:145–150
14. Naqvi AA, Khiari FZ, Liadi FA, Khateeb-ur-Rehman MA, Raashid AH Isab (2016) Moisture effect in prompt gamma measurements from soil samples. Appl Radiat Isot 115:61–66
15. Briesmeister JF (Ed) (1997) MCNP4B2 –A General Monte Carlo N-Particles Transport Code. Los Alamos National Laboratory Report, LA-12625. Version 4C, Los Alamos National Laboratory Report, LA-12625-M