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Determination of ^{226}Ra, ^{228}Ra and ^{210}Pb in NORM products from oil and gas exploration: Problems in activity underestimation due to the presence of metals and self-absorption of photons

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ABSTRACT

Typical calibration of solid environmental samples for the determination of ^{226}Ra, ^{228}Ra and ^{210}Pb entails the use of standard reference materials which have a very similar matrix. However, TENORM samples from the oil and gas exploration contain unusually high amounts of calcium, strontium and barium which can severely attenuate the photons of ^{210}Pb and ^{226}Ra with their characteristic 46.1 keV and 186.2 keV gamma-rays, respectively and to some extent ^{228}Ra with the characteristic gamma-rays of 911.2 keV and 969.0 keV. We used neutron activation analysis to evaluate the content of TENORM for calcium, barium and strontium and then used a software program SELABS to determine the self-absorption. Our results confirm that even in Petrie® containers with small dimensions the ^{210}Pb can be underestimated by almost by a factor of four while ^{226}Ra can be underestimated by 5%. The ^{228}Ra activities are virtually unaffected due to the higher energy gamma-rays. However, the implications for TENORM studies that employ large Marinelli® containers having sample sizes between 0.25 and 1.0 L may be severely compromised by the presence of high Z elements in elevated concentrations. The usual spectral interferences on ^{226}Ra, ^{228}Ra and ^{210}Pb coming from other radionuclides in the ^{234}U, ^{235}U and ^{238}U decay chains are virtually nonexistent due the very high activity levels of ^{226}Ra, ^{228}Ra and ^{210}Pb in the tens of thousands of Bq/kg.

1. Introduction

Naturally occurring radioactive material (NORM) is any material found in nature containing naturally formed radioactive isotopes. These isotopes include mainly the species present in the ^{235}U, ^{235}U and ^{232}Th decay chain series, ^{14}C, ^{40}K and ^{3}H. Activities of radioisotopes in NORM are typically low in undisturbed materials. The dose from this sort of NORM composes the majority of the dose received by a person each year at approximately 80% of the total dose (World Nuclear Association, 2011). However, there is a noticeably higher concentration of radioisotopes present in technologically enhanced NORM, called TENORM, which results directly from human industrial activities.

TENORM is formed in the process of mineral mining including phosphate production, where the end goal is to concentrate high quantities of metals or elements (e.g. phosphorous). However, TENORM has also become a widely recognized problem in the oil and gas industry. In the 1980's ^{226}Ra began to be noticed when scrap metal dealers would detect unacceptably high levels of radiation from oil-field piping (Zielinski and Otton, 1999). TENORM will develop in high concentrations in by-product oil and gas waste streams (Heaton and Lambley, 1995; Al-Masri and Suman, 2003; Al-Saleh and Harshan, 2008; Gazineu and Hazin, 2008). The NORM will chemically separate from other piped material in the process of the extraction of oil, resulting in high concentrations of ^{226}Ra, ^{228}Ra and ^{210}Pb and other radioisotopes in a densely caked layer on the inner surfaces of the piping (Zielinski and Otton, 1999). The activity of the ^{226}Ra from TENORM ranges from 185 to several tens of thousands Bq/kg of sample. By comparison, the NORM concentration of radium in rock and soil is, at a natural level, 18.5–185 Bq/kg (Zielinski and Otton, 1999). Disposal of TENORM becomes more problematic as higher concentrations of radioactivity demand even higher degrees of separation from the general populace. Very low levels of NORM can be dispersed along the surface, but higher concentrations require containment in abandoned wells or salt domes (Zielinski and Otton, 1999). ^{222}Rn a product of the decay of

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^{226}Ra is also a major component of dose to oil and gas workers from TENORM (Zielinski and Otton, 1999). Radon buildup is particularly hazardous in places where air ventilation is limited, such as underground mining operations. In the oil and gas industry radon tends to preferentially follow gas lines, and thus is also a major concern in the extraction of natural gas where it reaches concentrations of 5–200,000 Bq/m^3 (World Nuclear Association, 2011). In a recently published paper (Landsberger et al., 2012) it was determined that they there very high concentrations of barium and strontium in oil TENORM wastes which could interfere in the proper evaluation of activities due to self-absorption of photons often referred as self-attenuation. Gamma-rays at low energy ranges are especially susceptible to this self-attenuation effect (Robu and Giovani, 2009). As well coincidence summing corrections for the measurement of gamma-rays in natural decay series can also compromise accurate activity measurements (Garcia-Talavera et al., 2001). NORM and TENORM measurements are usually made in Petrie® containers holding 10–20 g or in large Marinelli® containers holding 250–1000 g of material. In the latter case photons can be severely attenuated with such large volumes of material. This phenomenon can be further increased with high Z elements such as barium and strontium. Typically, quality control in these measurements is done using reference materials with the usual concentrations of elements in soil, rocks or sediments (Xhixha et al., 2012). At present there is no TENORM reference material. The goal of this work is to investigate the determination of ^{226}Ra, ^{228}Ra and ^{210}Pb in TENORM waste, with high concentrations of the metals such as barium and strontium, from the oil fields in west Texas. These radionuclides were specifically chosen for their health effects impact in the drinking water supply and as ^{226}Ra and ^{228}Ra are radionuclides that are regulated by the US Environmental Protection Agency. Enviroklean Product Development Inc. (EPDI) is an environmental restoration company that specializes in TENORM clean-up and has generously supplied us with the material in an on-going industry-university collaboration.

2. Gamma-ray self-attenuation

Self-attenuation of gamma-rays is an important factor in measuring the activity of radioisotopes in any sample. A gamma-ray of any given energy that passes through any material will have a certain known probability of being attenuated. Simply, for a number of gamma-rays incident on a material, only a percentage of those photons will fully pass through the material. This is dependent on the density and composition of the target material (Robu and Giovani, 2009). This is more formally constructed as,

$$I = I_0 e^{-\mu x}$$

where μ is the linear attenuation coefficient of the material at the energy of the gamma-ray photon, I is the intensity of the gamma-rays exiting the material, I_0 is the intensity of the gamma rays incident on the material, and x is the linear thickness of the material (Robu and Giovani, 2009).

For a sample of NORM or TENORM it should be expected that the activity of radioisotopes present will be dampened by the attenuation of the total material in samples that exhibit large masses. There have a variety of techniques that have used diverse experimental and computational methods to determine the attenuation factors of differing energies and matrices (Cutshall et al., 1983; Xhixha et al., 2012; Bolivar et al.,1997). A computer code called SELFABS was utilized to determine the theoretical self-absorption fractions of gamma-rays that occur in the TENORM sample. A complete detailed mathematical description is given Jaegers and Landsberger (1990) and it applications to geological material is presented elsewhere (Dodoo-Amoo and Landsberger, 2001). Previous published work by Landsberger et al. (2102) using neutron activation analysis showed that concentrations of barium, calcium and strontium were 22.04%, 1.5%, and 5.28%, respectively. We performed calculations on the TENORM material using these values with the remaining matrix components comprising of oxygen, silicon, and smaller amounts of various other elements (Yaroshevsky, 2005) as shown in Table 1.

Table 1
Major constituents of solid sample.

Constituent	Weight fraction (%)
O	23.21
Na	2.57
Mg	1.35
Al	7.74
Si	30.35
K	2.87
Ca	1.50
Fe	3.09
Sr	5.28
Ba	22.04

3. Coincidence summing

For radionuclides that emit two or more gamma-rays within the resolving time of the gamma detector a well-known phenomenon known as coincidence summing occurs. In essence the two photons arrive to the detector at the same time yielding a so called *artificial* photon at higher energy lessening the intensity of the original gamma- or x-rays. Depending on the efficiency of the germanium detector and the geometrical position of the sample, coincidence summing can severely underestimate the intensity of the original photons. As an example the two gamma-rays of ^{60}Co, 1173.2 and 1332.4 keV add together resulting in a photon at 2505.6 keV. In NORM and TENORM samples, more efficient detectors are typically used with samples geometrically positioned right on or within a few cm of the detector. Coincidence summing has been very well studied by many groups and data for these effects are available in the literature (Sima and Arnold, 2012; Tomarchio and Rizzo, 2011; Vidmar and Kanisch, 2012; Lépy et al., 2010). Garcia-Talavera et al., 2001 have determined summing corrections for the natural decay series in gamma-ray spectrometry. We have focused our efforts solely on the summing coincidence effects and any other spectral interferences effects for ^{226}Ra, ^{228}Ra and ^{210}Pb.

4. Experimental

In order to investigate the activity gamma-ray spectroscopy was used to examine a TENORM sample with particularly high concentrations of barium and strontium. The sample analyzed was from sludge that had built up in the process of extracting oil. The solid material was sieved through a 250 μm pore size and dried at 105 °C dried for 24 h. A quantity of 20.34 g was weighed, placed in a plastic Petrie® dish with dimensions of 5 cm in diameter and 1 cm high, and sealed airtight for one month to achieve secular equilibrium.

The sample was counted for 12 h by an ORTEC® X germanium detector with an efficiency of 32.7% and FWHM of 2.0 keV at the 1.33 MeV ^{60}Co source. An efficiency curve in an identical geometry was measured by using a certified liquid source standard (Analytics) of multiple gammas over a range of energies. The program SELFABS was also used to adjust for any attenuation of photons in the water based standard solution. This was particularly important for gamma-rays below 100 keV. A background measurement was also taken to identify any photopeaks that could interfere with the

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activity measurements. There were virtually no spectral interferences from any background photopeaks. An efficiency curve is shown in Fig. 1. The activity for each radionuclide was determined using the common following equation:

$$A = \frac{CR}{\varepsilon(E)*I*BR}$$

where CR refers to the count rate measured, $\varepsilon(E)$ refers to the efficiency of the detector system at the particular energy of the gamma-ray, I refers to the intensity of the gamma-ray, BR is the branching ratio of a particular isotope, and A is the activity of the isotope.

5. Results and discussion

The gamma-ray spectra shown below in Figs. 2 and 3 are only for the major peaks of ^{210}Pb, ^{226}Ra and ^{228}Ra.

The transmission fraction (I/I_0) for the studied gamma-rays in the TENORM solid sample is shown in Table 2. From comparison calculation for NORM in typical soil samples is also shown. As can be seen for ^{210}Pb there is an underestimation of a factor of 3.76 while the underestimation for ^{226}Ra is about 5.5%. The differences for the photopeaks belonging to ^{228}Ra are virtually negligible.

Coincidence summing corrections were taken from Garcia-Talavera et al. (2001) for the 911 keV gamma-ray and 969.2 gamma-ray as 1.09 and 1.05, respectively for a similar Petrie® container holding fine sands. The work by Xhixha et al. (2012) gave a result of 1.024 for a Petrie® container. The diameter of the Petrie® container of the two above studies were 6 cm in diameter, very close to our 5 cm container. The height was not given in the Garcia-Talavera et al., 2001 paper, while the one by Xhixha et al. (2012) was 4.5 cm. The height of our container was 1 cm. Our final values are shown in Table 3 with corrections for coincidence summing using the Garcia-Talavera et al., 2001 results and our self-attenuation calculations. There are no coincidences summing effects for ^{226}Ra or ^{228}Ra. However, Gilmore (2011) provided data for a slight spectral interference on ^{210}Pb from ^{231}Pa and a strong spectral interference on ^{226}Ra from^{235}U and ^{230}Th. These later interferences are

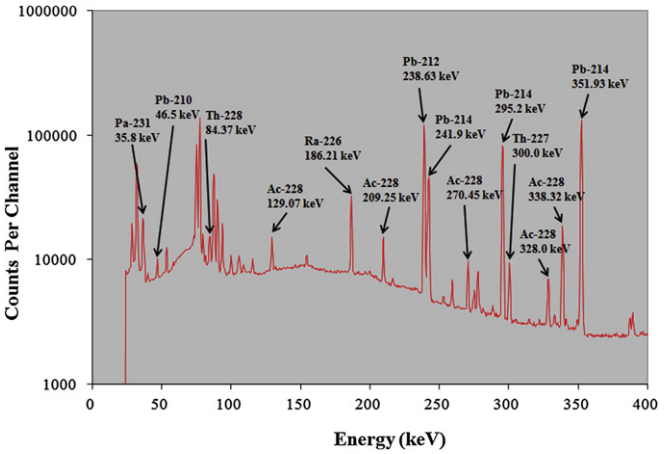

Fig. 2. Observed 30–400 keV gamma-ray energy spectrum showing the 46.5 and 186.2 photopeaks belonging to ^{210}Pb and ^{226}Ra, respectively.

well known. By looking at the TENORM spectrum in Fig. 3 on can see that the usual 1001.3 keV photopeak belonging to ^{238}U is non-existent. Therefore the contribution of ^{235}U which has an isotopic abundance 137 times less than ^{238}U, and it daughter ^{231}Pa has virtually no spectral interference on ^{210}Pb or ^{226}Ra. Similarly the interference of ^{230}Th a daughter from ^{234}U also has no interference on ^{226}Ra. The results are shown in Table 3. Total uncertainties were propagated by the statistical uncertainties in the photopeaks of the three radionuclides (3–5%) in the sample and efficiency standard along with the uncertainty of the activity levels (1–2%) provided by Analytics. An overall estimate of 5% uncertainty was given to each of the radionuclides. There was a 13% difference in the activities of the 911.2 and 969.2 keV photons belonging to ^{228}Ac. This may be due to the differences in branching ratios but those tend not to vary a lot in the published data. At present this 13% discrepancy is unaccounted. Therefore an average of the activities was taken for ^{228}Ra. The final uncertainty was the statistical uncertainties photopeaks (between 3 and 5%) and the uncertainty of the activities used in the efficiency curve.

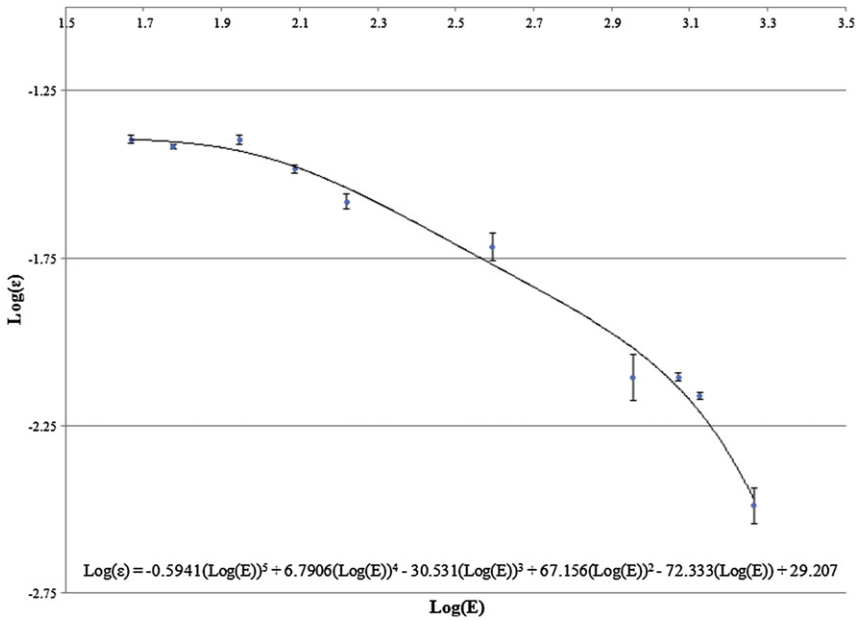

Fig. 1. Detector efficiency calibration using a liquid multi-gamma source. SELFABS was run for this standard to give efficiencies after correcting for self-attenuation. The polynomial fit for the efficiency is given in the equation in the figure.

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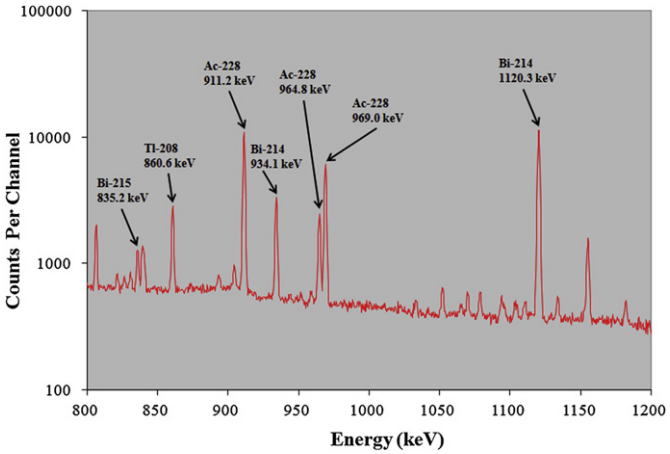

Fig. 3. Observed 800–1200 keV gamma-ray energy spectrum showing the 911.2 and 969.2 keV photopeaks belonging to ^{228}Ac in secular equilibrium with ^{228}Ra.

Table 2
Transmission fraction for gamma-rays in TENORM and NORM samples.

NORM radionuclide	Energy (keV)	Transmission fraction in TENORM solid	Transmission fraction in NORM soil
^{210}Pb	46.5	0.222	0.836
^{226}Ra	186.2	0.911	0.962
^{228}Ra	911.2	0.973	0.979
^{228}Ra	969.0	0.974	0.979

Table 3
Activities of TENORM sample.

NORM radionuclide	Activity (Bq/kg)
^{210}Pb	19,250 ± 962
^{226}Ra	90,190 ± 4510
^{228}Ra	23,286 ± 1164

6. Conclusion

We have demonstrated that there are potential pitfalls in the determination of ^{210}Pb, ^{226}Ra, and ^{228}Ra and as well as other radionuclides in TENORM solid samples from the oil and gas industry. Effects of the presence of high Z elements such as barium and strontium can add additional self-attenuation problems particularly for low energy gamma-rays. Large sample sizes between 0.25–1 L such those in Marinelli® containers may further affect accurate analysis. Coincidence summing effects also can vary due to the size of the containers. At present there are no reference materials for quality control for TENORM samples from the oil and gas industry or the mining sector. The use of reference materials from typical NORM soil or geological samples is not adequate for TENORM samples. In the future we will do a complete elemental analysis of several TENORM samples from the oil and gas industry in west Texas to better anticipate the self-attenuation problems. Lastly, coincidence summing effects need to be done for individual holders of different geometries.

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