

Analysis of naturally occurring radioactive material using neutron activation analysis and passive Compton suppression gamma-ray spectrometry

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Abstract. Naturally occurring radioactive material (NORM) still remains a problem in oil and gas exploration. Radioactive wastes from oil and gas drilling take the form of produced water, drilling mud, sludge, slimes, or evaporation ponds and pits. In many parts of the USA the soil contains radioactivity that is then concentrated in mineral scales on the pipes, storage tanks and other extraction equipment. The radionuclides ^{226}Ra and its one of daughter products ^{210}Pb and ^{228}Ra from ^{232}Th are the primary radionuclides of concern in the waste. We have investigated the concentrations of heavy metals in NORM using neutron activation analysis (NAA) as well as using passive radioactivity counting using Compton suppressed gamma-ray spectrometry. With a low-energy germanium counter and the Compton suppression system low detection limits were achieved to measure ^{226}Ra , ^{228}Ra and ^{210}Pb . Results have shown very elevated amounts for these radionuclides as well as the heavy metals of barium and strontium.

Key words: naturally occurring radioactive material (NORM) • ^{226}Ra • ^{228}Ra • ^{210}Pb • oil and gas industry

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Received: 9 September 2011
Accepted: 10 March 2012

Introduction

For more than two decades it has been well known that naturally occurring radioactive material exists in the oil and gas industry as a consequence of exploration and production. In 1991 Raloff [16] published an article on the new hot wastes in NORM and in 1992 Wilson *et al.* [20] described the health physics aspects of radioactive petroleum piping scale. Several detailed guidelines and overviews on the subject have been published by the International Association of Oil and Gas Producers [10], Canadian Association of Petroleum Producers [6], Kansas Department of Health and Environment [13], United States Geological Survey [17], New York State Department of Environmental Conservation [15] and the American Petroleum Institute [4]. More recently there has been published work on measurement of radiation levels in petroleum products and wastes in Riyadh City Refinery [3], radiological hazards of technologically enhanced NORM (TENORM) in waste petroleum pipes [1] and radiological assessment of oil refining industry [5]. With the rise of energy oil consumption and the value per barrel, exploration has increased world-wide at a very rapid rate. The same situation exists in west Texas where there are now thousands of new drilling operations planned and numerous in progress. However, the disposal of NORM wastes is expensive and can be a significant drain on commercial activities. Enviroklean Products Development, Inc. (www.epdi.biz) is a company that specializes in the decontamination of NORM wastes by reducing the volume

containing the radioactivity and thus reducing disposals costs. Remaining NORM wastes that are below legal limits are then re-injected into the ground. As part of a major study to characterize all aspects of NORM wastes and other non-oil and gas industry naturally elevated ^{226}Ra concentrations in drinking water, we have commenced a university–industry cooperation to address these environmental problems, as well as implementing worker and public health education.

Besides radioactivity measurements in soil, scale and processed water, neutron activation analysis (NAA) was employed to ascertain if any heavy metals are associated with the NORM wastes. In particular we investigated the use of a gamma-X detector, Compton suppression methods and thermal and epithermal NAA to determine the activities and heavy metals in small amounts of NORM wastes.

Experimental

Radioactivity counting

Soil, piping scales and processed water were prepared for radioactivity counting and NAA. Our prime consideration was to determine ^{226}Ra , ^{228}Ra and ^{210}Pb . The solid samples were sieved with a pore size of 250 μm to obtain homogeneity. The solid and processed water samples were placed in a 5 cm diameter and 1.5 cm height Petri® dish and heated sealed for one month to allow secular equilibrium to be achieved between ^{226}Ra and ^{222}Rn . The samples were counted on Ortec (Ametek) Gamma-X detector with an efficiency of 33% and FWHM (full width at half maximum) of 2.0 for the 1332 keV ^{60}Co photopeak. The use of a beryllium window on the germanium detector instead of the usual aluminum one yielded a much better efficiency for the determination of the 46.5 keV gamma ray belonging to ^{210}Pb . A complete description of the experimental set up is reported elsewhere [2].

The measurements of radioactivity in environmental samples can often be difficult mainly because of the self-absorption of photons especially low energy ones such as the 46.5 keV for ^{210}Pb and the 59.5 keV for ^{241}Am . This effect is even more dramatic when the sample sizes are very large as seen in Marinelli holders. There are effectively two ways to calibrate such a detection system. One is to use certified reference materials that have the appropriate interference free gamma rays of interest. This can be difficult to obtain with certified values at just a few per cent. Another way is to construct an activity efficiency curve and then calculate the activities. This method is potentially more accurate but great care must be taken to account for self-attenuation of the photons

Table 1. Radioactivity results for ^{210}Pb , ^{226}Ra and ^{228}Ra

Radionuclide	Sludge (Bq/kg)	Scale (Bq/kg)	Soil (Bq/kg)	Water (Bq/kg)
^{210}Pb	$5\,148 \pm 222$	$1\,370 \pm 74$	$22\,889 \pm 740$	815 ± 37
	$(139 \pm 6 \text{ pCi/g})$	$(37 \pm 2 \text{ pCi/g})$	$(618 \pm 20 \text{ pCi/g})$	$(22 \pm 1 \text{ pCi/g})$
^{226}Ra	$59\,000 \pm 300$	$2\,630 \pm 148$	$65\,296 \pm 3\,296$	$1\,481 \pm 74$
	$(1\,593 \pm 81 \text{ pCi/g})$	$(71 \pm 4 \text{ pCi/g})$	$(1\,763 \pm 89 \text{ pCi/g})$	$(40 \pm 2 \text{ pCi/g})$
^{228}Ac (^{228}Ra)	$28\,501 \pm 1\,493$	565 ± 40	154 ± 12	251 ± 16
	$(770 \pm 340 \text{ pCi/g})$	$(15 \pm 1 \text{ pCi/g})$	$(4.1 \pm 0.3 \text{ pCi/g})$	$(6.8 \pm 0.4 \text{ pCi/g})$

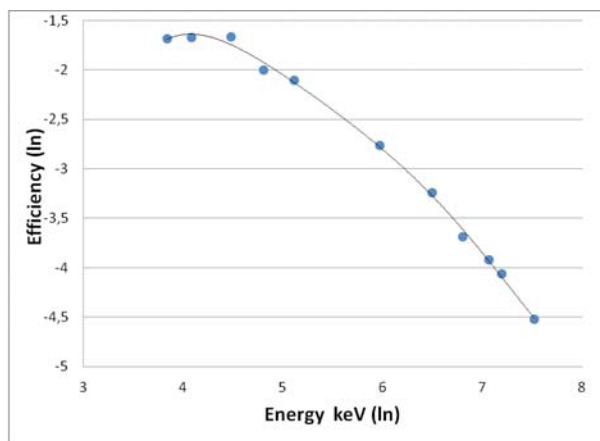


Fig. 1. Detector efficiency calibration using a 1 μCi mixed calibrated standard.

and the proper fitting of an efficiency curve. However, either method suffers from the self-absorption of gammas rays from unknown sources. For instance, if the unknown sample has a lot of material with high-Z (atomic) numbers such as Pb, then there can be serious underestimations of the calculated radioactivities. One way to overcome this deficiency is to place a source of photons having low to high energies and then calculate the self-absorption with and without the sample in the Petri® dish.

In our experiments we used a 1 μCi calibrated water based solution containing isotopes from 46 to 1836 keV to derive an efficiency curve as shown in Fig. 1. A program called SELFABS [11] was used to estimate the attenuation in the water and soil. For soil, the estimated concentrations of elements above 0.1% were based on universal published on crustal earth data [19]. The transmission factors were as follows: 45.2% for the 46.5 keV photon belonging to ^{210}Pb ; 76.8% for the 186.2 keV photon belonging to ^{226}Ra and 87.3% for the 911 keV photon of ^{228}Ac , which is in secular equilibrium with ^{228}Ra . All samples were counted for 12 h. The radioactivity results for soil, scale, sludge and processed water samples are shown in Table 1. A gamma-ray spectrum of passive counting of the sludge sample is shown in Fig. 2. A quality assurance on the efficiency curve was performed by analyzing the IAEA-375 radionuclides in soil [9]. Our result of $5024 \pm 163 \text{ Bq/kg}$ (Cs-137) (with all uncertainties propagated) is in good agreement with the consensus value of $5280 \pm 80 \text{ Bq/kg}$, which is $\sim 5\%$ higher. A simple sensitivity analysis reveals that the dominant factor for any variation in a result is the calculation of the calculated transmission factor (or self-absorption) of photons.

The analytical uncertainties based on counting statistics for the ^{210}Pb , ^{226}Ra and ^{228}Ra for the sludge, soil and scale varied between 0.1–6%. Detection limits for ^{210}Pb ,

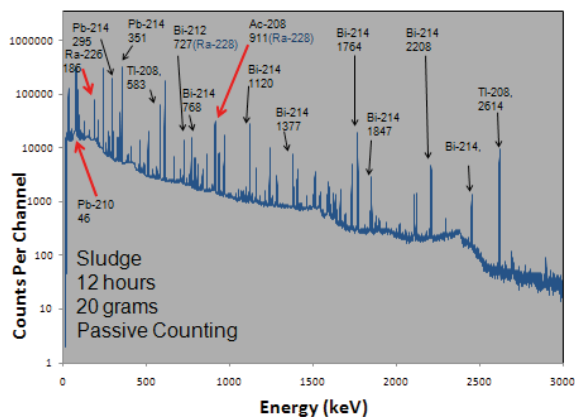


Fig. 2. Gamma-ray spectrum of passive counting of the sludge.



Fig. 3. Typical scale found in pipes in the field.

^{226}Ra and ^{228}Ra varied depending on the type of matrix that was determined. However, in all four cases there were adequate statistics to achieve good precision.

There are two additional interferences that were taken into consideration. One is the interference of the 185.2 keV gamma ray of ^{235}U on the 186.2 keV of ^{226}Ra . This later interference is well known and explained in detail by Gilmore [8]. However, in these NORM samples the activity of ^{235}U is from one to several orders of magnitude less than that of ^{226}Ra , thus having a negligible interference effect. The second systematic problem is coincidence summing. Again this is a well known effect and for naturally occurring radioactivity these corrections have been tabulated for Marinelli and Petri® holders [7]. For ^{210}Pb and ^{226}Ra the correction factors are negligible but the 911 keV photon for ^{228}Ac used to determine ^{228}Ra , there is a 9% effect. The results in Table 1 reflect this correction factor.

A preliminary assessment of scale residue radioactivity in pipes was made to estimate the amount of ^{226}Ra (only). A typical pipe is seen in Fig. 3. As can be surmised a calibration of such an awkward configuration may lead to erroneous results. To overcome this problem and reduce errors, a calibration as seen in Fig. 4 was set up. A 1 μCi certified ^{226}Ra source was placed and counted in nine separate positions in a con-

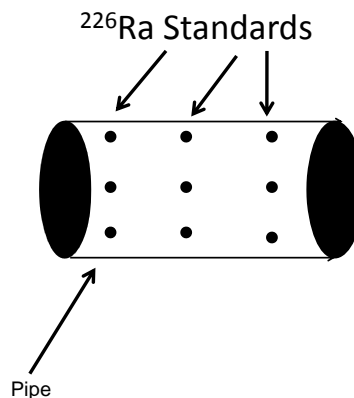


Fig. 4. ^{226}Ra calibration of a constructed cardboard. Black circles are the points of placement for the 1 μCi ^{226}Ra . An average activity for all the nine points was calculated to mimic the actual pipe itself with dimensions of 35 cm length and 6 cm base.

structed cardboard mimicking a similar shape of the pipe itself. An average ^{226}Ra concentration was then calculated and the pipe was counted for 12 h. Approximately 444 Bq (12 000 pCi) was measured inside the pipe. It was impossible to give a result in pCi/g since the radioactive residue is caked onto the pipes. However, it is clear that such measurements are difficult to perform.

Neutron activation analysis (NAA)

Dissolved radium mixes with barium, strontium, or calcium, to form hard and insoluble deposits form on the inside of pipes. This mixture occurs since all these elements occur in the Group II in the periodic table, all having only two electrons in their outer shells, and thus behaving chemically similar. Previous published data have shown the potential environmental impact of barium and radium discharges by produced waters from the “Bacia de Campos” oil-field offshore platforms, Brazil [12]. It has also been suggested that barium and strontium can be used as tracers for radium in soil-plant transfer studies [18]. Thus we performed NAA to determine the quantity of these two elements. For short-lived NAA, we determined Ca, Ba and Sr. Surprisingly, indium (In) was also detected in the sludge and scale at levels above crustal backgrounds.

Nuclear characteristics of the radionuclides determined are shown in Table 2. The radionuclide ^{48}Ca only has a good thermal neutron activation cross-section and thus epithermal NAA cannot be employed. Samples containing approximately 0.5 g were irradiated in a polyethylene vial and sent to the reactor via a pneumatic system. Calibration was done using individual certified liquid standards for the elements of interest. A typical spectrum along with irradiation, decay and counting

Table 2. Nuclear characteristics of Ba, Ca, In and Sr for neutron activation analysis products

Element	Nuclear reaction	Half-life
Barium	$^{138}\text{Ba}(n,\gamma)^{139}\text{Ba}$	83.8 min
Calcium	$^{48}\text{Ca}(n,\gamma)^{49}\text{Ca}$	8.7 min
Indium	$^{115}\text{In}(n,\gamma)^{116m}\text{In}$	54.2 min
Strontium	$^{86}\text{Sr}(n,\gamma)^{87m}\text{Sr}$	2.8 h

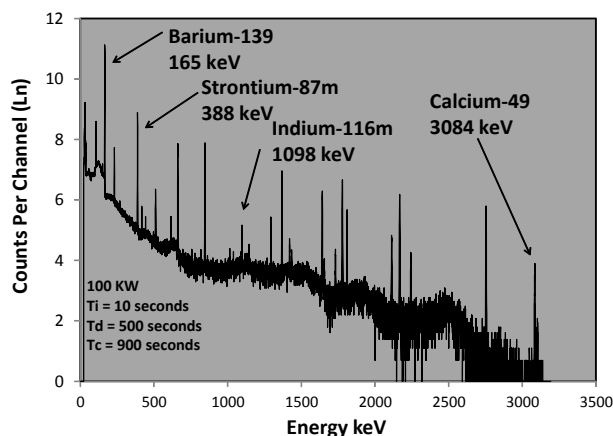


Fig. 5. Gamma-ray spectrum of thermal neutron activated sludge. Ti, Td and Tc are the irradiation, decay and counting times.

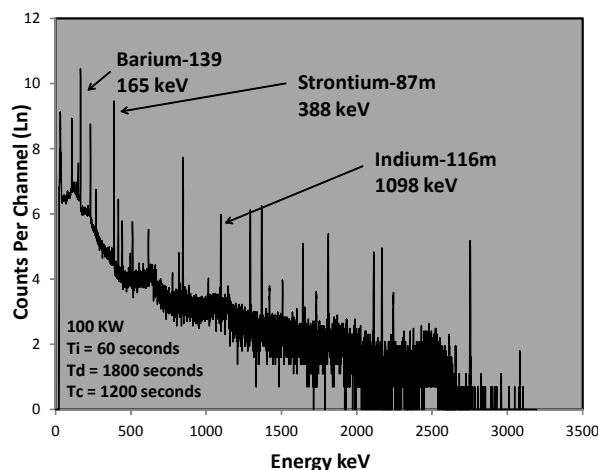


Fig. 6. Gamma-ray spectrum of epithermal neutron activated sludge. Ti, Td and Tc are the irradiation, decay and counting times.

Table 3. Elemental concentrations of NORM solids

Matrix	Barium (%)	Calcium (%)	Strontium (%)	Indium ($\mu\text{g/g}$)
Soil	18.54 ± 0.64	5.97 ± 0.09	1.95 ± 0.07	0.033 ± 0.003
Scale	1.68 ± 0.06	4.61 ± 0.11	1.09 ± 0.04	1.27 ± 0.02
Sludge	22.04 ± 0.76	1.50 ± 0.05	5.28 ± 0.20	0.88 ± 0.01

times for calcium determination is shown in Fig. 5 for thermal NAA. To enhance the determination of Ba, Sr and In epithermal neutrons were used. ^{86}Sr and ^{115}In have good resonance integral cross-sections [14] ($I_{\gamma}/\sigma_{\gamma}^0$) of 6.23 and 16.33, respectively. The radionuclide $^{87\text{m}}\text{Sr}$ decays with a single gamma ray of 388 keV while ^{139}Ba decays primarily with the 165 keV gamma ray, both of which are ideally suited for Compton suppression NAA [2]. Both these gamma rays are also in the region of highest detector efficiency (Fig. 2). A typical spectrum along with irradiation, decay and counting times for ^{139}Ba , $^{87\text{m}}\text{Sr}$ and $^{116\text{m}}\text{In}$ is shown in Fig. 6 for epithermal NAA. A perusal of both spectra reveals that at high levels of Ba, Sr, and In, thermal NAA can suffice, thus reducing the need for an additional step of epithermal NAA. However, the epithermal NAA method would be needed to be used for a larger range of concentrations going from background to high values. In fact, for the determination of indium in the soil samples, epithermal NAA was needed. Concentration values for these elements are seen in Table 3. For quality control National Institute for Standards and Technology (NIST) reference material soil 2711 was used. As seen in Table 4 our NAA values are in very good agreement with the NIST certified ones. The NIST value for indium is just an information value and not certified but the NAA result is in excellent agreement. Quite surprisingly the values for barium and strontium are very high, at least one order of magnitude above typical background levels.

Table 4. NAA results as compared to NIST values

Element	NAA value	NIST 2711 soil value
Barium	$795 \pm 56 \mu\text{g/g}$	$726 \pm 38 \mu\text{g/g}$
Calcium	$2.64 \pm 0.12\%$	$2.88 \pm 0.08\%$
Strontium	$229 \pm 19 \mu\text{g/g}$	$245.3 \pm 0.7 \mu\text{g/g}$
Indium	$1.1 \pm 0.1 \mu\text{g/g}$	$1.1 \mu\text{g/g}$

Conclusions

We have successfully established a protocol for the determination of ^{210}Pb , ^{226}Ra and ^{228}Ra in solid and liquid samples from naturally occurring radioactive material from oil and gas exploration sites using weights as low as 20 g of material. Detector efficiency calculations can be made with adequate care, however, gamma-ray self-absorption in samples is an important effect to take into consideration, especially when sample weights as high as twenty grams are used. Furthermore, we have shown that neutron activation analysis can be employed effectively to determine calcium, barium, strontium and indium from background to high levels in a complete non-destructive manner.

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