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Direct determination of ^{226}Ra in NORM/TENORM matrices by gamma-spectrometry

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The main shortcoming with the procedure to determine ^{226}Ra in a gamma spectrum of an environmental sample by means of the ^{214}Bi and ^{214}Pb photopeaks is the likelihood of ^{222}Rn leakage from the sample counting vial. An option to make such determination is to disregard the ^{226}Ra gamma-contributions to the spectrum, other than 186.2 keV (3.5%), subtracting the ^{235}U contribution to the ^{226}Ra+^{235}U peak at 186 keV. The use of this option to determine directly ^{226}Ra activity concentrations in environmental samples and in NORM/TENORM matrices will be presented and discussed.

Introduction

In the early days of gamma-spectrometry, in the late 40's, the high light yield of the thallium activated sodium iodide NaI(Tl) crystal allowed the first gamma-spectra to be taken from various samples.[1] The typical resolution of a NaI(Tl) crystal is about 45 keV at the ^{137}Cs photopeak at 661.7 keV (i.e., ≈7%), which follows the decay of this nuclide into ^{137m}Ba with an emission probability of 85.2%.[2] The low energy portion of a gamma-spectrum was then inscrutable for a long time. Using a gamma-spectrum obtained with a NaI(Tl) detector to determine the ^{226}Ra concentration by means of ^{214}Bi and ^{214}Pb photopeaks in an environmental sample implies an uncertainty of at least 50%.[3]

In the early 60's there was a remarkable improvement in peak resolution by the introduction of the lithium-drifted germanium Ge(Li) detectors.[4] This improvement made possible to determine the ^{226}Ra concentration by gamma-spectrometry using the 186.2 keV (3.5%) photopeak, once the ^{235}U 185.72 keV (52%) photopeak contribution to the ^{226}Ra+^{235}U peak centered at about 186 keV is subtracted. Thus, whenever a Ge(Li), a Gamma-X, or a hyper-pure germanium (HPGe) semi-conductor detector is available, it is possible to determine the ^{226}Ra concentration in the environmental samples. However, subtracting the ^{235}U 185.72 keV contributions to the ^{226}Ra+^{235}U peak is not an easy task.

Recently, the issue of environmental contamination with depleted uranium (DU) attracted the attention of several investigators back to the low energy region of gamma-spectra to find simple ways to determine the ^{235}U/^{238}U isotopic ratio.[5-8] Methods to measure ^{226}Ra in environmental samples via gamma-spectrometry benefit from the recent interest in the ^{235}U and ^{238}U series photopeaks.

This paper examines one of the spin-offs of such interest, which can be applied to measure ^{226}Ra in environmental samples in general, and in naturally occurring radioactive materials (NORM) or technologically enhanced NORM (TENORM) matrices in particular.

Experimental

The need for determining the ^{235}U/^{238}U isotopic ratio in environmental and biological samples is increasing, mostly after the Gulf War and the conflict in the Balkan, but will increase even further after the war in Iraq is over. As a consequence, the low energy region of gamma-spectra from environmental samples was revisited with renewed interest. Figure 1 represents a gamma-spectrum, up to 670 keV of a DU standard with 0.31%, obtained with a HPGe detector in a low background counting room with a radon reducing system, which is described elsewhere.[9] One can notice that the K_α (74.8; and 77.1 keV) and K_β (87.2; and 89.8 keV) Bi X-rays, and the photopeaks of ^{214}Pb (242; 295; and 352 keV), and those of ^{214}Bi (609; 768; 934; 1,378; and 1,765 keV) are absent from the spectrum.[9] Figure 2 represents a similar spectrum, but of a natural uranium (NU) standard (0.71%).[9] In the latter spectrum the same peaks appear with a slightly different intensity. In both cases, however, the photopeaks of ^{238}U at 63.3 keV, and of ^{235}U at 143.8 and 185.7 keV can be seen clearly.

In an environmental sample, like soil, the photopeak at 185.7 keV from the ^{235}U interferes with the 186.2 keV (3.5%), which results from the ^{226}Ra alpha decay to ^{222}Rn, forming a peak centered at about 186 keV. Thus it is necessary to subtract the 185.7 keV contribution from the peak area, if the ^{226}Ra activity concentration in the sample is to be known.

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Figure 3 represents a typical gamma-spectrum of a soil sample, up to the energy 250 keV. Gamma-spectra like this, which were initially taken for determining ^{137}Cs deposition in Brazilian soils,[10] were reanalyzed to make a preliminary assessment of the ^{226}Ra activity concentrations and the ^{226}Ra/^{238}U activity concentration ratios. The re-analyses of spectra allowed separating the contributions of ^{235}U (185.7 keV) and of ^{226}Ra (186.2 keV) in the photopeak area around the 186 keV peak in each spectrum.

The ^{238}U activity, which is relevant for the determination of the ^{226}Ra/^{238}U activity ratio, was estimated using the photopeak at 63 keV from ^{234}Th, discounted the contributions of ^{231}Th and ^{232}Th to the integral counting area surrounding this photopeak. Such a procedure is necessary because ^{238}U emits a single photopeak at 49.6 keV with a probability of only 0.064%. A detailed discussion about the problems that need to be overcome to use the 63 keV peak to measure the ^{238}U activity is presented elsewhere.[11]

An explanation of the reanalysis is described below. The area under the peak at the 186 keV results, after proper algebraic transformations, in an integral counting C(186 keV), which can be expressed as:[5]

$$C(186\ \text{keV}) = C(^{235}\text{U},\ 185.7\ \text{keV}) + \\ + C(^{226}\text{Ra},\ 186.2\ \text{keV}) \qquad (1)$$

where C(^{235}U, 185.7 keV) is the contribution to the integral counting due to the 185.7 keV photopeak; and C(^{226}Ra, 186.21 keV) is the contribution to the integral counting due to the 186.2 keV photopeak.

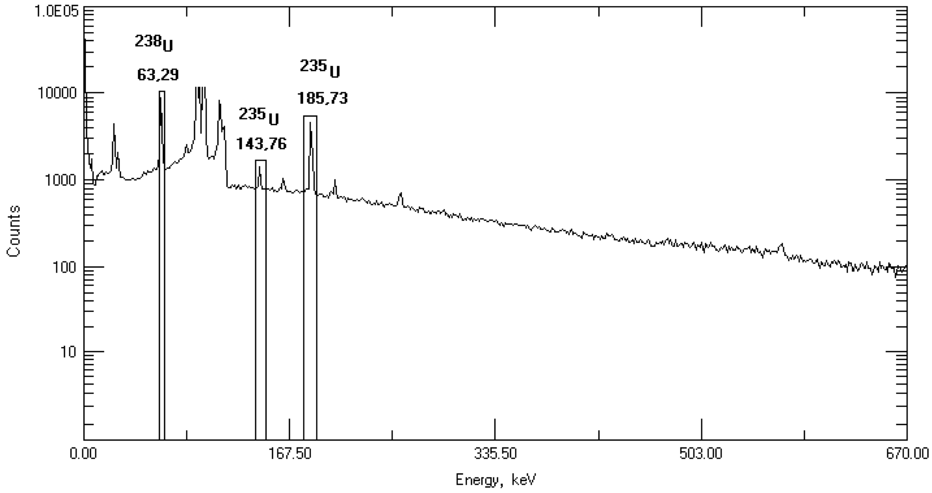

Fig. 1. Gamma-spectrum of a depleted uranium (0.31%) standard, up to the energy of 670 keV

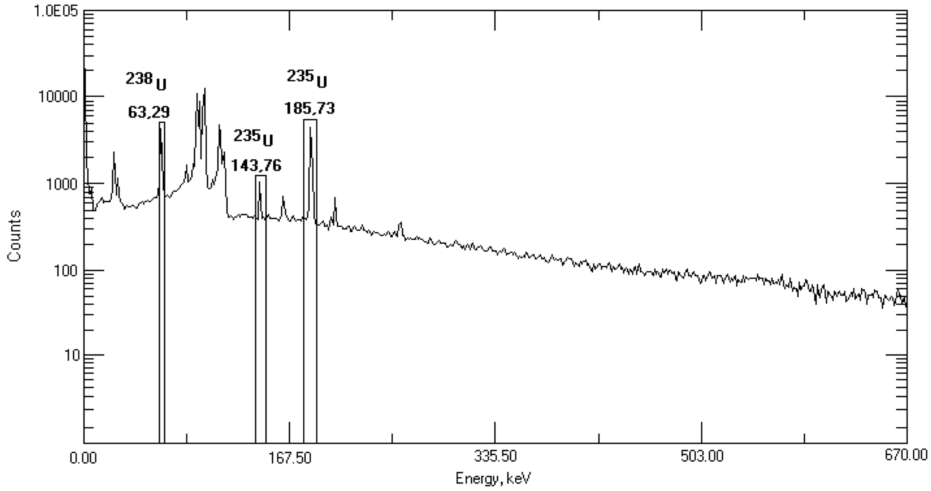

Fig. 2. Gamma-spectrum of a natural uranium (0.71%) standard, up to the energy of 670 keV

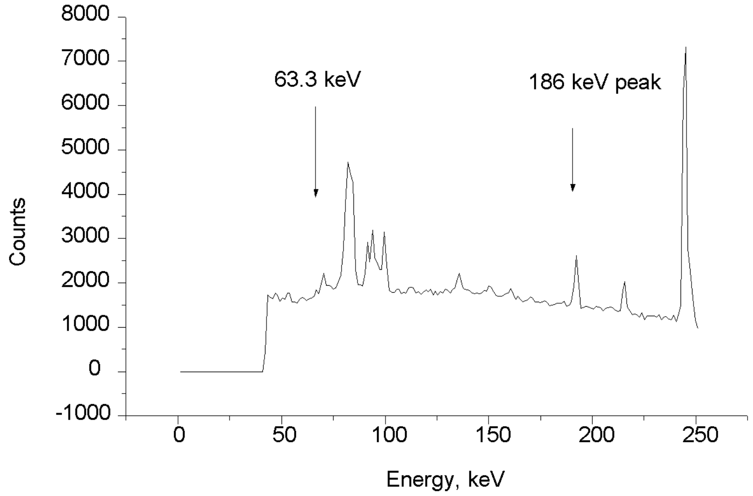

Fig. 3. Gamma-spectrum of a soil sample, up to the energy of 250 keV

Thus, when the contribution $C(^{235}\mathrm{U}$, 185.7 keV) is known, the contribution $C(^{226}\mathrm{Ra}$, 186.2 keV) becomes also known in Eq. (1). However, the contribution $C(^{235}\mathrm{U}$, 185.7 keV) needs to be determined indirectly by means of the integral counting from the 143.7 keV photopeak that follows the alpha-decay of ^{235}U (≈11%) into ^{231}Th, which appears isolated in most soil gamma-spectra. In some cases, however, coincidence summing corrections may be necessary when using the 143.7 keV photopeak for determining the ^{235}U contribution.[12]

Taking into account that the activity of ^{235}U in a sample does not depend on the way it is measured, one can write:

$$\frac{C(^{235}\mathrm{U},185.7)}{\varepsilon(185.7)0.57}=\frac{C(^{235}\mathrm{U},143.7)}{\varepsilon(143.7)0.11} \qquad (2)$$

Equation (2) allows one to determine the contribution $C(^{235}\mathrm{U}$, 185.72 keV). Substituting this contribution into Eq. (1), the estimated value $C(^{226}\mathrm{Ra}$, 186.2 keV) is obtained.

The uncertainty associated with the subtraction of $C(^{235}\mathrm{U}$, 185.72 keV) from the C(186 keV) is reflected in the estimated value $C(^{226}\mathrm{Ra}$, 186.2 keV). Typically, the higher the value $C(^{226}\mathrm{Ra}$, 186.2 keV) the lower the uncertainty associated with the subtraction, varying from 10% for higher value to about 30% for lower values, as one can see in Table 1.

Results and discussion

Soils samples were taken from sites spread from north to south in the Brazilian territory, but mostly along the parallel 20°S. Table 1 presents the ^{226}Ra activity concentrations listed with the latitude and longitude of the site of collection. Whenever more than one sample was collected in one site, or in nearby sites, the range of values was given. As it can be seen in Table 1, the measured ^{226}Ra values in Brazilian soils range from 4 to 218 Bq·kg^{-1}.

Table 2 lists ranges of ^{226}Ra activity concentrations in soil reported for several sites of the world to compare with the range obtained in this work. One can see from the data presented in Table 2 that the range of ^{226}Ra activity concentrations from Brazil does not differ significantly from those equivalent ranges for any other part of the world. The exception is China, which has the lowest and the largest values for ^{226}Ra activity concentrations in soils.

Table 1. ^{226}Ra activity concentrations in Brazilian selected soils

Latitude (S)	Longitude (W)	^{226}Ra, Bq·kg^{-1}
29°40’42”	51°07’50”	30 ± 10
08°10’52”	34°54’47”	10 ± 6 to 68 ± 13 (4)*
05°31’36”	47°29’30”	29 ± 3
12°31’39”	40°18’25”	127 ± 13
01°36’00”–02°02’24”	54°00’04”–54°24’39”	23 ± 6 to 209 ± 24 (8)
02°34’08”	54°43’13”	54 ± 28
03°09’09”–03°19’06”	60°09’11”–60°09’37”	25 ± 14 to 127 ± 30 (3)
09°58’29”	67°48’36”	63 ± 6
21°27’44”–21°31’40”	42°04’49”–42°04’49”	10 ± 4 to 218 ± 14 (4)
22°16’55”	42°31’52”	28 ± 10
21°02’39”–21°03’27”	40°55’24”–42°53’53”	32 ± 7 to 33 ± 8 (2)
23°02’34”	43°32’08”	7 ± 7 to 18 ± 5 (3)
22°13’13”	45°29’02”	33 ± 7
21°10’10”–21°53’01”	49°33’37”	4 ± 4 to 8 ± 3 (2)
22°21’24”	49°02’16”	4 ± 1
19°29’44”	57°25’41”	68 ± 6
20°27’52”–20°43’36”	53°31’30”–55°41’16”	4.1 ± 0.7 to11 ± 5 (3)

* Number in parentheses indicate the number of samples.

Table 2. Range of ^{226}Ra activity concentrations in soils from around the world

Region/country	Activity concentration range, Bq·kg^{-1}	
	^{226}Ra	Reference
Africa	5–180	UNSCEAR[13]
North America/USA	8–160	UNSCEAR;[13] MYRICK[14]
South America/Brazil	4–218	This work
East Asia/China	2–440	UNSCEAR[13]
West Asia	8–77	UNSCEAR[13]

The fact that the ^{226}Ra activity concentrations obtained in Brazilian soils do not differ considerably from other equivalent data is remarkable, but not surprising. After all, the ^{226}Ra activity concentrations spread over two orders of magnitude almost everywhere. This may reflect the diversity of geological formations, organic activity in the surface soil, run off of contaminated waters, re-suspension of sediments and/or flooding, among a myriad of other explanations.

One must bear in mind for example, that it is quite likely that the high values for ^{226}Ra activity concentrations in soils are related to natural radioactive anomalies or to NORM/TENORM contaminated sites. The highest value presented in Table 1 for ^{226}Ra, 218 Bq·kg^{-1}, corresponds to a sample taken from St. Antonio de Padua (21°27'44.3"S; 42°04'49.3"W), which is a site believed to have been contaminated in the past with phosphate fertilizers. The second highest value, 209 Bq·kg^{-1}, is from a soil sample collected in Monte Alegre (01°42'14.3"S; 54°13'49.0"W), with a radioactive anomaly nearby. The high value for ^{226}Ra activity concentration reported for China may actually reflect either a site contaminated with NORM/TENORM, or a nearby natural radioactive anomaly.

In view of those results, the authors and other colleagues became interested in examining the ^{226}Ra/^{238}U activity ratios for each soil sample measured, instead of just the ^{226}Ra concentration in soils. The latter are reported by UNSCEAR, and have relevancy for environmental studies usually concerning radiological protection. However, most data reported in the open literature, including by UNSCEAR, do not include the ^{226}Ra/^{238}U activity ratio for each individual soil sample. Such ratio, however, might be relevant for studies concerning geological formation, organic activity, and recent and historical climatologic changes.

Figure 4 shows the activity concentration ratios ^{226}Ra/^{238}U as a function of the approximate latitudes of the sites where the soil samples were reported to be collected.[10,15–17] Data on ^{226}Ra/^{238}U activity concentration ratios from soil samples collected near latitudes 40°N and 60°N are clearly close to 1; representing radioactive equilibrium.[16,17] On the other hand, data on ^{226}Ra/^{238}U activity concentration ratios from Brazil,[10] and from Sudan[15] are from lower latitudes. The ^{226}Ra/^{238}U activity concentration ratios for these soils spread between 0.11 and 11.

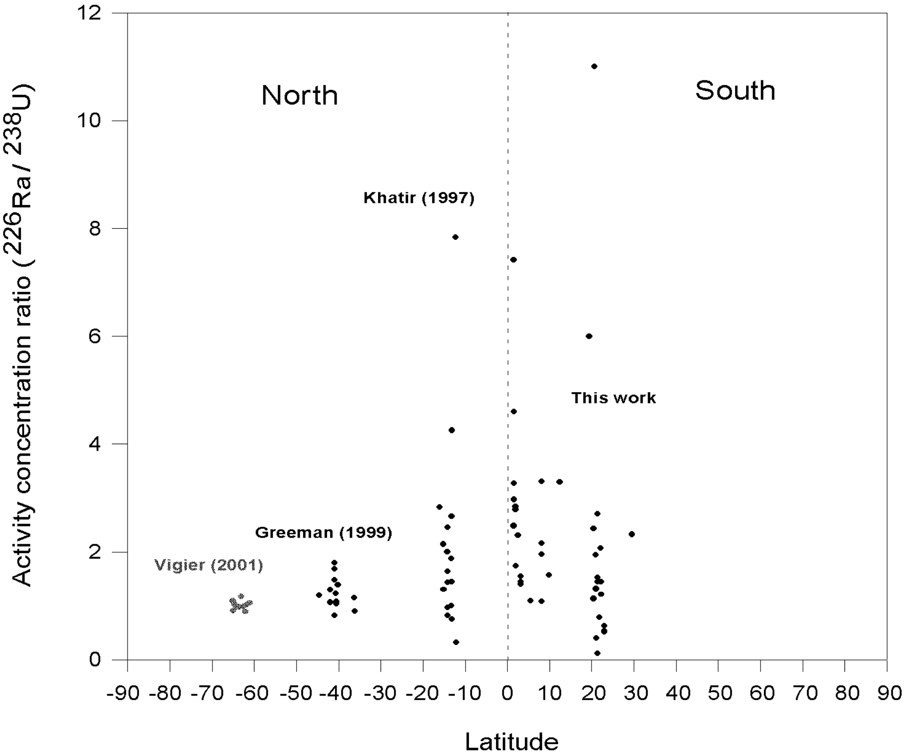

Fig. 4. Distribution of ^{226}Ra/^{238}U activity concentration ratios for soil samples as a function of the approximate latitudes of their collection sites

A further discussion about the meaning of the variation of the ^{226}Ra/^{238}U activity ratios is presented elsewhere.[10] More data, however, are necessary to establish the relevancy of this ratio for other applications. These authors suggest that investigators throughout report the ^{226}Ra/^{238}U activity concentration ratio, as well as the latitude and longitude of the collecting site of each sample.

Conclusions

A methodology was described to determine ^{226}Ra activity concentrations by analyzing, or reanalyzing, the low energy portion of gamma-spectra from environmental, including NORM/TENORM samples.

It was established that the ^{226}Ra activity concentrations range found in Brazilian soils do not differ significantly from equivalent data from other parts of the world.

The need to report the ^{226}Ra/^{238}U activity concentration ratio per sample with the data on ^{226}Ra activity concentration was stressed as a mean to better understand the variation of this ratio as a function of latitude.

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