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Estimation of ^{232}Th Concentration in Environmental Matrices by Tracking Activity of Major Daughter Products (^{212}Bi, ^{212}Pb and ^{228}Ac) with Time in a Hermetically Sealed Container

Singhal RK[1]*, Basu H[1], Saha S[1], Kumar A[2] and Pimple MV[1]

[1]*Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai, Maharashtra, India*
[2]*Health Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai, Maharashtra, India*

Abstract

Concentration of ^{212}Bi, ^{212}Pb and ^{228}Ac were tracked at different time intervals for 33 days in IAEA-RGTh^{-1} reference material having 2.89% Th and soil collected from ambient environment. In case of reference material, mean concentration of ^{232}Th evaluated using gamma energy line of ^{228}Ac (912 keV) and ^{212}Bi (728 keV) shows a deviation of only 0.05%, and 5.66% respectively from the certified mean value of ^{232}Th, whereas a large negative deviation of 29.9% was observed in the case of ^{212}Pb (239 keV). Th-232 concentration in soil sample as evaluated using above three different gamma lines shows a variation of only 10-13%.

Keywords: Thorium; Environmental matrices; Hermetically sealed; Gamma spectrometry

Introduction

Measurement of natural radioactivity content in the terrestrial environment is useful for the evaluation of the extent of direct and indirect exposure to human. Radioactivity in the soil due to anthropogenic radionuclides from nuclear facilities is indicative of the distribution and accumulation of radioactivity in the environment. On the other hand the natural radionuclides in the soil are a true representation of rock material beneath the surface soil [1,2]. The specific levels of terrestrial environmental radiation is related to the geological composition of each lithologically separated area, and to the content of thorium (Th), uranium (U) and potassium (K) of the rock from which the soil originate in each area [3]. In terms of natural radioactivity, it is well known, for instance, that igneous rocks of granitic composition are strongly enriched in Th and U (on an average 15 μg ml^{-1} of Th and 5 μg ml^{-1} of U) compared to rocks of basaltic composition (<1 ml^{-1} of U) [4].

Thorium is estimated to be about three to four times more abundant than uranium in the Earth's crust. Thorium is found in small amounts in most of the rocks and soils whereas granite rocks contain up to 80 μg g^{-1} of thorium [1]. Thorium is a naturally occurring radioactive element which undergoes alpha decay with a half-life of about 14.05 billion years. In nature, virtually all thorium is found as ^{232}Th. Other isotopes of thorium are short-lived intermediates in the decay chains of higher elements, and only found in trace amounts. Radon-220 (^{220}Rn) is one of its decay products and it is in gaseous form while radium and actinium are its secondary decay products. Because thorium oxide is highly insoluble, very little of this element is mobile in the aquatic environment [5,6]. Exposure to thorium internally leads to an increased risk of liver diseases. Thorium contribution is approximately 40% in the total external gamma exposure from the Earth crust. This is mainly due to Thallium-208 (^{208}Tl) and Actinium-228 (^{228}Ac) daughters from Thorium which are very hard gamma ray emitters.

Quantification of Thorium-232 (^{232}Th) in the environmental samples by gamma ray spectrometry is generally carried out by taking its fine dry powdered sample in a closed container which is hermetically sealed and kept to equilibrium for 30 days to develop a secular equilibrium between ^{232}Th and its major daughter products like ^{212}Bi (728 keV), ^{212}Pb (239 keV) and ^{228}Ac (912 keV). Content of thorium in the sample was determined by taking the average from all three gamma lines. In this study, we investigate the radioactivity buildup of the gamma lines of three major daughter product (^{212}Bi (728 keV), ^{212}Pb (239 keV) and ^{228}Ac (912 keV) of ^{232}Th with time and thereafter to evaluate the concentration of ^{232}Th in a hermetically sealed container having certified thorium ore (IAEA-RGTh-1) and soil sample collected from ambient environment.

Materials and Methods

Sample preparation

Ore sample: Dried ore sample [IAEA-RGTh-1 reference materials having 2.89% Th with floated silica powder of similar grain size distribution (<100 μm)] were weighed accurately and transferred to a cylindrical transparent polypropylene container (75 mm dia. and 75 mm H). Container was closed with a cover and sealed with the help of polypropylene sealing tape. Care has been taken that the container was hermetically sealed and there is no scope for the exchange of air with outside environment.

In a similar manner, the second set of samples was prepared after heating the ore at a temperature of 80°C for eight hours. The sample allowed to cool to room temperature before transferring to a cylindrical container.

Soil sample: Samples of surface soil were collected as per the protocols of IAEA Technical report series 295 (1989) [7]. A representative surface soil samples [0-15 cm] were taken. Soil samples were cleaned by removing the stones and decay plants leaves and thereafter dried and pulverized and kept in oven at 110°C. Dried soil were pulverized in a mixer and sieved through a mesh size of 2000 μm. About 250 g of meshed soil samples were transferred to a cylindrical transparent polypropylene container (75 mm dia. and 75 mm H), weighed, sealed and analysed for gamma emitting radionuclides.

***Corresponding author:** RK Singhal, Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400 085, Maharashtra, India, Tel: +912225505050; E-mail: rsinghal@barc.gov.in

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Instrument details: Detection system based on high-purity germanium (HPGe) N type coaxial detector (Model: GCD-50 220N) coupled with a 16K multi-channel analyser (MCA: ITech Instrument) was used for the gamma ray counting. The detector has relative efficiency of 50% for 1.33 MeV to NaI (Tl) detector and is placed into U type cryostat integrated with a dewar vessel. Typical parameters of the semiconductor detector are given in Table 1.

Determination of ^{232}The concentrations in certified ore and soil sample by tracking the activity of ^{212}Pb, ^{212}Bi and ^{228}Ac with time.

Hermetically sealed sample containers were placed on the active volume of a shielded high-purity germanium (HPGe) detector and activity measured for a counting time of 2000 s in case of thorium ore, while 60000 s in the case of soil sample. The naturally occurring radionuclides considered in the present analysis of the measured γ ray spectra are ^{212}Pb (239 keV and a gamma yield of 43.1%), ^{212}Bi keV and a gamma yield of 6.64%), ^{228}Ac 912 keV and gamma yield of 29%). Under the assumption that secular equilibrium has been attained between ^{232}Th and their daughter products, the concentration of ^{232}Th was determined from the average concentrations of ^{212}Pb and ^{228}Ac in the samples [4,8]. The environmental gamma-ray background at the laboratory site was determined using an empty standard counting box kept on the detector window inside the graded shielding. The energy resolution (FWHM) achieved in the calibration measurements was 1.8 keV at 1.33 MeV reference transition of ^{60}Co Depending on the background of the measured spectra, the Minimum Detectable Activity (MDA) of ^{232}Th was calculated to be 0.18 Bq kg^{-1} for the counting time of 80000 s.

Results and Discussion

Direct determination of ^{232}Th in solid sample without any chemical treatment using semiconductor gamma ray spectrometer is very difficult because ^{232}Th does not have intense gamma rays (lines) of its own. However ^{232}Th activity can be carried out using its progeny. Long-lived thorium decays initially to ^{228}Ra, which has a 6.7 year half-life; the longest lived of all the radioactive progeny that follow. Thus, in a pure sample of ^{232}Th, if no physical or chemical processes are ongoing that would disturb the ^{232}Th-^{228}Ra equilibrium, it would require about 35 years before the ^{228}Ra achieved about the same activity as the ^{232}Th. The ^{228}Ra decay produces only an extremely low yield and low-energy gamma ray, which would not be reliable for making an estimate of ^{232}Th. The decay product of ^{228}Ra is ^{228}Ac; the ^{228}Ac has a 6.17 hour half-life so it grows into the ^{228}Ra quite quickly and will achieve activity equilibrium with the ^{228}Ra and the ^{232}Th, both of which are solids under normal conditions. As a general belief, if the sample is hermetically sealed it is assumed that there is no ongoing processes that would disrupt the equilibrium [4,7,8].

The progenies that follow ^{228}Th in the decay chain would also achieve this equilibrium if none of the decay products were lost during the observation time. One of the progeny is ^{220}Rn, a noble gas that might escape from the sample matrix under some circumstances. The ^{220}Rn has only a 55-second half-life so its potential for escape before decaying to solid ^{216}Po is not as great as it would be if it had a longer half-life but, depending on the sample chemical and physical characteristics, some radon might escape if the sample is not sealed to present such losses. Naturally, any loss of radon will negate the approach to equilibrium of the subsequent progeny, including the ^{212}Pb and ^{212}Bi and the activities of these may not be equivalent to the activity of the ^{232}Th [4-6].

Quantification of Th-232 using gamma spectrometry

While quantifying a radionuclide by using gamma spectrometry, the preference will be given to only those lines which were free from interferences. In general thorium in powdered soil and rock samples was quantified using ^{212}Pb (239 keV and a gamma yield of 43.1%), ^{212}Bi (728 keV and gamma yield of 6.64%) and ^{228}Ac (912 keV and gamma yield of 29%). While doing so, it was assumed that secular equilibrium between ^{232}Th and their decay products was reached. In case of secular equilibrium the daughter half-life is usually much shorter than that of the parent nuclide: i.e., $\lambda_1<\lambda_2$ where $\lambda_i=(\ln_2/T_{1/2})_i$, λ_i is the decay constant for the 'i'th radionuclide. Consequently, the activity of the

S No	Typical Parameters	Values
1	Gamma ray energy range	3-3000 KeV
2	Energy resolution	800 eV at 5.9KeV; 2060 eV at 1332KeV
3	Peak to Compton ratio	61:1
4	Optimal operating voltage	-3500V
5	Sensitive area	64.3 mm (Diameter), 64.3 mm (Depth)
6	Relative efficiency (%)	50
7	Aluminum end cap thickness	0.7 mm
8	Input window material	Polymer coated carbon
9	Graded shielding for ultra-Low background	10 cm lead thickness and is jacketed by a 9.5 mm steel outer housing. The graded liner consists of a thin layer of 10 mm thickness and a copper layer of 1.5 mm thickness.
10	Spectroscopic System	Make: Orion Itech Instruments having 7.0 inter winner software to analyze the gamma spectra.
11	Typical background counts for a counting time of 60 000 second in case of	
	Radionuclides	**Counts**
	^{228}Ac (911.07 keV)	40.1
	^{212}Bi (727.17 keV)	26.6
	^{212}Pb (238.63keV)	398.3
	^{234}Th (92.38 keV)	723.8
	^{214}Pb (351.92 kev)	168.1
	^{214}Bi (609.31 keV)	159.1
	^{40}K (1461.23 Kev)	163.4

Table 1: Typical parameters of the n-type HPGe detector.

parent does not decrease markedly over many daughter half-lives. In this case, the solution of Bateman's equation for a parent-daughter pair, simplifies to $N_2\lambda_2=N_1\lambda_1(1-e^{-\lambda_2 t})$ where N_1 and N_2 are the number of radioactive atoms of the parent and daughter nuclides respectively, λ_1 and λ_2 are the respective decay constants, and t is the elapsed time [9]. Then for values of t much greater than the daughter half-life $N_2\lambda_2=N_1\lambda_1$. This condition is termed as secular equilibrium. The concentration of ^{232}Th was determined from the average concentrations of ^{212}Pb, ^{212}Bi and ^{228}Ac in the samples assuming the existence of secular equilibrium. Two of the radionucides ^{212}Bi and ^{212}Pb are the progeny of ^{220}Rn which is a gas while ^{228}Ac is directly in the secular equilibrium with ^{232}Th. Figure 1 gives the variation in counts for all three radionuclides observed at different time intervals after hermetically sealing the container. From Figure 1 it is clear that there is only minor variation in counts with time in all the radionuclides (^{212}Bi, ^{212}Pb and ^{228}Ac). The observed minor variation of 1-3% is statistical in nature. From the observation, it can be concluded that there is no substantial buildup of ^{212}Bi and ^{212}Pb with time in the container.

Table 2 gives average activities of thorium (Bq kg^{-1}) evaluated from all three gamma lines at different time intervals. It is clear that mean concentration of ^{232}Th evaluated using gamma energy lines ^{228}Ac (912 keV) and ^{212}Bi (728 keV) shows only 0.05% and 5.66% deviation respectively from the certified mean value of ^{232}Th whereas a large negative deviation of 29.9% was observed in the case of ^{212}Pb (239 keV). This negative deviation cannot be attributed to non-development of secular equilibrium in the container as the number of counts shows only minor variations throughout the measurement period of 33 days.

Figure 2 give the variation in counts with time in case of gamma lines ^{212}Pb (239 keV and a gamma yield of 43.1%), ^{212}Bi (728 keV and gamma yield of 6.64%) and ^{228}Ac (912 keV and gamma yield of 29%) for soil sample. From this Figure, it's clear that there is only minor variation in number of counts with time for all the above three gamma lines. As discussed above, this variation is statistical in nature. Corresponding concentration ^{232}Th at different intervals is given in Table 3. Mean value of ^{232}Th is 89.38 ± 1.14, 116.20 ± 6.82 and 97.45 ± 2.87 Bg kg^{-1} as evaluated from the gamma line of ^{212}Pb (239 keV), ^{212}Bi (728 keV) and ^{228}Ac (912 keV) respectively. This experimental evidence corroborate that there is no buildup of activity during the period of observation of 33 days.

In order to see weather similar effects were observed in case of uranium estimation in case of soil sample, counts of gamma line of ^{234}Th (92.79 keV), ^{214}Pb (352.36 keV) and ^{214}Bi (609 keV) were monitored at different time intervals immediately after sealing the container. Figure 3 give the variation in counts with time for the above three gamma lines. From this figure it's clear that there is no build of activity with time as number of counts shows only minor variation which is mainly statistical in nature and theses observation again strengthen the fact that equilibrium is not disturbed. In general, in case of soil samples collected from ambient environment, disequilibrium may results from geochemical sorting, whereby a process acts to move a parent or daughter into or out of a system at a rate which is significant relative to the half-life of the daughter [10]. The decay chains in deeply buried, unweathered materials are generally in equilibrium [11]. Most soils consist of a hydrodynamically unstable mix of fine and coarse particles [12]. Experimental finding clearly indicating that equilibrium in the thorium and uranium decay chain has been observed in soil, it is highly unlikely that particle sorting processes would disturb the level

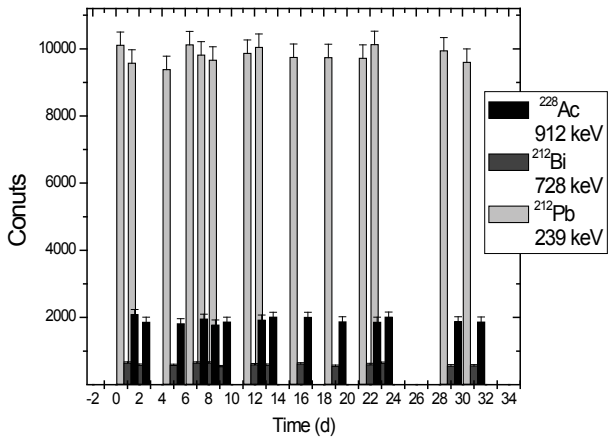

Figure 1: Variation in counts observed in 2000 seconds for gamma line of ^{212}Bi (728 keV), ^{212}Pb (239 kev) and ^{228}Ac (912 keV) with time in hermetically sealed container having thorium ore.

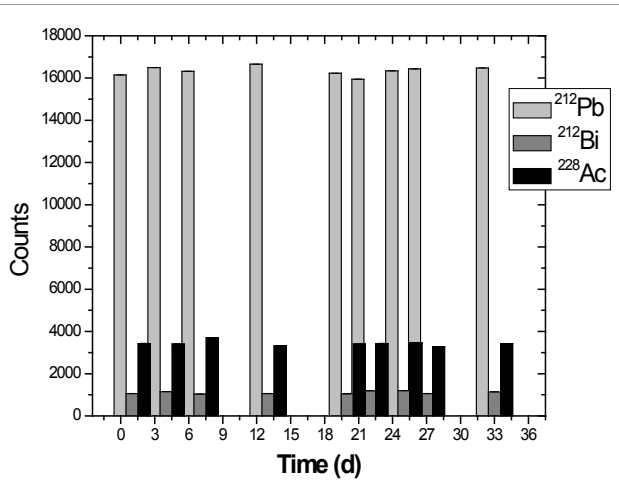

Figure 2: Variation in counts observed in 60000 second for gamma line of ^{212}Bi (728 keV), ^{212}Pb (239 kev) and ^{228}Ac (912 keV) with time in hermetically sealed container having soil.

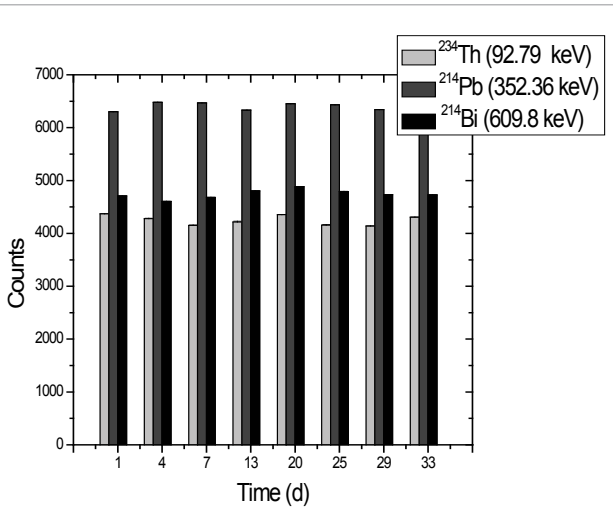

Figure 3: Variation in counts observed in 60000 second for gamma line of ^{234}Th (92.79 keV), ^{214}Pb (352.36 kev) and ^{214}Bi (912 keV) with time in hermetically sealed container having soil.

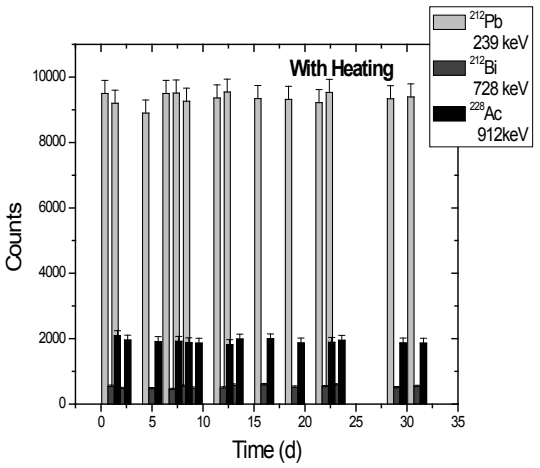

Figure 4: Variation in counts observed in 2000 second for gamma line of ^{212}Bi (728 keV), ^{212}Pb (239 kev) and ^{228}Ac (912 keV) with time in hermetically sealed container having Thorium ore.

of equilibrium in soil collected from ambient environment [13-16]. However, disequilibria have been reported from diverse sedimentary depositional environments [17-20]. Tracking the activity ^{212}Bi, ^{212}Pb and ^{228}Ac after heating the thorium ore.

Radon (^{222}Rn) is the gaseous product of the decay of the radium and being gaseous in nature it is diffused inside the grains of ore. In order to remove earlier remains of radon if any in ore grains, sample were heated in an oven at a temperature of 90°C for eight hours and after cooling at room temperature the sample was transferred to the same cylindrical containers as used in the previous study. The similar patterns of counts were observed and thus there was no build of these radionuclides (Figure 4) were observed in 33 days. But it was interesting to note that there was 5% less counts in the case of ^{212}Pb and ^{212}Bi as compared to counts obtained without heating which may be within experimental limits or due to diffusion of radon from the ore grains due to external heating.

Quality assurance of the measurements

For the purpose of quality assurance, a control sample from

Time (days) elapsed after hermetically sealing of the container	Concentration of ^{232}Th (Bq kg^{-1}) based on gamma line of:		
	^{212}Pb	^{212}Bi	^{228}Ac
0	2370	3478	3267
5	2205	3442	3124
9	2270	3236	3236
16	2280	3489	3459
22	2284	3588	3207
33	2255	3376	3217
Mean value (Bq kg^{-1})	2277.33 ± 53.71	3434.81 ± 119.42	3251.67 ± 112.21
Certified mean value of Th-232: 3250 ± 270 Bq kg^{-1}			

Table 2: Evaluated concentration of ^{232}Th (Bq kg^{-1}) based on counts obtained for gamma energy lines ^{228}Ac (912 keV) and ^{212}Bi (728 keV) and ^{212}Pb (239 keV) at different time intervals in case of Thorium Ore.

Time (days) elapsed after hermetically sealing of the container	Concentration of ^{232}Th (Bq kg^{-1}) based on gamma line of:		
	^{212}Pb	^{212}Bi	^{228}Ac
0 (before sealing the container)	88.76	112.15	98.06
4	88.74	111.39	96.76
7	90.35	120.57	96.32
13	89.40	108.69	104.31
20	91.22	111.26	93.68
22	88.87	110.24	96.19
25	87.34	125.68	96.98
27	89.48	125.83	97.94
33	90.26	119.98	96.78
Mean value	89.38 ± 1.14	116.20 ± 6.82	97.45 ± 2.87

Table 3: Evaluated concentration of ^{232}Th (Bq kg^{-1}) based on counts obtained for gamma energy lines ^{228}Ac (912 keV) and ^{212}Bi (728 keV) and^{212}Pb (239 keV) at different time intervals in case of soil.

Radionuclides	Recommended value (IAEA-312)		Measurement Results
	Mean value	95% Confidence interval	
^{232}Th (mg kg^{-1})	91.4	81.3 – 101.5	95.9 ± 1.12
^{238}U (mg kg^{-1})	16.5	15.7 -17.4	15.3 ± 0.02

Table 4: Quality control measurements using the reference soil material IAEA-312.

a reference soil material (IAEA-312) was prepared in an identical geometry, and treated with respect to the measurement and analysis procedure as an unknown sample. Samples were counted without waiting for any equilibration period. The results obtained and the recommended values are summarized in Table 4. As can be seen from this table, the recommended mean values of Th and U and the measured values were in good agreement, demonstrating a good performance of measurement and analysis technique used.

Conclusion

Work carried out under this programme clearly indicates that quantification of thorium by gamma spectrometry using gamma line, ^{212}Pb (239 keV) ^{212}Bi (728 keV) ^{228}Ac (912 keV) can be done in ore/soil sample without any time delay for development of secular equilibrium. As these samples have not gone through any chemical treatment, therefore the secular equilibrium which is already prevailed is not disturbed. Similar pattern was observed in case of uranium estimation by using gamma lines of ^{234}Th (92.79 keV), ^{214}Pb (352.36 keV) and ^{214}Bi (609 keV).

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