Possibility of rapidly reporting ^{226}Ra activity in ^{226}Ra-^{222}Rn samples with unknown equilibrium factor by γ spectrometer

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Abstract This paper reports the observed changes for equilibrium factors between ^{226}Ra and ^{222}Rn with sealing time of the samples. The samples include soil, raw coal, mineral water, cement, rock, etc. Especially the conceptions of "pre-equilibrium time" and "pre-equilibrium factor" have been put forward and methods of measuring and processing data have been given which can be used for rapidly reporting activity of ^{226}Ra in samples with unknown equilibrium factor. It is definitely concluded that, using methods given in the paper, a test report will be completed in 3~7 days, instead of one month, after receiving the sample whose activity is not lower than LLD of the spectrometer.

Keywords γ spectrometer, ^{226}Ra-^{222}Rn sample, Secular radioactive equilibrium

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1 Introduction

In determining of radioactivity of natural radioactive nuclide ^{226}Ra in environment samples, the spectroscopy workers almost all adopt the method to determine activity of ^{226}Ra. Usually, instead of measuring the characteristic γ-ray emitted by ^{226}Ra itself, they measure those (e.g. 352 keV or 609 keV) emitted by its daughters. This mode is based on an essential condition that radioactive equilibrium between ^{222}Rn and ^{226}Ra has been established or formed. Because half-lives of ^{226}Ra and ^{222}Rn are 1600 years and 3.82 days respectively, their equilibrium belongs in secular radioactive equilibrium. It is generally regarded that radioactive equilibrium has been formed when the equilibrium factor between the daughter and its parent nuclide is larger than 97%. As a rule, in most of γ spectrometric laboratories where natural radioactive nuclides including ^{226}Ra are measured the prepared samples should be sealed for 6~7 half-lives of ^{222}Rn, i.e. about 25 days before they are measured. Consequently, the expected time to give test results of samples will be about one month in determining natural radioactive nuclides of environmental samples including ^{226}Ra, for example soil, coal, building materials, crops, etc. But, for various reasons, in the cases frequently encountered it is expected to give the test results in a time as short as possible. Perhaps as it cannot be helped, or, being prompted by benefit, some laboratories, which are ordered or required by some clients, measure and process data according to the equilibrium mode while activities between ^{226}Ra and ^{222}Rn have not been in equilibrium, and then give a test report too early. Obviously, their behavior is not scientific and serious, for the results given by them are not fully unsuspected. But can't we do something to give the test report not only on the base of reliability but also with as short time as possible? We have observed changes of the equilibrium factors between ^{226}Ra and ^{222}Rn with samples and their preparation methods, and studied possibility to rapidly report activity of ^{226}Ra in samples with unknown equilibrium factor by γ spectrometer.

2 Changes of equilibrium factors of ^{226}Ra-^{222}Rn with time in some samples

2.1 Soil samples

Changes of equilibrium factors between ^{226}Ra and ^{222}Rn in 3 soil samples with time have been observed, and the results are listed in Table 1. All data are referred to count rate (s^{-1}) of the peak area of γ ray at 352 keV. The dried and non-dried soils from Shijiazhuang city were all taken from the same sample

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bag, in which the soil sample collected from 30 cm deep under earth's surface was put. The difference between dried and non-dried samples lies in the fact that the former was toasted at 105 °C for 24 h in the oven, and the latter was raw soil with a water content of 15.1%. It should be indicated that the non-dried soil sample was measured from the third day after having collected and at the same time the rest in the sample bag was dried to become the dried sample, and the water content in it before drying was also determined.

In Table 1, "non-dried soil from Tsinghua" was collected from a building site of Tsinghua University. The soil has been air-dried for 7 d after digging out from about 2 m deep under earth's surface, so it was more porous and with lower humidity than the above soil.

2.2 Raw coal and mineral water samples

Changes of equilibrium factors between ^{226}Ra and ^{222}Rn in 2 raw coal samples with time have been observed. The raw coal was obtained from a coal mine in Datong city of Shanxi Province. Here, the raw coal was screened out by a 60 mesh screen. After that, a part of them was immediately put into the sample box, sealed and measured, and the other part was toasted at 85 °C for 24 h in the oven, and then sealed in the sample box and observed. The water content in the non-dried coal sample was 17.3%. Results observed are given in Table 2.

Table 1 Changes of equilibrium factors between ^{226}Ra and ^{222}Rn in sealed soil samples with sealing time for different samples and preparation methods of samples

Sealing time (d)	Soil from Shijiazhuang		Non-dried soil from Tsinghua University
	Dried soil	Non-dried soil	
1	0.0342±0.0009	0.0433±0.0017	0.0245±0.0006
2	0.0361±0.0020		
3		0.0483±0.0022	0.0259±0.0006
4	0.0376±0.0008	0.0457±0.0009	
5	0.0396±0.0008		
7	0.0405±0.0009	0.0479±0.0009	
8	0.0410±0.0009		
10	0.0443±0.0006		0.0276±0.0006
11	0.0443±0.0009		
12			0.0264±0.0006
13		0.0460±0.0009	
14	0.0440±0.0008		
16		0.0474±0.0010	
17		0.0475±0.0009	
22	0.0430±0.0009	0.0462±0.0009	

*The underlined data indicate that the equilibrium between daughter and parent has already been set up. (The same below in Tables 2, 3 and 4.)

Change of equilibrium factors between ^{226}Ra and ^{222}Rn in a mineral water sample with time had been observed earlier and the results are listed at the last column in Table 2.[1]

Table 2 Changes of equilibrium factors between ^{226}Ra and ^{222}Rn in sealed raw coal and mineral water samples with sealing time and preparation method of samples

Sealing time (d)	Count rate of the peak area of γ ray at 352 keV (cps.)		Activities of ^{214}Pb (10^{-3} Bq·L^{-1})
	Dried soil	Non-dried soil	Mineral water
1	0.0110±0.0004	0.0084±0.0004	<7.0
2			<7.0
3	0.0139±0.0004	0.0103±0.0004	9.47±5.1
4	0.0148±0.0004		12.0±5.5
6			15.8±5.7
7	0.0157±0.0009	0.0105±0.0004	18.1±6.2
9		0.0112±0.0004	21.5±6.0
10			22.2±6.5
11		0.0108±0.0004	
12			22.0±6.2
13			26.2±6.6
16	0.0178±0.0009	0.0111±0.0004	26.0±7.0
17			27.8±6.9
18		0.0112±0.0004	28.8±6.8
19			30.8±7.2
20	0.0155±0.0004		
21	0.0164±0.0005		
22	0.0179±0.0006		
23	0.0181±0.0005		
24	0.0174±0.0006		
27	0.0164±0.0003		
29			36.1±7.5
30			36.2±6.7

2.3 Cement and rock samples

Changes of equilibrium factors between ^{226}Ra and ^{222}Rn in 2 cement samples with time have been observed, and their results are listed in Table 3. The cement marked with "Weima" was produced by the Weima Cement Plant in Fengrun County of Hebei Province. Some part was toasted (dried) at 105 °C for 24 h in the oven, and the other part was not toasted (non-dried).

A rock sample from the Xinjiang Uygur Autonomous Region was also observed, and its results are listed together in Table 3. This sample was prepared as follows: first, the rock was smashed and ground into powder, and then screened by a 100 mesh screen and immediately put into the sample box to be measured.

Table 3 Changes of equilibrium factors between ^{226}Ra and ^{222}Rn in sealed cement and rock samples with sealing time for different samples and preparation methods of samples

Sealing time (d)	Count rate of the peak area of γ ray at 352 keV (s^{-1})		
	Weima tablet cement		Granite rock
	Dried cement	Non-dried cement	Non-dried powder
1	0.0415±0.0008	0.0407±0.0007	0.0516±0.0008
2			0.0520±0.0007
3		0.0376±0.0007	0.0533±0.0009
4	0.0429±0.0007	0.0402±0.0007	
5		0.0455±0.0012	0.0525±0.0005
6	0.0441±0.0006	0.0458±0.0009	
7	0.0434±0.0007		
9		0.0453±0.0009	
11		0.0442±0.0005	
12		0.0450±0.0008	

2.4 Factors of influencing equilibrium between ^{226}Ra and ^{222}Rn

By comprehensive analyses of Tables 1~3, we have obtained the following results: (1) in all observed samples, there was no any sample which had achieved a full equilibrium at the beginning of sealing time; (2) even if for the same kind of sample, such as soils, their equilibrium levels were not quite the same in non-dried condition; (3) except for the sample of mineral water concentrated by evaporation, almost all samples had equilibrium factors larger than 0.5 at sealing beginning time, while equilibrium factor for the concentrated mineral water was less than 0.19. But which factors ever influence the equilibrium between ^{226}Ra and ^{222}Rn in samples? According to the description in Ref. [2] and to the sample preparation process mentioned above the influence factors may be classified into two kinds: processing and non-processing factors. The former is related to sample preparation, such as smashing, grinding, screening, toasting and evaporating of samples, while the latter includes environmental factors before sample preparation, for example, ground temperature, atmospheric temperature and pressure, humidity, wind speed, precipitation and frequency and other meteorological factors; porosity of sample matter in natural or stored state and diffusion factor of ^{222}Rn gas in them; and other physics-chemistry characters with respect to separation, adsorption and resolution of radon gas.

It should be indicated that above factors can take effect both independently and complexly, and the influence levels are dependent on the characters of the sample itself and the specific historical environment the sample has stayed in. These acts are not only complex, but also difficult to expect and control. Therefore it is also difficult to analyze quantitatively or estimate the equilibrium factor of the samples in advance. In fact, we can not obtain the true equilibrium factor of a concrete sample unless a practical determination has been completed. Under normal conditions, it can not be avoided almost that the equilibrium factor of ^{226}Ra-^{222}Rn before sample preparation is changed with all sorts of preparation process of environment samples or building material samples. Therefore, except for the extremely individual cases, it is not reasonable to measure and process data using the equilibrium mode before the ^{226}Ra-^{222}Rn equilibrium is achieved. Here, the "extremely individual cases" imply that the sample matter has not only reached the equilibrium of ^{226}Ra-^{222}Rn before sample preparation but the equilibrium factor would not been changed with the preparing process of sample.

3 Rapid determination of ^{226}Ra in samples with non-equilibrium ^{226}Ra-^{222}Rn

3.1 Measuring principle

As is described above, for environmental samples containing mixed natural radioactive nuclides of ^{238}U, ^{232}Th, ^{226}Ra, ^{40}K and their daughter nuclides, the method of determining ^{226}Ra is often used. The point of this method is to measure characteristic γ rays from daughters ^{214}Pb or ^{214}Bi, instead of direct characteristic γ ray from ^{226}Ra with energy of 186 keV. This is due to the fact that the interfering emission from ^{235}U with energy of 185.7 keV is not easily corrected in the case of unknown equilibrium factor between ^{238}U and ^{226}Ra.

The equilibriums of ^{226}Ra-^{222}Rn and ^{222}Rn-^{214}Pb, ^{214}Bi all belong to secular radioactive equilibrium. But the time of establishing equilibrium is different: the former needs about 27 d, while the latter only needs 3 h (here, 7 half-lives are adopted in all computation). Although it is equally valid to determine either parent or daughters, it will take long time to begin measuring the activity of ^{222}Rn when the equilibrium between them is already established. Here, we have described, based on the decay law of the parent and its daughter nuclides in a secular equilibrium system, a method, with which the parent's activity can be measured before the equilibrium is set up. The principle diagram for this method is shown in Fig.1. Based on the decay law in the secular radioactive equilibrium, the activities of daughter and its parent nuclides can be expressed as

$$A(t) = A_0 \bullet (1 - \mathrm{e}^{-\lambda t}) \tag{1}$$

where A_0 stands for activity of parent nuclide; $A(t)$ stands for activity of daughter nuclide at time t; and λ stands for decay constant of daughter nuclide.

For almost all samples at the initial sealing time, as indicated in Tables 1~3, activities of the daughter nuclide do not equal "0", and various samples have different equilibrium factors, which do not equal "1" in most cases. In order to indicate this feature in practical samples, Eq.(1) is rewritten as

$$A(t_i) = A_0 \bullet (1 - \mathrm{e}^{-\lambda(t_0 + t_i)}) \tag{2}$$

where $t_i\,(\geqslant 0)$ is called "sealing-equilibrating time", which begins at the moment of sample's sealing; $t_0\,(\geqslant 0)$ is called "pre-equilibrium time", which equal the time needed for reaching the equilibrium level at the moment of sample's sealing, and the corresponding equilibrium factor called "pre-equilibrium factor"; $A(t_i)$ stands for the activity of daughter nuclide at t_i.

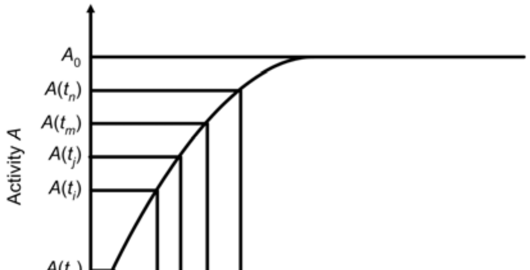

Fig.1 Change of activity of daughter nuclide with sealing time in a secular radioactive equilibrium system.

Obviously, when $t_0 = 0$, Eq.(2) will become Eq.(1), which corresponds to the change of activity of daughter nuclide beginning from "zero activity". When $t_0 > 0$, Eq.(2) will not equal Eq.(1), which corresponds to the change of activity of daughter nuclide beginning from "some activity (≠0)". So, Eq.(1) is a special case of Eq.(2).

Except for A_0 and t_0, all other parameters in Eq.(2) are the parameters that can be determined directly through one measurement or from the computation. Once t_0 of a practical sample is decided, activity of the parent nuclide in the sample will be obtained by

$$A_0 = \frac{A(t_i)}{1 - \mathrm{e}^{-\lambda(t_0 + t_i)}} \tag{3}$$

In order to decide parameter t_0, a method of eliminating the unknown parameter can be adopted. By measuring at different time we obtain the activity of the sample at time $t_j\,(\geqslant 0, \neq t_i)$:

$$A(t_j) = A_0 \bullet \left[1 - \mathrm{e}^{-\lambda(t_0 + t_j)}\right] \tag{4}$$

To resolve the simultaneous equations consisting of Eq.(2) and (4), we get

$$\frac{A(t_i)}{A(t_j)} = \frac{1 - k_i \bullet \mathrm{e}^{-\lambda t_0}}{1 - k_j \bullet \mathrm{e}^{-\lambda t_0}} \tag{5}$$

where $k_i \equiv \mathrm{e}^{-\lambda t_i}$; $k_j \equiv \mathrm{e}^{-\lambda t_j}$. Then t_0 can be found:

$$t_0 = \frac{1}{\lambda} \bullet \ln \frac{k_i \bullet A(t_j) - k_j \bullet A(t_i)}{A(t_j) - A(t_i)} \tag{6}$$

This means that, according to a simple theory, activity of the parent nuclide ^{226}Ra in a sample, whose equilibrium factor between ^{226}Ra-^{222}Rn is unknown in fact, can be obtained rapidly through twice measurements at different time. Thus, shortening the time for reporting true ^{226}Ra activity information becomes possible.

3.2 Practical formulae applied in rapid determination

It should be pointed out that $A(t_i)$ mentioned above is activity of the daughter at a certain time, t_i. But, in common measuring practice, collecting data for a spectrum always needs a period of time (specially for a sample with very low activity), during which the activity of ^{222}Rn in the sample can not be considered as unchanged because the equilibrium usually has not been established in the duration. We have therefore recommended the following formula which takes into account the change of ^{222}Rn activity in the measuring period:

$$C(t_i,t_j)=\int_{t_i}^{t_j} A_0\bullet(1-\mathrm{e}^{-\lambda(t_0+t)})\,\mathrm{d}t \tag{7}$$

Integrating Eq.(7) we obtain

$$C(t_i,t_j)=A_0\bullet\left[T(i,j)-\frac{E(i,j)}{\lambda}\bullet\mathrm{e}^{-\lambda t_0}\right] \tag{8}$$

where $T(i,j)\equiv t_j-t_i$; $E(i,j)\equiv\mathrm{e}^{-\lambda t_i}-\mathrm{e}^{-\lambda t_j}$.

Similarly, the counts in the sample spectrum for a period of time from t_m to t_n can be expressed as

$$C(t_m,t_n)=A_0\bullet\left[T(m,n)-\frac{E(m,n)}{\lambda}\bullet\mathrm{e}^{-\lambda t_0}\right] \tag{9}$$

Where $T(m,n)\equiv t_n-t_m$; $E(m,n)\equiv\mathrm{e}^{-\lambda t_m}-\mathrm{e}^{-\lambda t_n}$.

Dividing Eq.(8) by Eq.(9), we gain

$$\frac{C(t_i,t_j)}{C(t_m,t_n)}=\frac{T(i,j)-\dfrac{E(i,j)}{\lambda}\bullet\mathrm{e}^{-\lambda t_0}}{T(m,n)-\dfrac{E(m,n)}{\lambda}\bullet\mathrm{e}^{-\lambda t_0}} \tag{10}$$

Through further transformation, we have

$$\mathrm{e}^{-\lambda t_0}=\frac{\lambda\bullet\left[C(t_m,t_n)\bullet T(i,j)-C(t_i,t_j)\bullet T(m,n)\right]}{C(t_m,t_n)\bullet E(i,j)-C(t_i,t_j)\bullet E(m,n)} \tag{11}$$

$$t_0=\frac{1}{\lambda}\ln\frac{C(t_m,t_n)\bullet E(i,j)-C(t_i,t_j)\bullet E(m,n)}{\lambda\bullet\left[C(t_m,t_n)\bullet T(i,j)-C(t_i,t_j)\bullet T(m,n)\right]} \tag{12}$$

Then according to Eq.(8), the activity of parent nuclide in the sample can be obtained:

$$A_0=\frac{C(t_i,t_j)}{T(i,j)-\dfrac{1}{\lambda}\bullet E(i,j)\bullet\mathrm{e}^{-\lambda t_0}} \tag{13}$$

4 Applicability of the rapid determination method

The theory base for rapidly determining ^{226}Ra in the non-equilibrium samples of ^{226}Ra-^{222}Rn has been given above. Now we will give a practical example to verify the applicability of the method.

Here, we have taken the results for the dried-soil observed at different time listed in Table 1. The first reason for this is that more data have been observed for the sample, and the second reason is that its equilibrium has been set up through a long time (9~10 d) after sample sealing. These factors are undoubtedly quite profitable for testing and verifying the study in the work. The parameters needed in the computation applying Eqs. (11)~(13) and some computing results are given in Table 4. Table 5 gives values of $\mathrm{e}^{-\lambda t_0}$ and activity A_0 which are computed with the method described in Section 3.2. In Table 5, (A_0-2), (A_0-4), (A_0-5) and (A_0-7) express the calculated activities based on the peak counts observed, respectively, in 2, 4, 5 and 7 d after the sample sealing. It may be seen through the activity results in Table 5 that they are agreed very much with the data underlined in Table 4, indicating the equilibrium having been established in the sample. It is shown that the developed method for measuring a non-equilibrated sample and rapidly reporting accurate activity data in equilibrium can be successfully applied in practice.

5 Discussion and conclusion

In the example listed in Table 5 we have calculated 6 $\mathrm{e}^{-\lambda t_0}$ values from 6 calculating combinations, each of which was formed by choosing any two from four time spans (i.e. 2, 4, 5, 7 d) (C_4^2=6). Observing carefully all data in Table 5, we have found that there are some remarkable differences in the results of $\mathrm{e}^{-\lambda t_0}$ and activities (A_0-2), (A_0-4), (A_0-5) and (A_0-7), but all activities obtained by using the average value of $\mathrm{e}^{-\lambda t_0}$ agree well with each other. These facts tell us that in order to obtain accurate and reliable results and avoid the influence of large statistical fluctuation of counts, which could be met in a single group measurement, we had better adopt the average value of $e^{-\lambda t_0}$ in the calculation. Accordingly, we suggest that at least three time spans be chosen to measure an unknown secular equilibrium sample. Thus, constituting at least 3 (C_3^2=3) calculating combinations will be possible and the average $e^{-\lambda t_0}$ and $\overline{A_0}$ values will be easily calculated.

Now we can make the following conclusions: (1) For a non-equilibium ^{226}Ra-^{222}Rn sample, although it is still impossible to "give a test report on the same day when the sample is received" (as someones often claim on internet), we can ensure that, with the method described in the paper, a reliable and accurate report will be provided in 3~7 d, instead of about one month, thus the waiting time will be shortened greatly. (2) Since any radiation detector has its detection lower limit (LLD), it will be very difficult to measure a sample with too low activity. In a non-equilibrated sample, activity of the daughter nuclide is usually lower than that in an equilibrium sample, which may set some obstruction for using this method to rapidly report the ^{226}Ra activity accurately. (3) Obviously, the method described above can be applied not only to the non-equilibrium ^{226}Ra-^{222}Rn system, but also to other similar secular radioactive equilibrium systems.

Table 4 The parameters observed in the established equilibrium of ^{226}Ra-^{222}Rn for the dried soil sample from Shijiazhuang city*

Sample sealing time (d)	Storing time of spectrum (Y.M.D.h.m)	Measuring beginning time t_i, t_m (s)	Measuring finishing time t_j, t_n (s)	(t_j-t_i) or (t_n-t_m)	Net areas of the peak (counts)	Count rate of the peak ±1σ (cps)
1	02.07.10	3600	65505	61905	2115	0.0342±0.00085
2	02.07.11.11:13	168949	180780	11831	427	0.0361±0.00203
4	02.07.13.07:45	267251	341100	73849	2776	0.0376±0.00081
5	02.07.14.09:09	343116	432540	89424	3545	0.0396±0.00077
7	02.07.16.08:31	524195	603060	78865	3191	0.0405±0.00090
8	02.07.17.09:16	613315	692160	78845	3232	0.0410±0.00086
10	02.07.19.09:48	696245	866880	170616	7551	0.0443±0.00058
11	02.07.20.09:26	867473	951690	84487	3742	0.0443±0.00086
14	02.07.23.08:31	1120663	1207860	87197	3840	0.0440±0.00077
22	02.07.31.10:34	1822129	1906440	84311	3625	0.0430±0.00087

*In the table the beginning time of sample sealing is estimated at A.M.9:00 of July 9, 2002, with an error of no more than 1 h.

Table 5 Calculated $e^{-\lambda t_0}$ and A_0 values based on the parameters listed in Table 4

Calculated value	Calculating combinations according to different sealing time before observation						Average values Ⅰ	Average values Ⅱ
	2-4	2-5	2-7	4-5	4-7	5-7		
$e^{-\lambda t_0}$	0.22053	0.31326	0.25989	0.47983	0.29119	0.14132		0.28434
A_0-2	0.04255	0.04604	0.04396	0.05400	0.04516	0.03996	0.04528	0.04489
A_0-4	0.04255	0.04505	0.04357	0.05036	0.04443	0.04062	0.04443	0.04424
A_0-5	0.04394	0.04604	0.04481	0.05036	0.04552	0.04229	0.04549	0.04536
A_0-7	0.04339	0.04476	0.04396	0.04744	0.04443	0.04229	0.04438	0.04432
$\overline{A_0}$ ±1S	0.04490 ±0.003						0.04490 ±0.0006	0.04470 ±0.0005

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