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SELECTIVE DETERMINATION OF EXTREMELY LOW-LEVELS OF THE THORIUM SERIES IN ENVIRONMENTAL SAMPLES BY A NEW DELAYED COINCIDENCE·METHOD

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An attempt was made to apply a delayed coincidence method for the absolute determination of trace quantities of the thorium series. This method is based on selective counting of the relatively short lived nuclide ^{216}Po (half-life 145 ms) in the thorium series members. For this purpose, a "list mode" time analyzing system combined with a liquid scintillation counter was assembled by means of a conventional microcomputer. A multiple time analysis was employed in the processing and data compilation of delayed coincidences to distinguish them from the true coincidences due to random events.

From a time spectrum, the decay component of ^{216}Po (145 ms) can be selectively measured. Absolute activities of its progenitors, ^{224}Ra and ^{228}Th as well as ^{220}Rn, can be determined even in the presence of the background radiations of the almost equivalent activity-strength of concomitant uranium series.

INTRODUCTION

A delayed coincidence technique was applied to measure half-lives of extremely short-lived nuclides ranging from 10^{-11} to 10^{-4} s (1, 7). This technique can be used to determine the activity of the short-lived nuclide without eliminating background radiations provided that the detection efficiencies are known for the radiations populating and de-populating the nuclides. The feasibility of this technique in identifying and assaying trace quantities of ^{228}Th and its daughter nuclides was demonstrated by the use of the 304ns half-life of ^{212}Po in the thorium decay chain by McBeth et al. (8) (see Figure 1). Cross and McBeth (9) also determined the ^{226}Ra series by means of the 164 μs half-life of ^{214}Po. However, the measurement of half-lives shorter than those in the microsecond region requires fast-timing electronic equipment because short-lived nuclides emit beta-rays, of which the detection efficiencies are difficult to precisely determine.

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On the other hand, an alternative method for assaying the ^{228}Th series was presented by Cross et al. (10) that used ^{216}Po with a half-life of 145ms (see Figure 1). In their correlation counting (CC) technique, the activity of the short-lived nuclide is deduced from deviation in the statistical properties of the counting rate distributions due to the presence of correlated events. However, the CC technique is known to give poorly reproducible results.

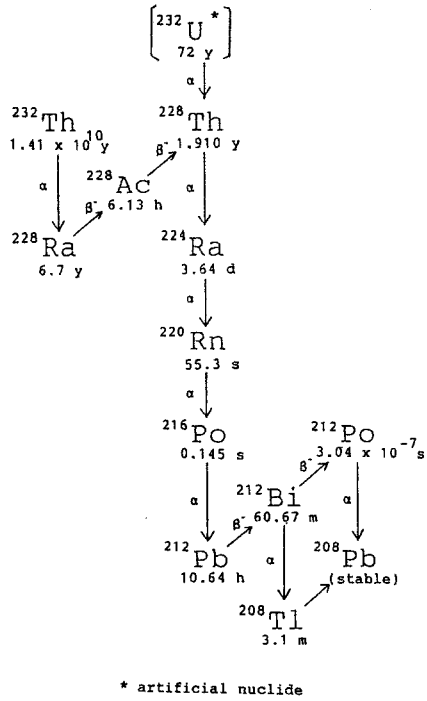
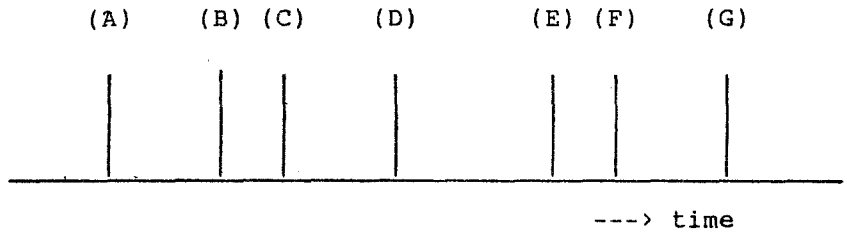


Figure 1. Thorium (4n) decay series

In this paper, an attempt was made to apply a new delayed coincidence in assaying ^{216}Po (145ms) in the thorium series members using a liquid scintillation counter and a microcomputer. In this measurement, whenever a decay event is detected, it is recorded on the computer memory as a "time list." The time interval distributions (hereafter called "time spectrum") between the events in the recorded "time list" data was used to evaluate the absolute activity of thorium series members. The principles and applications of the present delayed coincidence method with mulitple time analysis are outlined below.

PRINCIPLES

The determination of the half-life of a short-lived nuclide is performed by measuring the distribution of time intervals between the nuclear decay events populating and de-populating the nuclides. In many cases, Time to Amplitude Converter (TAC) is employed to measure the time intervals. This device converts a time interval between a "start-event" and a "stop-event," to a pulse height. If an event is selected as a "start event," the next event is always selected as "stop-event." This is called a "single period time analysis" as shown in Figure 2.



(1) Single period time analysis

(A)-(B), (B)-(C), (C)-(D), (D)-(E), ...

(2) Multiple time analysis

(A)-(B), (A)-(C), (A)-(D), (A)-(E), ...
(B)-(C), (B)-(D), (B)-(E), (B)-(F), ...
(C)-(D), (C)-(E), (C)-(F), ...

Figure 2. Conceptual expression of the delayed coincidence measurement of indistinguishable parent-daughter pairs. (a): Single period time analysis, (b): Multiple time analysis. Symbols (A), (B), . . and (G) represent the time when each decay event is detected

When there are short-lived daughter nuclides together with the relatively long-lived parent in the presence of background radiations, and if the parent and daughter radiations are distinguishable, the time intervals between the detected events are distributed as follows (9, 11, 12):

$$P(t)\cdot dt = [\, C \cdot (1-\beta\,\varepsilon_d)\cdot \exp(-Ct) + \beta \cdot \varepsilon_d\cdot(C+\lambda)\cdot \exp(-(C+\lambda)t)\,]\cdot dt,$$

$$\beta = \varepsilon_p \cdot A_p / N_s \qquad (1)$$

Where p(t) is the probability that the time interval appears between t and t+dt, C is the mean background rate, ε_p and ε_d are detection efficiencies for the parent and daughter, respectively, β is the fraction of parent type events, λ is the decay constant of the daughter, and A_P and N_S are the disintegration rates of the parent channel, respectively. The first term in this Equation represents the chance coincidences, and the second refers to the true coincidence distributions. From Equation 1, the true coincidence does not decay with its own decay constant, λ, but follow the factor C+λ. The activity, A_P, can be computed by fitting the measured time spectrum by a form $N_{sp}(t)\cdot dt$ in Equation 1.

If $\lambda >> C$, Equation 1 can be simplified to the following:

$$p(t)dt = [\, B_S + A_S \cdot \exp(-\lambda t) \,]\, dt \qquad (2)$$

where B_S and A_S are $C(1-\beta\cdot\varepsilon_d)$ and $\beta\cdot\varepsilon_d\cdot\lambda$, respectively, and they consist of all constants. For the measurement of half-lives in the time range of less than about 10^{-5}s, Equation 2 is valid because the condition $\lambda >> C$ can always be fulfilled. However, for the measurement of half-lives and determination of the activity of longer-lived nuclides, the approximation in Equation 2 is not profitable.

Whenever values of λ and C in Equation 1 are comparable, it is difficult to distinguish the true coincidence distributions from the chance coincidence distributions. Furthermore, it is impossible to distinguish the decay of ^{220}Rn and ^{216}Po by liquid scintillation counting. In measuring half-lives longer than 10^{-4} s, some true coincidence events will be blocked by random chance coincidences (5).

In a multiple time analysis (6), when an event is detected as a "start-event," all delayed events within a given time period are accepted as "stop-events" as shown in Figure 2. Thus, the system has essentially no coincidence losses. In addition, distinguishing the parent and daughter decays is not required. A time spectrum is compiled from the time differences between a "start-event" and a "stop-event" by processing the "time list" data. The true coincidence behaves as an exponential function which follows a decay curve with the intrinsic half-life, while the chance coincidence term gives a constant background. When short-lived daughter nuclides and the parents co-exist along with many additional background radiations, the time intervals will be distributed as follows:

$$p(t)dt = [\, \varepsilon_p\cdot\varepsilon_d \cdot A_P\cdot\exp(-\lambda t) + B_c \,]\, dt \qquad (3)$$

where A_P is a disintigration rate of the parent nuclide, and B_c is a parameter that represents chance coincidence distribution.

Therefore, it is easy to distinguish the true coincidence distributions from chance coincidence distributions and identify the nuclide by fitting the measured time spectrum in Equation 3.

EXPERIMENTAL

List Mode Time Measuring System

A low-background liquid scintillation counter with an anti-coincidence background reduction system (Aloka LSC-LB1) was employed. The intrinsic background counting rate of the system was about 1 cpm or less.

Amplified dynode pulses from the photomultiplier of the LSC are discriminated to reduce the contribution of background radiations such as beta-rays. The discrimination level was selected in order that the alpha particles populating and depopulating ^{216}Po were detected with 100% efficiency. The discriminated pulses are fed into an 1024 channel multichannel analyzer (MCA, Norland 5300) to measure the pulse height distribution, followed by the time analysis of logical output from the MCA in the digital time analyzer which was made to record the time whenever an event was detected. A block diagram of the time measuring system is shown in Figure 3.

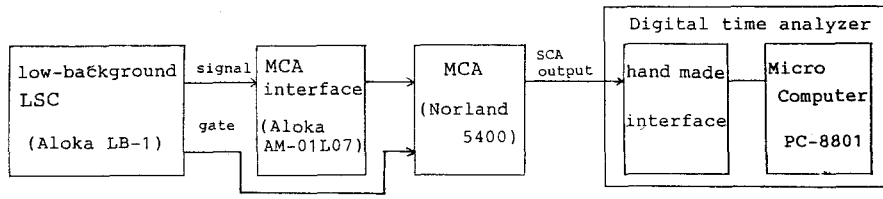


Figure 3. Block diagram of the apparatus employed in the "list mode" time measurement

The digital time analyzer consisted of a laboratory-made interface (primarily counter/timer circuit) and a microcomputer (NEC, PC-8801). Clock pulses of 500 Hz frequency were counted in a "time register," an internal standard timer, all through the time measurements. On the arrival of each logic pulse corresponding to a decay or background event, the internal timer in the "time register" was read and written into the "time list" within a certain fixed area of the computer memory. These processes were controlled by computer programs. The stored time data was written to disk files when the area was full; the "time list" was then initialized and the measurement restarted. At the end of each measurement, all the time data was saved in the disk files and the circuit was reset.

Sample Preparation

As a standard source for the thorium series, a ^{232}U stock solution in radioactive equilibrium was used; ^{210}Po was used as a source for random events.

An aliquot of the ^{232}U solution (3M HNO_3) was loaded into an Aquasol-II (New England Nuclear), in a 20 ml glass counting vial. Samples containing ^{232}U and chemically purified ^{210}Po were also prepared to study the effects of co-existing radioactive nuclides on activity determination.

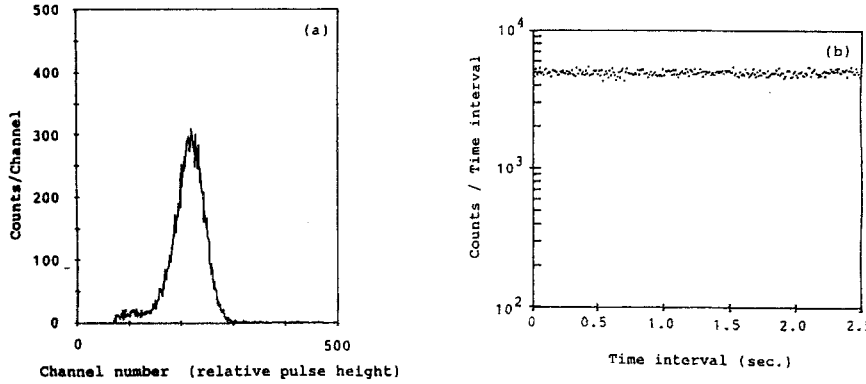


Figure 4. (a). Pulse height distribution and (b): Time spectrum from ^{210}Po loaded in Aquasol-II

Delayed Coincidence Measurement

After the measurement, time differences between one event and its delayed events within a certain time range were compiled from the "time list" data files.

In this multiple time analysis, a time spectrum accumulated in a certain measuring time, t_m, is distributed as follows:

$$N\,p(t) = B + A\exp(-\lambda t) \tag{4}$$

where t is the length of time interval, N is the total number of counts, p(t) is the probability that the time interval has a length between t and t+dt, B is the number of chance coincidences, λ is the decay constant of ^{216}Po, and A is the parameter referring to the disintegration of the parent nuclide, ^{220}Rn. It was assumed that detection efficiencies for alpha particles from both ^{220}Rn and ^{216}Po were 100%. The accumulated time spectrum was fitted in Equation 4 by a least squares method. The absolute activity of ^{220}Rn ($A(^{220}Rn)$) was calculated as follows:

$$A(^{220}Rn) = A/\lambda/t_m \text{ (dps)} \tag{5}$$

RESULTS AND DISCUSSION

Time Spectrum of Random Events and ^{232}U With Daughters

Figure 4(a) shows the pulse height distribution for ^{210}Po in the Aquasol-II. A distinctive peak due to the 5.3 MeV alpha particles de-populating ^{210}Po was observed. It was confirmed that alpha particles can be detected with 100% efficiency in liquid scintillation counting.

The time spectrum for ^{210}Po is shown in Figure 4(b). Flat distribution was clearly observed

which showed the counting rates were not dependent on the time interval between the events. Since the time range in measuring time intervals of the events is negligibly small compared to the 138 d half-life of ^{210}Po, one can regard the decay of ^{210}Po as a purely random event within the present measuring time interval.

Figure 5 shows the pulse height distribution from a sample containing ^{232}U and its daughter nuclides in equilibrium. The lower end of the energy distribution was discriminated to reduce the contribution of beta-rays and the other background radiations. Complex peaks due to alpha particles emitted by ^{232}U, ^{228}Th, ^{224}Ra, ^{220}Rn, ^{216}Po, and ^{212}Po (compare with Figure 1) are observed as essentially one peak on the continuous background. Thus, it is difficult to distinguish an alpha particle from a particular de-populating nuclide from that of another one by their energy alone.

The time spectrum from the same sample was obtained as shown in Figure 6(a). In the time range less than about 0.5 s, the increment of time interval distribution was clearly observed beyond the statistical fluctuation in the flat distribution due to chance coincidences. This evidently implies the presence of a short-lived nuclide.

Figure 6(b) shows the time spectrum after the chance coincidence portions were subtracted. The counts per channel decreased exponentially with the increasing channel number corresponding to the time interval length. The half-life obtained by a least squares fitting program was 142 ± 5 ms,

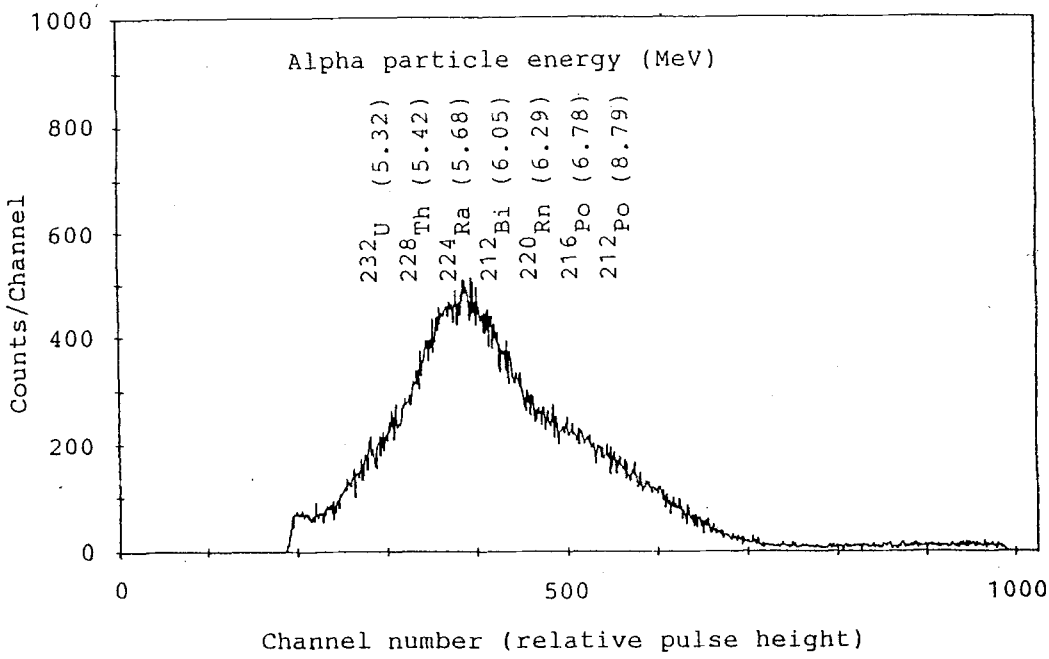


Figure 5. Pulse height distribution from ^{232}U loaded in Aquasol-II

which verified the presence of ^{216}Po. According to the result, the decay of ^{216}Po in a thorium decay series can be detected by the use of the multiple time analysis.

The results shown in Figure 6(b) certainly support the possibility of determining half-lives in the 10^{-1} second region by the present multiple time analysis. Furthermore, the alpha particles populating and de-populating the nuclides, originating from ^{220}Rn and ^{216}Po, respectively, could be detected with 100% efficiency. This means that the absolute activity of preceding nuclides, including ^{224}Ra, ^{228}Th, and ^{232}U, could be determined by this method if the system is in radioactive equilibrium.

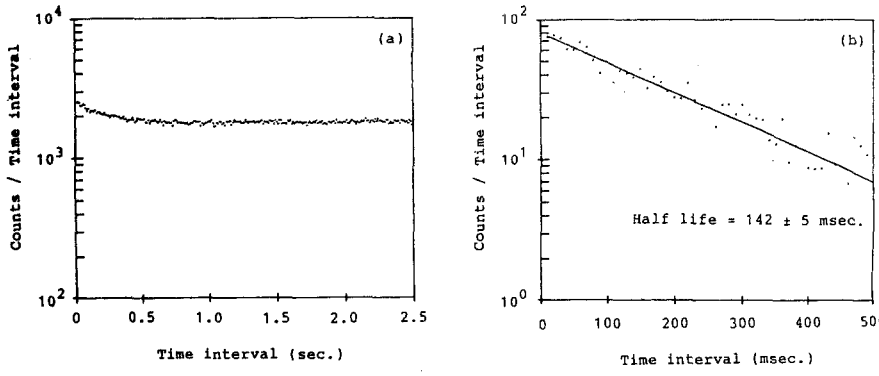


Figure 6. (a). Time spectrum from ^{232}U and its daughters loaded in Aquasol-II.
(b). Time spectrum with chance coincidences subtracted.
The solid line represents the results of a computer fit to the data

Activity determination of ^{232}U

To examine the feasibility of determining the activities of thorium series nuclides, several standard samples which contained different aliquots of ^{232}U standard solution ranging from 5.5 x 10^{-3} to 7.4 x 10^{-1} Bq were measured for the ^{232}U activity.

In Figure 7, evaluated activities for ^{220}Rn from each sample were plotted against respective activities of the added ^{232}U. A measuring time was chosen in the range of 60,000 to 131,000 s depending on the activity strength. A linear relationship demonstrates the reliability of this method in the determination of absolute activities for thorium series members. The relative standard deviation of the evaluated activity was 2% under the experimental condition where the activity of ^{233}U was 0.22 Bq and where the measuring time was 60,000 s.

Effects of Random Events on Activity Determination

As described above, the activity of ^{220}Rn in the thorium decay series could be determined by multiple time analysis for the samples containing only the thorium series nuclides. However, this is an exceptive ideal condition. To apply this method to the ordinary environmental samples, the effect of

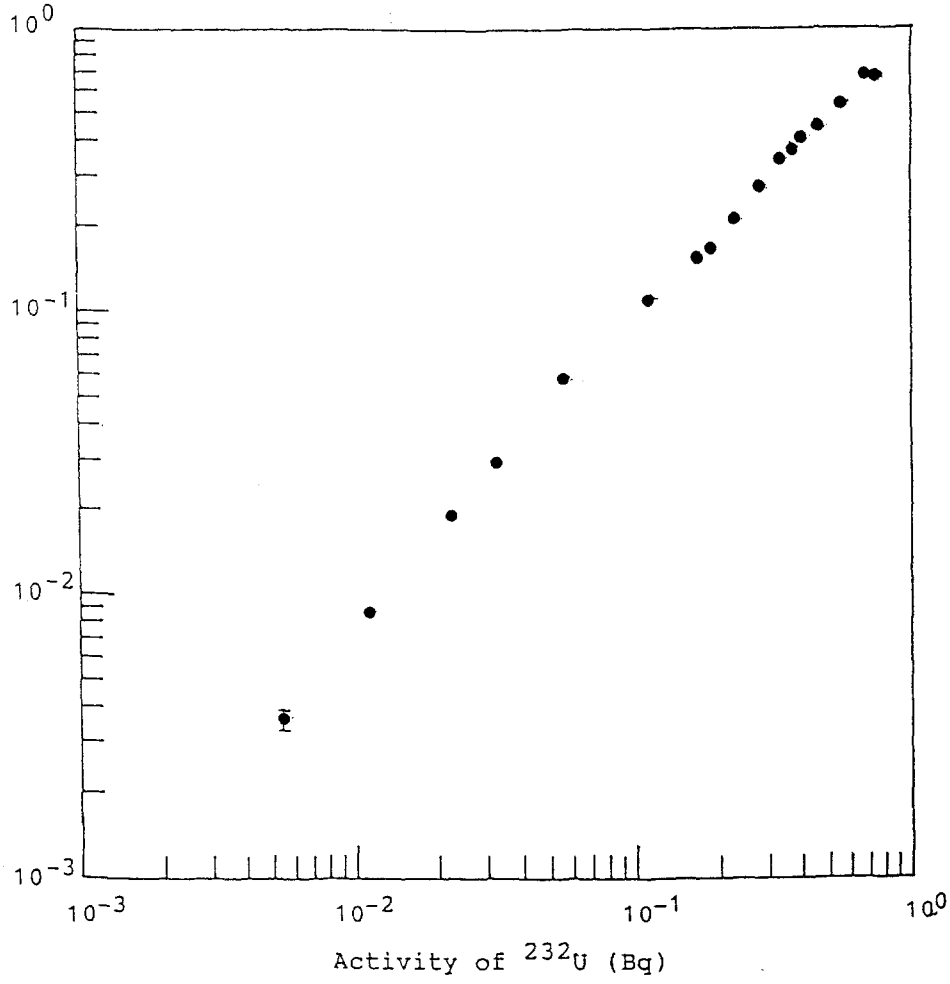


Figure 7. Relationship of activities between ^{232}U added as standard and ^{220}Rn determined by delayed coincidence measurement

background radiations including a co-existing uranium series must be considered in determining activities of the thorium series. For this purpose, several samples containing ^{232}U with its daughter nuclides were measured with ^{210}Po added as a representative contaminant. The composition and activity values obtained from the time spectra for each sample are summarized in Table 1.

From Table 1, the calculated activities remained constant in spite of an increase in the activity of ^{210}Po in the sample, although the error tended to increase. This implies that the evaluation of the true coincidences from a measured time spectrum is not significantly affected by the increase of chance coincidences in the present experimental regions. Therefore, it would be interesting to determine

Table 1

Activity determination of ^{220}Rn by the delayed coincidence method for the samples which are spiked with ^{232}U and ^{210}Po

Sample No.	Measuring time (sec.)	A(^{232}U) (Bq)	A(^{210}Po)* (Bq)	A(^{220}Rn) (calculated) (Bq)
1	7×10^4	4.07×10^{-2}	0	$(3.85 \pm 0.09) \times 10^{-2}$
2	6×10^4	4.07×10^{-2}	0.95×10^{-1}	$(4.32 \pm 0.12) \times 10^{-2}$
3	6×10^4	4.07×10^{-2}	1.90×10^{-1}	$(4.40 \pm 0.14) \times 10^{-2}$
4	6×10^4	4.07×10^{-2}	2.85×10^{-1}	$(4.41 \pm 0.20) \times 10^{-2}$
5	1×10^4	4.07×10^{-2}	3.79×10^{-1}	$(3.93 \pm 0.49) \times 10^{-2}$
6	1×10^4	4.07×10^{-2}	4.74×10^{-1}	$(3.01 \pm 0.63) \times 10^{-2}$
7	1×10^4	4.07×10^{-2}	5.69×10^{-1}	$(6.60 \pm 0.64) \times 10^{-2}$
8	1×10^4	4.07×10^{-2}	6.64×10^{-1}	$(3.82 \pm 0.73) \times 10^{-2}$

* ^{210}Po was used as a representative contaminant. The ratio $A(^{232}U)/A(^{210}Po)$ is in larger range than 0.06.

activity of the thorium series in the presence of the uranium series nuclides or other background radiations provided that there exist no other nuclides with half-lives of - 10^{-1} s.

Thus, the theoretical prediction and the experimental results indicate that 10^{-2} Bq ^{220}Rn in the thorium decay chain can be determined with an accuracy of 20% with a counting time 1.5 x 10^5 s under the condition that the background counting rate is about 1 cps or less. This accuracy was estimated from the relative standard deviation of repeated measurements.

Application of Delayed Coincidence Method to Natural Samples

A determination of ^{228}Th activity in water from a hot spring collected from Tamagawa hot spring (Akita prefecture, well-known as a typically high concentration of radioactive elements in Japan). After being stored for about two months, a 40 ml sample was mixed with 60 ml of Aquasol-II in a 100 ml teflon vial.

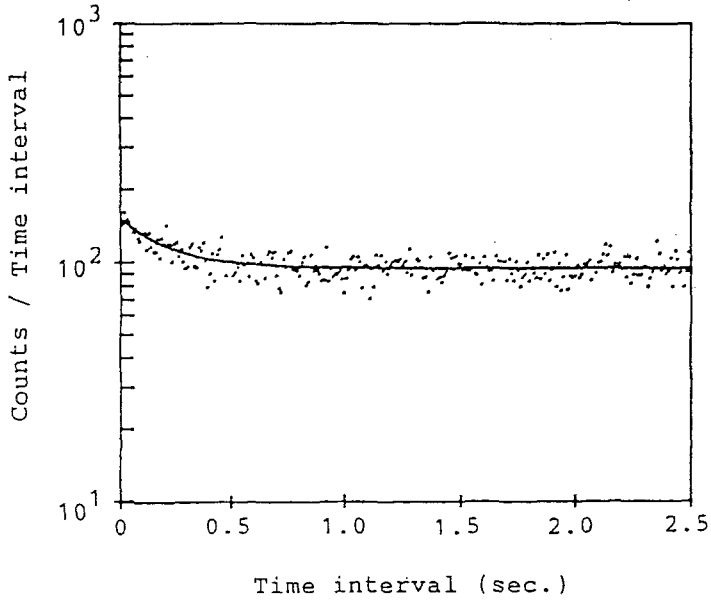


Figure 8. Time spectrum from a water samples collected from Tamagawa hot spring. 40 ml of the sample was used for analysis. The solid line represents the result of a computer fit to the data. measuring time is 1.31 x 10^5 sec. Evaluated activity of ^{228}Th is (2.26 ± 0.14) x 10^{-1} Bq/l

The time spectrum obtained from the sample is shown in Figure 8. In the time region of less than about 0.5 s, the distribution clearly exceeds the statistical variation of the flat distribution as seen in time regions larger than 0.5 s. Since there are no other radioactive nuclides with half-lives on the order of 10^{-1} second in the thorium series except ^{216}Po, this excess portion certainly suggests the presence of the thorium series nuclides. Recently, the existence of ^{224}Ra and ^{228}Th in radioactive disequilibrium

was also ascertained in the same hot spring water by the present method as well as in precipitation from the hot water (13, 14). The solid curve represents the result of a least-squares fit to the experimental data. The activity of ^{228}Th equilibrated with ^{220}Rn and ^{216}Po in the sample was evaluated to be (9.04 $\pm$ 0.56) x 10^{-2}Bq or (2.26 $\pm$ 0.14) x 10^{-1}Bq/1 without any tedious chemical procedures to purify or enhance thorium series.

CONCLUSION

A "list mode" time analyzing system was assembled to apply the delayed coincidence method to the absolute determination of trace quantities of the thorium series nuclides in enviroment samples.

It was found that 0.01 Bq of ^{220}Rn in the thorium series in radioactive equilibrium could be determined with an accurary of 20% with a measuring time of 1.5 X 10^5 s under the condition that the total counting rate, including background activities from other radioisotopes like the uranium series, was about 1 cps.

It was possible to evaluate the activities of ^{228}Th by measuring the delayed coincidence of the parent-daughter pairs, ^{220}Rn - ^{216}Po.

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