Comparison of radon doublet alpha spectra measured in water using chi-square and maximum likelihood methods

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Abstract

Radon doublet alpha spectra were measured in water using the chi-square and maximum likelihood methods and the measurement results were compared. Radon measurements were made with a high-resolution alpha liquid scintillation spectrometer ORDELA 8100AB. The chi-square method introduced significant systematic deviations in cases of low-count statistics whereas the maximum likelihood method yielded good results in all cases. Thus, radon concentration in water can be determined more accurately using the maximum likelihood method.

1. Introduction

Precise estimates of radon (^{222}Rn) concentrations in drinking water and ground water have become necessary in recent years. These estimates are based on measurements of alpha and/or gamma rays of radon and its daughter nuclides. We have recently developed a alpha liquid scintillation spectrometric method using the ORDELA 8100AB spectrometer[1]. In this method, alpha rays of radon are measured directly, before radioactive equilibrium has been reached between radon and its daughters. Since the alpha peaks of ^{222}Rn and its daughter nuclide ^{218}Po overlap, the radon peak area is determined by peak curve fitting, which has traditionally been done using the chi-square method because of its simplicity. Recently, the maximum likelihood method has become popular for decay curve fitting[2]. Several reports have noted that systematic deviations are introduced when the chi-square method is applied to radioactive data, which usually follow a Poisson distribution. This is especially true with low-count statistics, whereas the maximum likelihood method gives good results[3–5] over a wide range of radioactive counts.

In the present work, double Gaussian fitting with a linear background for the alpha doublet of ^{222}Rn 5.49 MeV and ^{218}Po 6.00 MeV was carried out to obtain the radon peak area by means of the chi-square method and the maximum likelihood method. We investigated mainly the estimation of parameter values (known as "point estimation" in statistics) and compared the results to determine the radon concentration in water accurately. Some examples of radon measurement in water are given.

2. Experimental

Radon in 1 L of sample water was extracted into 3 mL of liquid scintillator consisting of 4g of 2,5-diphenyloxazole, PPO, dissolved in 1 L of xylene, and then 1 mL of the scintillator was transferred to a 1 mL glass counting vial. Alpha rays with an energy of 5.49 MeV emitted from the decay of radon in the vial

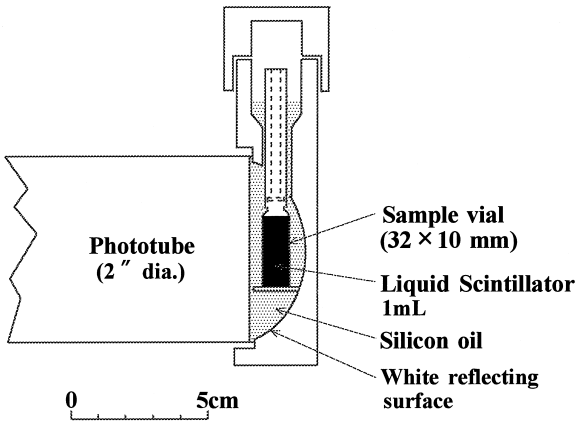

Fig. 1 Cross-section of the detector portion of the alpha liquid scintillation spectrometer ORDELA 8100 AB. One mL of liquid scintillator is put into a 1 mL glass counting vial.

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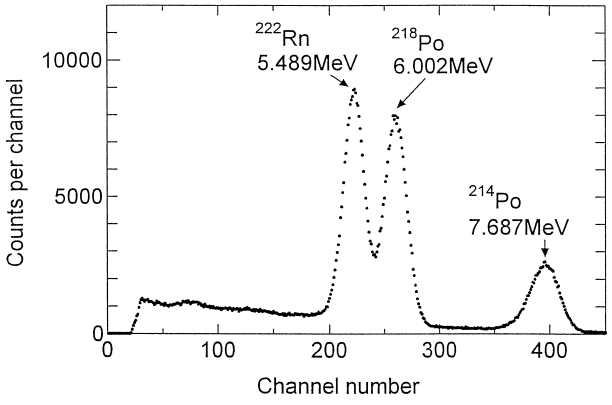

Fig. 2 Typical alpha liquid scintillation spectrum of radon and its daughters for 3600 sec measuring time. Radon concentration in water sampled at Onomichi-Trackstation was 2311 BqL^{-1}.

were directly measured with a high-resolution alpha liquid scintillation spectrometer ORDELA 8100AB, shown in Fig. 1[6]. This method was described in detail previously[1]. The typical energy spectrum of radon and its daughters in ground water having a high radon concentration is shown in Fig. 2. The alpha peaks of ^{222}Rn 5.49 MeV and daughters ^{218}Po 6.00 MeV and ^{214}Po 7.69 MeV were superimposed on the beta and gamma continuum of the daughters ^{214}Pb and ^{214}Bi. In the present work, the ground water was sampled at Kagamiyama (where the radon concentration is about 26 BqL^{-1}), near Hiroshima University. Radon measurements were made for 60 minutes once a day for 20 days to provide doublet alpha spectra for analysis.

3. Analysis

3.1 Peak-shape function of alpha doublet

Since the peak of a single-energy alpha ray obtained with the detector system in the present work is essentially symmetrical and is described by a Gaussian curve[6], the doublet of ^{222}Rn and ^{218}Po fully dissolved in the liquid scintillator is described by a double Gaussian curve of the same peak width. Fig. 2 shows how the ^{214}Po 7.69 MeV peak spreads slightly to the low-energy side due to a wall effect. That is because some of the ^{214}Pb and ^{214}Bi has adhered to the wall of the vial before the ^{214}Po emitted its alpha ray[7]. Beta-gamma background is represented by a straight line in the region of the alpha peaks. Therefore, the peak-shape function for this alpha doublet has the form of two Gaussian curves plus a linear function for the channel number $x_i (i = 1,...,n)$ and can be expressed as follows :

$$f(x_i) = a_1 exp\{-a_2(x_i - a_3)^2\} + a_4\{-a_2(x_i - a_5)^2\} + a_6 + a_7 x_i . \quad (1)$$

The first and second terms express the ^{222}Rn and ^{218}Po peaks. The third and fourth terms express the background part. The quantities a_j are the free parameters that would be searched in the analysis. The parameters a_1, a_4 and a_3, a_5 represent the peak heights and peak positions. The parameter a_2 is connected to the peak FWHM Γ, which is a common value for ^{222}Rn and ^{218}Po peaks, by the relation :

$$\Gamma = 2\sqrt{\frac{ln2}{a_2}}. \quad (2)$$

The parameters a_6 and a_7 represent the intercept and slope of the background part. Consequently, the radon peak area S is given as

$$S = a_1\sqrt{\frac{\pi}{a_2}}. \quad (3)$$

3.2 Maximum likelihood method

Since the number of counts in each channel follows the Poisson distribution, the probability to obtain the number of counts $y_i (i = 1,...,n)$ in the channel x_i is given by

$$P(y_i) = \frac{m_i^{y_i}}{y_i!} exp(-m_i), \quad (4)$$

where m_i is the parent mean of y_i. Then the likelihood function L is expressed as

$$L = \prod_{i=1}^{n} \frac{\{f(x_i)\}^{y_i}}{y_i} exp\{-f(x_i)\} \quad (5)$$

The best fitted $f(x)$ could be obtained when this likelihood function is maximized. Usually, it is convenient to use the natural logarithm of the likelihood function expressed as follows :

$$ln L = \sum_{i-1}^{n} \{y_i \, ln f(x_i) - f(x_i) - ln(y_i!)\} \quad (6)$$

The optimum values of the free parameters a_j can be obtained by the following simultaneous equations, which are likelihood equations :

$$\frac{\partial ln L}{\partial a_j} = 0, (j = 1,...,7) \quad (7)$$

Since the log likelihood function $ln L$ is non-linear with respect to a_j, an iterative fitting procedure

similar to ref. 3 for the linearization was carried out. The initial values of the free parameters a_j were obtained on MCA's display to guarantee fast convergence and get reliable results. Parameter searching stopped when the log likelihood function $\ln L$ found a maximum. The uncertainties of parameters were approximately derived from the error matrix[8]. This method is denoted by MXL.

3.3 Two chi-square methods

The chi-square method is widely used to analyze the nuclear radiation spectrum assuming a normal distribution with the same value of the parent mean and the parent variance according to eq. (4). The quantity chi-square is defined by

$$\chi^2 = \sum_{i=1}^{n} w_i [y_i - f(x_i)]^2, \qquad (8)$$

where w_i is the weight for the datum y_i. The most probable values for free parameters are determined by minimizing the chi-square. Generally, the weight w_i is given by $1/\sigma_i^2$, where σ_i is the standard deviation for the datum y_i. Since the parent variance is not known, the weight is deduced in various ways[3, 9]. In the present work Neyman's chi-square is adopted replacing w_i by $1/y_i$. When the value of y_i is zero, w_i is taken as unity so as to prevent the weight being infinite.

The chi-square method suffers from potential problems, especially when the data consists of low-count statistics. One of these problems is due to the discrepancy between the Poisson and normal distributions. It seems that agreement is good as long as the number of counts is above 5[10], but Y. Jading and K. Riisager have shown that this is not true for determination of the parameter value[5]. Another problem is due to the weighting used in the fitting. For Neyman's chi-square, since the weights are large for datum points over the fitted curve and small for datum points under the curve, the fitting function is pulled down and the fitted area is underestimated. This is referred to as the "pull-down effect", as described below.

The chi-square function is non-linear with respect to a_j, so a linearization method similar to MXL was carried out. This method is denoted by LSQ1. Moreover, the pull-down effect causes the simultaneous fitting of peak and background to give smaller background values, so we subtracted the background and performed double Gaussian chi-square fitting for the spectrum data. The background was represented by a straight line, which was determined by averaging the low- and high-energy sides of the doublet. The weight was calculated from the original data in the same way as in LSQ1. This method is denoted by LSQ2.

4. Results and discussion

Fig. 3 shows typical results for curve fitting. When the statistics are good, as in Fig. 3(a), the three different analytical methods agree well on which is the best-fitted function, except the small background in LSQ1 due to the pull-down effect. When the statistics are poor as in Fig. 3(b), the pull-down effect makes the FWHM of the chi-square fit smaller than that of the maximum-likelihood fit and sometimes reduced the peak height. The radon peak area is therefore underestimated in LSQ2, while LSQ1 may yield a closer estimate of the peak area because the pull-down effect shifts the background downward.

It was confirmed that MXL preserves total counts in the fitting region and the free parameters are

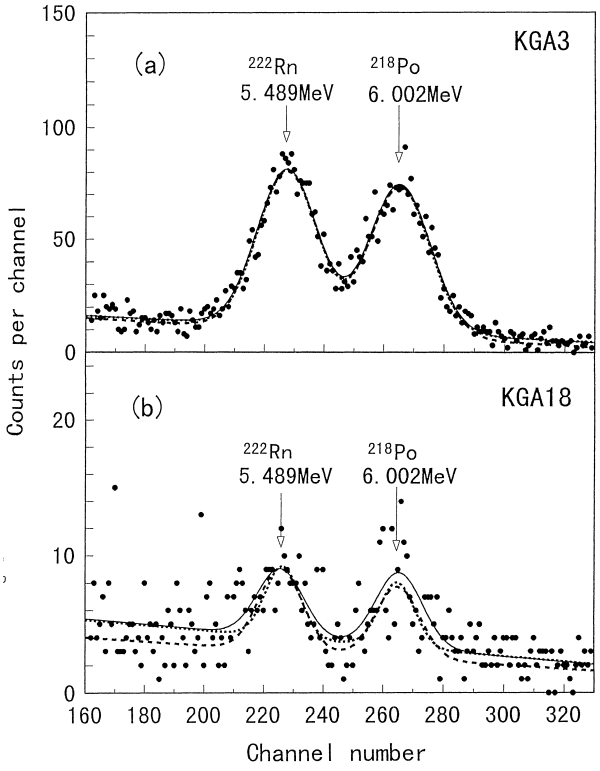

Fig. 3 Typical results for curve fitting for doublet alpha spectra of radon. The solid lines represent the best-fitted functions by MXL, the dashed lines ones by LSQ1 and the dotted lines ones by LSQ2 : (a) third-day spectrum ; (b) eighteenth-day spectrum.

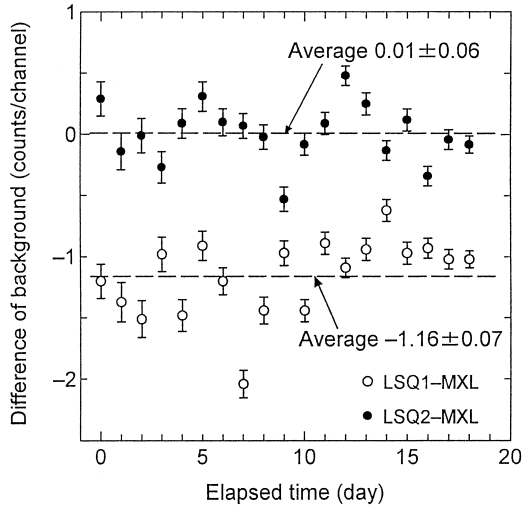

Fig. 4 Differences in background obtained by three different methods as a function of elapsed time. Each point indicates the difference in background counts per channel between maximum likelihood fit and two chi-square fits, calculated by averaging the background in the region of the radon peak.

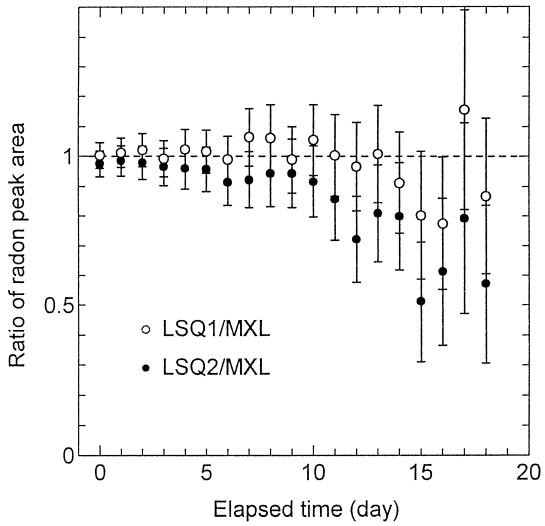

Fig. 5 Ratios of radon peak area determined by three different analysis methods as a function of elapsed time. Each point indicates the ratio of radon peak area of chi-square fit to MXL.

unbiased. The differences of background determined by LSQ1, LSQ2, and MXL are shown in more detail in Fig. 4 as a function of elapsed time corresponding to from 13.4 to 3.4 (counts/channel). It was found that the difference between LSQ1 and MXL is approximately unity, which is consistent with the result of ref. 5. It was also found that the results of LSQ2 and MXL almost agree. These findings mean that the background term includes most of the bias in LSQ1 and the discrepancy of the peak term becomes large in LSQ2.

Ratios of the radon peak area of two chi-square fits to MXL are shown in Fig. 5 as a function of elapsed time corresponding to from 2486 to 96 (counts) of radon peak area (a_1=102.5～4.7) determined by MXL. It may be stated that :

a) the result of LSQ2 is always underestimated due to the pull-down effect,
b) it deviated beyond the error limit after the twelfth day with below 263 (counts) of radon peak area ($a_1 \leq 10.9$),
c) the result of LSQ1 is close to that of MXL containing the background reduction problem,
d) the result of LSQ1 is sometimes underestimated in poor statistics because of the strong pull-down effect of the radon peak.

5. Application

Radon concentration in water can be calculated using the effective efficiency which is determined experimentally for radon in 1 mL of scintillator[1]. Some examples of radon concentration measurement are given in Table 1. Radon concentrations determined by three different methods almost agree in the cases of Nos. 1 and 2, but the deviations between them are significant in the case of No. 4. A reliable estimate of radon concentration in water can be made by means of the maximum likelihood analysis of the

Table 1 Radon concentration in ground water obtained by alpha−liquid scintillation spectrometry and analyzed by three different analysis methods.

No.	Place	Meas. time (sec)	^{222}Rn peak count* (counts)	a_1* (counts)	Radon concentration (BqL^{-1})		
					MXL	LSQ1	LSQ2
1	Innoshima	3600	5998	232.2	75.3 ±1.9	75.6 ±1.9	75.2 ±1.9
2	Kagamiyama	3600	2035	88.8	26.3 ±1.0	26.6 ±1.0	26.0 ±1.1
3	Yuge	3600	1393	56.5	17.9 ±0.8	18.1 ±0.8	17.3 ±0.8
4	Taguchi	3600	162	6.1	1.98±0.36	1.59±0.32	1.01±0.35

*) ^{222}Rn peak count and peak height a_1 are obtained by MXL.

radon alpha doublet.

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