原　　著

陽イオン交換樹脂による温泉水中のラジウムの定量

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Determination of Radium Concentrations in Hot-Spring Waters with Cation Exchange Resin

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Abstract

　　Experimental conditions are discussed for a new analytical method for determining ^{226}Ra and ^{228}Ra concentrations in hot-spring waters. The method is aimed to be applicable to the field works. The acidity of the sample water is adjusted to 0.1 M HCl and Ra isotopes are collected by the cation exchange resin in a successive ion exchange procedures of batch operations : the second ion exchange procedure is applied to the same sampled water after the removal of the resin in the first procedure. The concentration of Ra isotopes in the sample water can be estimated from the amount of Ra isotopes recovered in the two operations by calculation. The amounts of ^{226}Ra and ^{228}Ra on the resin are obtained by a γ-ray spectrometry for the 351 keV γ-ray from ^{214}Pb and for the 911 keV γ-ray from ^{228}Ac, both in radioactive equilibrium with precursors, respectively. The present estimation method is applicable to 5 l of hot-spring waters having ^{226}Ra concentrations of larger than 10 mBq/l, and may be applicable to the ordinary underground waters of less than 1 mBq/l by using 50 l of sample water.

Key words : radium concentration, hot-spring water, cation exchange resin, field work, gamma-ray spectrometry

要　　旨

　温泉水中の ^{226}Ra および ^{228}Ra を定量する新しい方法を開発するための実験条件を検討した．本方法は野外調査時に応用することを目的としている．試料水の酸濃度を 0.1 M HCl 調整した温泉水試料に対し，陽イオン交換樹脂をバッチ法で用い，回収操作を 2 回連続して行うことにより回収量を求め，計算によりラジウム濃度を求めることができる．樹脂に回収された ^{226}Ra と ^{228}Ra の量は，ガンマ線スペクトロメトリーにより ^{226}Ra と ^{228}Ra と放射平衡になった ^{214}Pb の 351 keV のガンマ線と ^{228}Ac の 911 keV のガンマ線を測定することにより求められる．この方法により，^{226}Ra として 10 mBq/l 以上含む温泉水試料では 5 l，1 mBq/l 以下の濃度の地下水試料では 50 l を対象にすればラジウムの定量が可能である．

キーワード：ラジウム，温泉水，陽イオン交換樹脂，野外調査，ガンマ線スペクトロメトリー

1. Introduction

Several techniques have been reported in the literature on the determination of the concentrations of ^{226}Ra in thermal spring waters or natural waters, including the coprecipitation with BaSO$_4$ or with PbSO$_4$ followed by α-ray spectrometry, γ-ray spectrometry and liquid scintillation spectrometry (Sato *et al,* 1975 ; Honma and Murakami, 1977 ; Horiuchi and Murakami, 1978 ; Environment Agency of Japan, 1978 ; Horiuchi *et al.,* 1979 ; Horiuchi, 1981 ; Moron *et al.,* 1986 ; Yamamoto *et al.,* 1989 ; Hancock and Martin, 1991 ; Burnett and Tai, 1992 ; Yamamoto *et al.,* 1994). "Guide to the analysis of mineral spring waters" appeared in *J. Soc. Eng. Mineral Springs, Jpn,* issued in 1978 recommends the procedure of the coprecipitation of ^{226}Ra with BaSO$_4$ followed by the measurement of ^{222}Rn in equilibrium with ^{226}Ra by a liquid scintillation spectrometer (Environment Agency of Japan, 1978).

However, Ba reagents frequently contain small but significant amounts of ^{226}Ra of several fractions of 1 Bq/g. As the amount of ^{226}Ra impurity in BaCl$_2\cdot$2H$_2$O reagents from 3 major makers in Japan was found to be in the range of 20–100 mBq/g, several tens mBq of ^{226}Ra might be mixed by the coprecipitation with several tens mg of Ba. Yamamoto *et al* (1989) who found the amount of ^{226}Ra impurity in Ba reagents ranged 100–400 mBq/g proposed the procedure to eliminate ^{226}Ra impurity from Ba compounds by cation exchange separation using CyDTA (cyclohexanediaminetetraacetic acid) as eluant. An α-ray spectrometry was applied for ^{226}Ra separated from the coprecipitating Ba compounds thus purified. These observations show that the separation procedure including coprecipitation of Ra with Ba compounds is generally not preferable in the determination of a minute amount of ^{226}Ra of less than 1 mBq/l in the water sample. Forthermore, most of these methods have difficulties in applying them to the field works because of their tedious chemical procedures which need the transportation of a large amount of sample water to the laboratory for the isolation of ^{226}Ra by a series of chemical procedures.

The experimental conditions of a new easy field work method for the isolation and measurement of ^{226}Ra and ^{228}Ra in thermal spring waters or underground waters are studied. This method consists of two procedures : (1) collection of Ra isotopes by cation exchange resin for the isolation, and (2) the determination of ^{226}Ra and ^{228}Ra by γ-ray spectrometry.

2. Experimentals

Most of the present studies on experimental conditions for chemical procedures with cation exchange resin were made by use of Ba instead of Ra, mainly because the amount of the waste water containing ^{226}Ra should be in minimum size. Barium was determined by the atomic absorption spectrometry.

2.1 Collection

Collection rate of Ba on resin was investigated with the solution of 3 and 30 ppm concentrations. The acidity of the solution was adjusted to 0.1 M HCl and cation exchange resin of Dowex 50W-X8, #20-50, in H-form, was employed. The amount of water volume was set to be 5 l or 50 l.

Collection rate was observed with the 3 methods described below :

Method (1) : A 30 g of resin was put into a 5 l of the solution directly and the solution was stirred for 15 min.

Method (2) : A 30 g of resin was put into a 50 l of the solution directly and the solution was stirred for 15 min.

Method (3) : A 30 g of resin was placed within a plastic tube. A 50 l of the solution was circulated for 15 min through the tube at a flow rate of 6 l/min with the aid of a portable pump.

The collection rates *vs* the operating time is given in Fig. 1. Figure 1 indicates that the Method (1) is effective in case where the amount of the water sample is as small as 5 l, while the Method (3) is favorable for the water samples of a larger amount than 50 l.

2.2 Estimation of Ra concentration in sample water

The time required for the ion exchange equilibrium between a large volume of sample water and a small amount of resin will be longer than 1 hour. However, a short time as possible is usually required for the operation in the field work. Assuming that the temperature and chemical properties of the large volume of sample water may not change
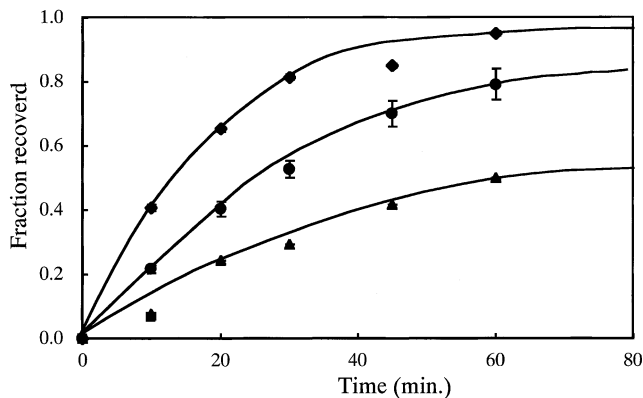

Fig. 1 Recovery curve of Ba by cation exchange resin.
◆ : Method (1) ; ▲ : Method (2) ; ● : Method (3).

significantly after a shot-time collection operation, the Ra content in the water samples can be estimated by the amount of Ra recovered by the two successive ion exchange procedures operated in the fixed time from the same water sample by using the following equations :

$$C_1 = C_0 \cdot \alpha \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(1)$$
$$C_2 = (C_0 - C_1) \cdot \alpha \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(2)$$
$$\therefore \alpha = 1 - (C_2/C_1) \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(3)$$
$$\therefore C_0 = C_1 / [1 - (C_2/C_1)] \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(4)$$

where C_0 : Total quantity of Ra in the initial water sample, which can be converted into the concentration by the volume of sampled water.

C_1 : Quantity recovered from the initial sample water by the 1st operation.

C_2 : Quantity recovered by the 2nd operation from the remaining water sample after removal of the resin used in the 1st operation.

α : Collection efficiency in the fixed operation time for the water sample.   The collection efficiency is assumed to be the same for the two successive operations. The operation time was set to the 15 min for the present estimation.

2.3   Interference of coexisting ions

Calcium and Fe are one of the major constituents usually existing in the natural waters. Though some thermal spring waters contain Ca more than 500 ppm, most of the concentrations of 2,350 thermal spring waters from 30 localities in Japan are reported to be less than 100 ppm (Hirakawa *et al.*, 1977). Frequency distribution of concentrations of Ca and Fe are shown in Fig. 2.
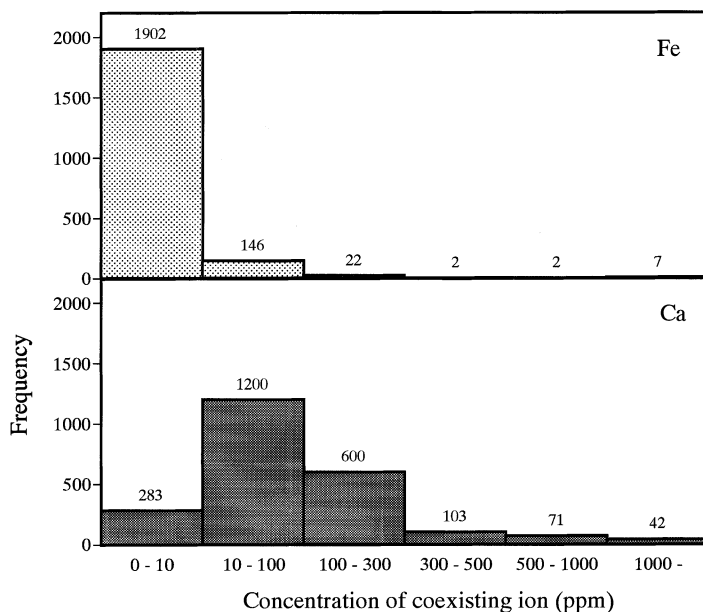

Fig. 2   Frequency distribution of concentration of Ca and Fe ion in Japanese thermal waters. (after Hirakawa *et al.*, 1977).
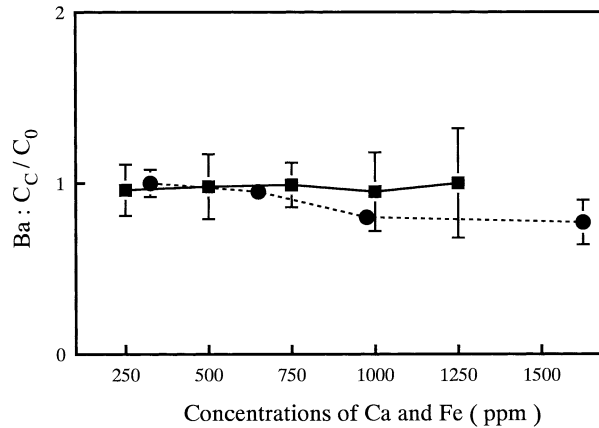
Fig. 3　Concentration of coexisting ions and ratio of C_C to C_0.　■ : Ca ;　● : Fe

Interference of the coexisting ions to the present method was studied with the 0.1 M HCl solutions of 30 ppm Ba by mixing a following range of Ca and Fe ions with the solution : the concentrations of Ca were adjusted to 250, 500, 750, 1,000 and 1,250 ppm, and those of Fe were adjusted to 300, 650, 950 and 1,600 ppm. The calculated concentrations (C_C) estimated from C_1 and C_2 by eq. (4) are compared with the known initial concentration C_0 in Fig. 3. As the C_C's for different Ca and Fe concentrations are approximately equal to the initial C_0 within their concentration range up respectively to 1,250 and 650 ppm, the interference of coexisting ion to the present method of estimation can be ignored as far as the samples are the ordinary natural waters.

2.4　Collection of Ra isotopes

The phosphorite from Florida, U.S.A., was used throughout the following studies. This phosphorite containing 3 Bq/g of ^{226}Ra was dissolved in 6 M HCl to prepare the stock solution of ^{226}Ra. Initially, the U impurity was eliminated from the stock solution with UTEVA Resin, an extraction chromatograph material supplied by Eichrom Industries, Inc., U.S.A., because the 186 keV γ-ray from ^{235}U interferes the 186 keV spectral line from ^{226}Ra. An aliquot of the ^{226}Ra solution thus refined was poured into a vessel, in which a 30 g of cation exchange resin (Dowex 50W-X8, #100-200, in H-form) had been placed in advance in order to obtain the initial quantity of ^{226}Ra (C_0). The acidity of another aliquot was adjusted to 0.1 M HCl and the volume of the solution was adjusted to 5 l. After the solution and a 30 g of cation exchange resin were mixed, the mixture was stirred for 15 min. The resin that collected ^{226}Ra was taken out from the solution to measure C_1 in eq. (1). The second collection procedure was applied to the remaining solution after the removal of the resin in the first operation and the resin was taken out to measure C_2 in eq. (2). Each recovered resin was dried and packed into containers for γ-ray measurement and were stored for one month in order that ^{222}Rn attained to be in radioactive equilibrium with ^{226}Ra. Radioactivities of ^{226}Ra and ^{214}Pb in equilibrium with ^{222}Rn were determined by γ-ray spectrometry.

2.5 Gamma-ray spectrometry

Gamma-ray intensities were measured with an HPGe semiconductor detector. The counting efficiency for γ-rays in the present detector was estimated by the efficiency curve constructed by using the relative counting efficiencies for the *plural* γ-rays from a *single* nuclide such as [152]Eu, ^{60}Co and [138]La, together with the normalizing point at the 1,460 keV γ-ray from [40]K in the chemical reagent of KCl. The logarithmic relationship between the relative counting efficiency and the γ-ray energy was made to fit to the quadratic function by the method of least squares and was normalized at 1,460 keV. Radioactivities of [226]Ra, [214]Pb, [214]Bi and [228]Ac were determined respectively by the 186 keV, the 351 keV, the 609 keV and the 911 keV γ-rays.

2.5.1 The use of the 351 keV γ-ray from [214]Pb equilibrated with [226]Ra

Though the 186 keV γ-ray from [226]Ra itself can be used for the determination of [226]Ra, the branching ratio of the 186 keV γ-ray is only 3.6%. On the other hand, as that of the 351 keV γ-ray from [214]Pb is 37.6%, the indirect detection of [226]Ra by the 351 keV γ-ray from [214]Pb in equilibrium with [226]Ra is more effective than the direct use of the 186 keV γ-ray from [226]Ra. If U coexists in the sample water, the 185.7 keV γ-ray from [235]U may interfere the determination of the 186.2 keV γ-ray from [226]Ra, U should be removed before the ion exchange procedure of [226]Ra as described before in [2.4]. In addition, as the correction factors due to absorption and self-absorption of the higher energy γ-rays are smaller, the use of the 351 keV from [214]Pb is preferable for the spectrometry.

2.5.2 Escape of [222]Rn from the sample container

Measurement of [214]Pb and [214]Bi for [226]Ra was made to confirm whether [222]Rn is completely in a radioactive equilibrium with [226]Ra in the container.

Ion exchange resins by which [226]Ra was collected were packed into containers made of 3 different materials : polypropylene, glass and steel.

The establishment of the equilibrium of [222]Rn with [226]Ra in the sample container is checked by the activity ratio of [214]Pb to [226]Ra and [214]Bi to [226]Ra. The measured activity ratios for 3 different containers are given in Table 1.

(1) Container of polypropylene (65 mmϕ, 15 mmH) : The activity ratio has showed to be about 0.75, indicating that one fourth of the equilibrated [222]Rn escapes through the material (polypropylene) of the container wall of 1.0 mm thick.

Table 1   Concentrations of [226]Ra, [214]Pb and [214]Bi (in cps), and activity ratios of [214]Bi and [214]Pb to [226]Ra

Container	[226]Ra (186keV)	[214]Pb (351keV)	[214]Bi (609keV)	[214]Pb/[226]Ra	[214]Bi/[226]Ra
Polypropylene	1.22±0.33	—	0.89±0.04	—	0.73±0.20
	2.12±0.33	—	1.63±0.33	—	0.77±0.12
Glass culture dish	1.39±0.12	—	0.52±0.02	—	0.37±0.04
	0.79±0.10	—	0.06±0.01	—	0.08±0.02
Steel (Tin can)	0.89±0.31	0.98±0.05	0.88±0.05	1.10±0.39	0.99±0.35
	5.21±0.54	5.00±0.10	4.38±0.10	0.96±0.10	0.84±0.09
	3.60±0.53	3.03±0.08	2.72±0.09	0.84±0.13	0.76±0.11
	0.87±0.29	1.00±0.05	0.93±0.05	1.15±0.39	1.07±0.36

(2) Container of glass (70 mmϕ, 16 mmH) : This container is a pair of glass culture dish having the wall of 2.0 mm thick and it was sealed with silicone. Different and small activity ratios are observed. Major part of the ^{222}Rn formed from ^{226}Ra can easily escape through the possible cavity between the wall and the sealing material or through the sealing material itself.

(3) Container of steel (60 mmϕ, 10 mmH) : This container is a tin can having a thin wall of 0.25 mm thick. The activity ratios indicate that ^{222}Rn exists in radioactive equilibrium with ^{226}Ra. As this type of can is available commercially, the use of tin cans is useful for the routine measurement.

3.　Results and discussion

3.1　Ra concentrations of some hot-spring waters

Eleven hot-spring water samples from Tamagawa, Masutomi, Sarugajo, Arima, Onogawa, Misasa and Hijiori hot-springs were used for the experiment. Radium was separated by Method (1) in [2.1] for the hot-spring waters of 5–10 l and by Method (3) for the well water of 50 l. Results are given in Table 2. Concentration of the well water in Table 2 was deduced from the 609 keV γ-ray from ^{214}Bi, because the 351 keV γ-ray from ^{214}Pb was not determined due to the larger Compton background than the 609 keV from ^{214}Bi. While C_1 in eq. (1) was obtained for all of the sample, C_2 was not always obtained, because the collection efficiency is so large that C_2 was not detected. In this case, α was assumed to be unity in the estimation of the concentration. Different collection efficiencies (α) were observed for different water sources which may due to the different properties of respective sample waters. The concentrations of ^{226}Ra deduced from the 186 keV spectral line were observed significantly larger than those of ^{214}Pb, because the 186 keV spectral line was possibly overlapped with the 186 keV

Table 2　Concentrations of ^{226}Ra and ^{228}Ra in several hot-spring waters and one well water (in mBq/l). Activity ratios of ^{228}Ra/^{226}Ra are given for some of hot-spring waters

Sample water	^{226}Ra (^{214}Pb)	^{228}Ra (^{228}Ac)	α	^{226}Ra reported	^{228}Ra/^{226}Ra
Tamagawa	60±8	1120±110	0.89±0.06	55–270 (Yokoyama, 1955)	18±3
Masutomi 1	9±2	—	—	160–300 (Horiuchi and	—
Masutomi 2	46±5	56±10	0.90±0.02	Murakami, 1978)	1.2±0.3
Masutomi 3	980±80	2140±130	0.27±0.03	37±5 (Yamamoto *et al.*, 1994)	2.2±0.2
Sarugajo	38±3	—	—	6–110 (Sato *et al.*, 1975)	—
Arima 1	186±13	64±26	0.58±0.03	37–7750 (Yokoyama, 1955 ;	0.34±0.14
Arima 2	63±9	46±13	0.46±0.06	Ikeda, 1955)	0.73±0.23
Onogawa 1	322±33	495±60	0.32±0.03		1.5±0.2
Onogawa 2	257±14	533±40	0.59±0.03		2.1±0.2
Misasa	50±2	106±5	—	37–550 (Yokoyama, 1955)	2.1±0.1
Hijiori	12±2	30±3	—		2.5±0.5
Well water (*)	0.64±0.15	—	—		—

(*) Well water from Meiji University, Kawasaki

Table 3　Ra concentrations obtained in different experimental conditions

	Volume (l)	Resin (mesh)	^{226}Ra (^{214}Pb)	^{228}Ra (^{228}Ac)	α (^{214}Pb)
Masutomi 3-1	10	20-50	980±80	2410±130	0.27±0.03
Masutomi 3-2	5	100-200	1026±23	2673±63	0.92±0.01
Onogawa 1-1	10	20-50	322±33	495±60	0.32±0.03
Onogawa 1-2	5	100-200	267±8	469±17	0.91±0.02

Table 4　Ra concentrations obtained in the field work and in the laboratory work

	^{226}Ra (^{214}Pb)	^{228}Ra (^{228}Ac)	^{228}Ra/^{226}Ra
Onogawa 2 (lab.)	257±14	507±24	2.0±0.1
Onogawa 2 (field)	257±23	533±40	2.1±0.2
Hijiori (lab.)	10±2	32±3	3.2±0.7
Hijiori (field)	12±2	30±3	2.5±0.5

γ-ray from ^{235}U coexisting in the sample waters. The concentrations of ^{214}Pb and ^{228}Ac represent those of ^{226}Ra and ^{228}Ra, respectively. The concentrations estimated presently are in the same order of magnitude as the reported values. Different activity ratios of ^{228}Ra/^{226}Ra were observed in the variuos water samples from different water source.

Though different collection efficiency (α) was obtained in different combination of the volume for sample water and the mesh-size for collecting resin for the sample of Masutomi 3 and Onogawa 1 as shown in Table 3, the two estimated Ra concentrations agreed well with each other, indicating that the present estimation method is effective even when different collection efficiency is obtained for any experimental condition of isolation.

3.2　Application to field works

The Ra concentrations estimated in an *in-situ* separation were compared with those determined by the separation method carried out in the labortory for the same water samples transported. The Method (3) described in [2.1] was applied to 50 l water samples from Onogawa and Hijiori hot-springs. The good agreement between two data (lab. and field) shown in Table 4 suggests that the present field work analytical method is applicable enough.

Acknowledgements

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