PERGAMON

Applied Radiation and Isotopes 55 (2001) 221–227

Applied Radiation and Isotopes

www.elsevier.com/locate/apradiso

A convenient method for discriminating between natural and depleted uranium by γ-ray spectrometry

Miki Shoji[a,*], Yasunori Hamajima[b], Kiyofumi Takatsuka[c], Hiroshi Honoki[a], Tomoko Nakajima[a], Takashi Kondo[d], Takashi Nakanishi[b]

[a] *Radioisotope Research Center, Toyama Medical and Pharmaceutical University, 2630 Sugitani, Toyama 930-0194, Japan*
[b] *Department of Chemistry, Faculty of Science, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan*
[c] *Radioisotope Laboratory, Toyama University, 3190 Gofuku, Toyama 930-8555, Japan*
[d] *Department of Radiological Sciences, Faculty of Medicine, Toyama Medical and Pharmaceutical University, 2630 Sugitani Toyama 930-0194, Japan*

Received 17 January 2000; received in revised form 19 October 2000; accepted 30 November 2000

Abstract

A convenient method for discriminating between natural and depleted uranium reagent was developed by measuring and analyzing the γ-ray spectra of some reagents with no standard source. The counting rates (R) of photoelectric peaks of γ-rays from nuclides with the same radioactivity divided by their emission probability (B) are expressed as a function of γ-ray energy. The radioactivities of ^{234}Th and ^{234m}Pa and 21.72 times that of ^{235}U are equal to the radioactivity of ^{238}U in natural uranium. Therefore, the plot of 21.72-fold R/B for ^{235}U should be on a curve fitted to the points for ^{234}Th and ^{234m}Pa in natural uranium. Depleted uranium with a ^{235}U isotopic composition of less than 0.68% could be discriminated from natural uranium in the case of a reagent containing 4.0 g of uranium.

Keywords: Discrimination; Natural uranium; Depleted uranium; Uranium mineral; γ-ray spectrometry; Radioactive equilibrium; Bateman solution

1. Introduction

Natural uranium is defined as uranium-containing materials in which the isotopic composition of ^{235}U in uranium atoms is equal to that of the natural isotopic abundance (0.72%). Depleted uranium is uranium in which the isotopic composition of ^{235}U is below 0.72%. Discrimination between natural and depleted uranium is important for the proper management of nuclear fuel materials. One way to achieve this is a comparison of the γ-ray spectrum of an unknown sample with that of a natural uranium sample. This method needs a reference uranium standard that should be authenticated to be of natural isotopic composition. It should also be of reagent grade because natural uranium minerals are not suitable for the purpose. The natural uranium minerals contain ^{226}Ra and its daughter nuclides in the ^{238}U decay chain and ^{231}Pa and its daughter nuclides in the ^{235}U decay chain. The γ-rays from ^{226}Ra (186.10 keV) in the ^{238}U decay chain obstruct those from ^{235}U (185.72 keV) (Firestone and Shirley, 1996) in the case of uranium minerals. Another disadvantage of the method is that the influence of absorption of γ-rays by samples themselves and their containers should be corrected because the samples and their containers are of different shapes and materials.

In this report, we present a method for discriminating between natural and depleted uranium of reagent grade by measuring and analyzing the γ-ray spectrum of the sample without any standard reference sources. The

*Corresponding author. Tel.: +81-76-434-7191, fax: +81-76-434-5004.
E-mail address: shojim@ms.toyama-mpu.ac.jp (M. Shoji).

0969-8043/01/$ - see front matter
PII: S0969-8043(00)00391-2

method is based on the principle that the counting efficiency of photoelectric peaks of γ-rays can be expressed as a function of γ-ray energy under specified measuring conditions.

2. Experimental

2.1. The basis of the procedure

The counting rate (R) of a photoelectric peak in a γ-ray spectrum is related to the disintegration rate (A) of a nuclide by the equation

$$R = ABE_S GE_D, \quad (1)$$

where B is the number of γ-ray photons emitted at a disintegration of the nuclide (emission probability), E_S the efficiency of γ-rays passing through the source and container, G the geometrical efficiency of the measuring system, and E_D the efficiency of a detector detecting γ-rays as a photoelectric peak (Gilmore and Hemingway, 1995). Eq. (1) can be transformed as follows:

$$R/B = AE_S GE_D. \quad (2)$$

For multiple kinds of γ-rays emitted from a nuclide in a sample, A and G are common and constant, and E_S and E_D are expressed as functions of γ-ray energy. Therefore, R/B is expressed as a function of γ-ray energy, and the plot of the R/B values against the γ-ray energy should be a smooth curve.

When the disintegration rate of nuclide N_l ($l = 1, 2, 3, \ldots$) contained in a sample is A_l, the γ-rays emitted from nuclide N_l are γ_{lm} ($m = 1, 2, 3, \ldots$), and the counting rate and emission probability of γ_{lm} are R_{lm} and B_{lm}, Eq. (2) is modified for γ_{lm} as

$$\frac{R_{lm}/B_{lm}}{A_l} = E_S GE_D. \quad (3)$$

When the ratio of $A_1, A_2, \ldots, A_l, \ldots$ is $a_1 : a_2 : \cdots : a_l : \cdots$, Eq. (3) is transformed to

$$\frac{R_{lm}/B_{lm}}{a_l} = kE_S GE_D, \quad (4)$$

where k is a constant value.

If the quantitative relationship among disintegration rates of nuclides in a sample ($a_1 : a_2 : \cdots : a_l : \cdots$) is known, the corrected R/B values according to the relationship $((R_{lm}/B_{lm})/a_l)$ for these nuclides are expressed as a function of γ-ray energy, and can be plotted on the same curve. In cases in which the corrected R/B values for a sample cannot be plotted on the same curve, the quantitative relationship among nuclides does not hold for the sample.

2.2. Quantitative relationships among nuclides contained in natural uranium

This procedure was applied to uranium samples of reagent grade. Uranium was discovered in 1789 by Klaproth, and it can be considered that uranium reagent has been manufactured from uranium minerals at least since that time. Radionuclides contained in uranium reagent just after manufacture are thought to be ^{238}U, ^{235}U and ^{234}U. The natural isotopic abundances for ^{238}U, ^{235}U and ^{234}U are 99.2745, 0.7200 and 0.0055%, respectively (Firestone and Shirley, 1996), and the ratio of the radioactivities of these nuclides calculated from their isotopic abundances and half-lives is 21.72 : 1 : 21.90 in that case.

Listed in Table 1 are radionuclides produced from ^{238}U, ^{235}U and ^{234}U and their radioactivities at 211 years after manufacture of uranium reagent, as calculated from their half-lives (Firestone and Shirley, 1996) and the Bateman solution, which gives the number of atoms of any daughter nuclides in successive decays starting with the pure first parent nuclide in the decay chain (Chase and Rabinowitz, 1962).

In the ^{238}U decay chain, ^{234}Th, ^{234m}Pa and ^{234}Pa are in secular equilibrium with ^{238}U in 1 year and the radioactivities of ^{238}U, ^{234}Th and ^{234m}Pa are equal. The decay ratio from ^{234m}Pa to ^{234}Pa is 0.13%, and the radioactivity of ^{234}Pa is 1.3×10^{-3} times that of ^{238}U. The radioactivity of ^{234}U produced from ^{238}U is 6.0×10^{-4} times that of ^{238}U after 211 years, and the radioactivity of ^{230}Th and its daughter nuclides is negligible.

In the ^{235}U decay chain, ^{231}Th is in secular equilibrium with ^{235}U in 2 weeks and the radioactivities of the two nuclides are equal. The radioactivity of ^{231}Pa is 4.5×10^{-3} times that of ^{235}U after 211 years, which corresponds to 2×10^{-4} times that of ^{238}U in the case of natural uranium. The radioactivity of ^{227}Ac and its daughter nuclides is less than 4×10^{-3} times that of ^{235}U (2×10^{-4} times that of ^{238}U in the case of natural uranium).

The radioactivities produced from ^{234}U at 211 years after manufacture are 1.9×10^{-3} for ^{230}Th and 8.6×10^{-5} for ^{226}Ra compared to that for ^{234}U. When the period of time after manufacture is shorter than 211 years, the radioactivities of nuclides produced from parent nuclides do not exceed the values listed in Table 1.

Therefore, the radionuclides contained in uranium reagent are considered to be ^{238}U, ^{234}Th, ^{234m}Pa, ^{234}Pa, ^{235}U, ^{231}Th, ^{234}U and ^{230}Th. Among these nuclides, ^{234}Th and ^{234m}Pa are in secular equilibrium with ^{238}U, and the disintegration rates of these three nuclides are equal for uranium reagent manufactured more than 1 year ago. The ratio of disintegration rates of ^{235}U/^{238}U is 1/21.72 in natural uranium. Accordingly, the ratio of disintegration rates of ^{234}Th, ^{234m}Pa and ^{235}U is 1 : 1 : 1/21.72 in natural uranium.

Table 1
Half-lives and radioactivity of daughter nuclides produced from ^{238}U, ^{235}U and ^{234}U at 211 years after manufacture from uranium mineral calculated using Bateman solution

Parent nuclide	Daughter nuclide	Half-life	Radioactivity
^{238}U		4.468×10^9 yr	1.0
	^{234}Th	24.10 days	1.0
	^{234m}Pa	1.17 min	1.0
	^{234}Pa	6.70 h	1.3×10^{-3}
	^{234}U	2.455×10^5 yr	6.0×10^{-4}
	^{230}Th	7.538×10^4 yr	5.8×10^{-7}
	^{226}Ra	1.6×10^3 yr	1.7×10^{-8}
	^{222}Rn	3.8235 days	1.7×10^{-8}
	^{218}Po	3.10 min	1.7×10^{-8}
	^{214}Pb	26.8 min	1.7×10^{-8}
	^{214}Bi	19.9 min	1.7×10^{-8}
	^{214}Po	164.3 μs	1.7×10^{-8}
	^{210}Pb	22.3 yr	1.1×10^{-8}
	^{210}Bi	5.013 days	1.1×10^{-8}
	^{210}Po	138.376 days	1.1×10^{-8}
^{235}U		7.038×10^8 yr	1.0
	^{231}Th	25.52 h	1.0
	^{231}Pa	3.276×10^4 yr	4.5×10^{-3}
	^{227}Ac	21.773 yr	3.8×10^{-3}
	^{227}Th	18.72 days	3.8×10^{-3}
	^{223}Ra	11.435 days	3.8×10^{-3}
	^{219}Rn	3.96 s	3.8×10^{-3}
	^{215}Po	1.781 ms	3.8×10^{-3}
	^{211}Pb	36.1 min	3.8×10^{-3}
	^{211}Bi	2.14 min	3.8×10^{-3}
	^{207}Tl	4.77 min	3.8×10^{-3}
^{234}U		2.455×10^5 yr	1.0
	^{230}Th	7.538×10^4 yr	1.9×10^{-3}
	^{226}Ra	1.6×10^3 yr	8.6×10^{-5}
	^{222}Rn	3.8235 days	8.6×10^{-5}
	^{218}Po	3.10 min	8.6×10^{-5}
	^{214}Pb	26.8 min	8.6×10^{-5}
	^{214}Bi	19.9 min	8.6×10^{-5}
	^{214}Po	164.3 μs	8.6×10^{-5}
	^{210}Pb	22.3 yr	6.4×10^{-5}
	^{210}Bi	5.013 days	6.4×10^{-5}
	^{210}Po	138.376 days	6.4×10^{-5}

2.3. Data analysis

When the "a" value for ^{234}Th and ^{234m}Pa in Eq. (4) is one, the "a"value for ^{235}U is 1/21.72 in natural uranium. The plot of R/B values for ^{234}Th and ^{234m}Pa and 21.72 times the R/B values for ^{235}U against γ-ray energy should lie on the same curve in natural uranium. In the case of depleted uranium, the ratio of the disintegration rate of $^{235}U/^{238}U$ is smaller than 1/21.72, and the plot of 21.72 times the R/B values for ^{235}U should be under the curve drawn for ^{234}Th and ^{234m}Pa.

The energy and emission probability of γ-rays utilized in this analysis and of those overlapping with them are shown in Table 2 (Firestone and Shirley, 1996). It is considered that the overlapping γ-rays listed in Table 2 do not practically affect the counting rates of photoelectric peaks of γ-rays utilized in this analysis, because the product of the radioactivity of nuclides emitting them (Table 1) and their emission probability (Table 2) is fairly small.

The 21.72-fold R/B values derived from ^{235}U γ-rays and R/B values derived from ^{234}Th and ^{234m}Pa γ-rays were plotted on the vertical axis against γ-ray energy on the horizontal axis with a logarithmic scale for both. Because the photoelectric peaks of γ-rays of 92.38 and 92.80 keV from ^{234}Th were not separated from each other, each B value was summed up and the resulting R/B value was plotted in the position of average energy. For the photoelectric peaks of 202.12 and 205.31 keV γ-rays from ^{235}U, the R/B value was calculated in the same

Table 2
γ-Rays utilized in discrimination analysis and overlapping γ-rays emitted from nuclides contained in uranium reagents

	Utilized γ-ray		Overlapping γ-ray					
Nuclide	Energy (keV) and emission probability (%)		Nuclide, energy (keV) and emission probability (%)					
^{234}Th	63.29	(4.84)	^{234m}Pa	62.70	(1.2×10^{-3})	^{234}Pa	62.70	(1.5)
	92.38	(2.81)	^{231}Th	63.86	(0.023)	^{235}U	64.37	(0.01)
	92.80	(2.77)	^{231}Th	93.02	(0.045)			
^{235}U	143.76	(10.96)	^{230}Th	143.87	(0.0488)	^{234}Pa	143.78	(0.32)
	163.33	(5.08)	^{231}Th	163.10	(0.155)	^{234}Pa	164.94	(0.054)
	185.72	(57.2)	^{231}Th	183.5	(0.0329)	^{234m}Pa	184.7	(1.7×10^{-3})
	202.11	(1.08)	^{230}Th	186.05	(8.8×10^{-3})	^{234}Pa	186.15	(1.76)
	205.31	(5.01)	^{231}Th	188.76	(3.2×10^{-3})			
			^{234m}Pa	203.12	(1.02×10^{-3})	^{234}Pa	203.12	(1.23)
			^{230}Th	205.1	(5.2×10^{-6})			
^{234m}Pa	258.26	(0.0728)	^{234}Pa	257.2	(0.05)			
	766.36	(0.294)	^{234}Pa	766.4	(0.07)			
	1001.03	(0.837)						

way. A smooth curve should be drawn which is fitted to the points plotted for γ-rays from ^{234}Th and ^{234m}Pa. The function of the curve was approximated to polynomials in $\ln(R/B)$ against $\ln(E_\gamma)$ as follows:

$$\ln(R/B) = c_0 + c_1\ln(E_\gamma) + c_2\{\ln(E_\gamma)\}^2 + \cdots + c_n\{\ln(E_\gamma)\}^n,$$

where E_γ is the γ-ray energy and $c_0, c_1, c_2,$ etc., are coefficients determined by the least-squares method. The curve was fitted to the points separately above and below its knee in practice, using a quadratic function below the knee and a linear function above the knee in a way that ensured that the two curves met reasonably convincingly.

The R/B value in the position of 185.72 keV (equal to the energy of γ-rays from ^{235}U) on the curve was defined as R/B(N), which corresponds to the 21.72-fold R/B value for 185.72 keV γ-rays from ^{235}U in natural uranium. The 21.72-fold R/B value derived from 185.72 keV γ-rays from ^{235}U obtained by measurement of the sample was defined as $R/B(\mathrm{S})\pm s$ (s is $21.72\sigma/B$, where σ is a unit standard deviation of R of 185.72 keV γ-rays from ^{235}U in the sample). If the value of R/B(N) is between $(R/B(\mathrm{S})-s)$ and $(R/B(\mathrm{S})+s)$, the sample should be natural uranium. If the value of R/B(N) is more than the value of $(R/B(\mathrm{S})+s)$, the sample should be depleted uranium. The isotopic composition of ^{235}U can also be estimated from the value of $R/B(\mathrm{S})/R/B(\mathrm{N})$.

2.4. γ-Ray spectrometry of uranium samples

The γ-ray spectra of uranium samples were acquired in their containers using an n-type closed-end coaxial high-purity germanium detector with a beryllium end cap and a 0.3-μm-ion-implanted layer (EG & G Ortec, GMX-23195, Oak Ridge, TN) equipped with a 4096 channel multichannel analyzer (Seiko EG & G, MCA 7700, Matsudo, Japan). The detector was 55.0 mm in diameter and 56.3 mm in length. The γ-ray spectra were acquired and analyzed using MCA emulating and γ-ray analyzing software DS-P200/W32 (Gamma Studio, Seiko EG & G). Samples were placed at 10 cm from the detector end cap to minimize true coincidence summing (Gilmore and Hemingway, 1995). The detector was shielded with 100 mm thickness of lead with a steel frame and an internal graded shield consisting of 2 mm thickness of cadmium, 20 mm thickness of copper and 5 mm thickness of acrylate resins. The interior dimensions of the shield were 300 mm depth × 300 mm width × 670 mm height.

3. Results and discussion

γ-Rays emitted from ^{234}Th, ^{234m}Pa and ^{235}U as listed in Table 2 were utilized in this analysis. γ-Rays from ^{238}U (49.6 keV) were not used because of the small emission probability (7.5×10^{-4}) and severe self-absorption (Firestone and Shirley, 1996). The photoelectric peaks of γ-rays listed in the left-hand side of Table 2 do not overlap with those of principal γ-rays from other radionuclides in the sample. γ-Rays which might affect the counting rates of photoelectric peaks of γ-rays utilized in this analysis are listed on the right-hand side of Table 2. However, they do not practically affect the counting rates of photoelectric peaks of ^{234}Th, ^{234m}Pa and ^{235}U γ-rays considering that the product of the radioactivity of nuclides emitting them (Table 1) and their emission probability (Table 2) are relatively small compared to those of aimed γ-rays. The γ-rays most affecting the aimed γ-rays are the 163.10 keV γ-rays from

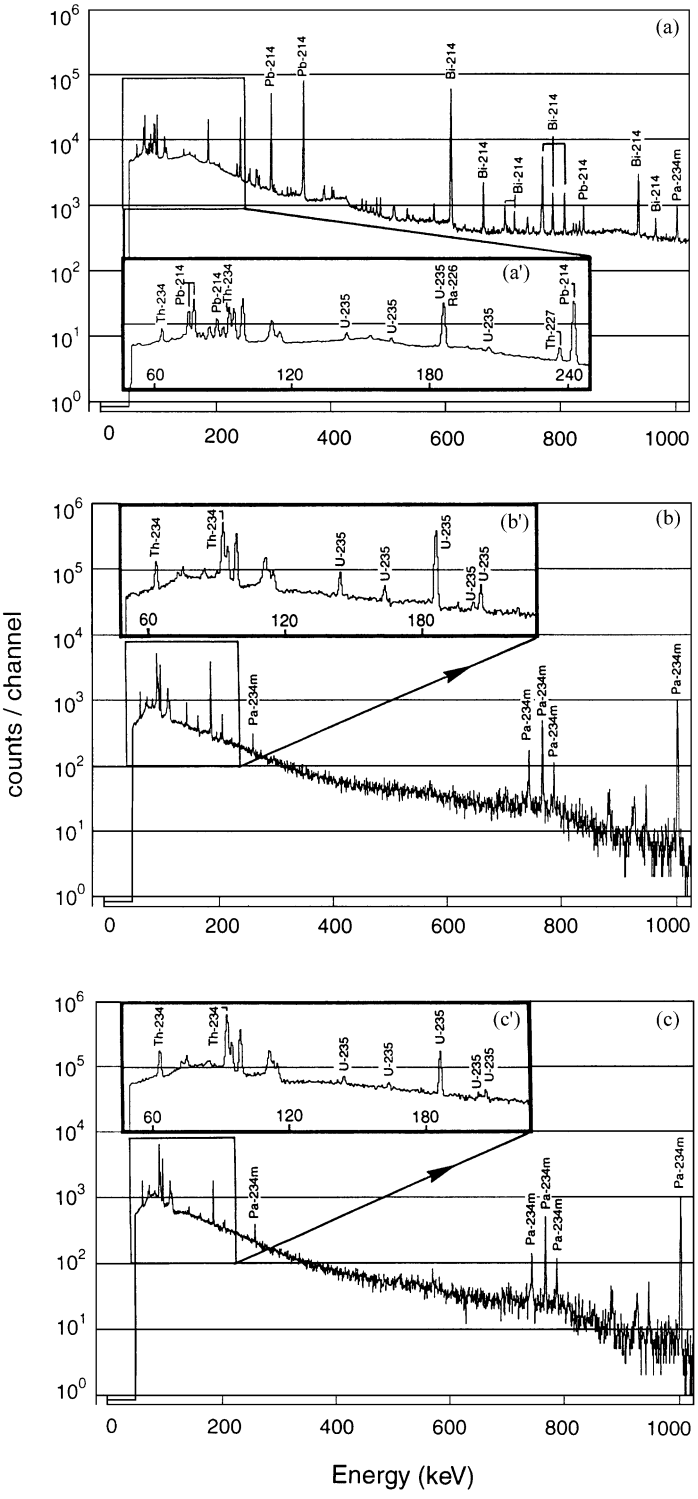

Fig. 1. γ-Ray spectra of natural and depleted uranium samples: (a) and (a′), natural uranium mineral; (b) and (b′), natural uranium reagent; (c) and (c′), depleted uranium reagent. Measurement conditions are described in the text.

^{231}Th, for which the counting rate of the photoelectric peak corresponds to about 3% of that of 163.33 keV γ-rays from ^{235}U. Photoelectric peaks of X-rays appear in the spectra. The photoelectric peaks of X-rays were not used in this analysis because they contain fluorescent X-rays emitted from uranium atoms excited by α-rays and β-rays (Early et al., 1975).

The γ-ray spectra obtained from uranium minerals and uranium reagent that were confirmed to be natural or depleted based on their label and history are shown in Fig. 1. Photoelectric peaks of γ-rays emitted from ^{235}U and ^{226}Ra overlapped at 186 keV, and many photoelectric peaks of γ-rays from ^{227}Th, ^{214}Pb and ^{214}Bi were observed in the spectrum of the uranium mineral (Fig. 1(a) and (a′)). The photoelectric peak of 351.92 keV γ-rays from ^{214}Pb (emission probability, 0.358) and that of 609.31 keV γ-rays from ^{214}Bi (emission probability, 0.448) were not detected when the reagent containing 4.0 g of uranium was measured in a glass bottle at 10 cm from the detector for 18,000 s. It is suggested that the photoelectric peak of 186.10 keV γ-rays from ^{226}Ra (emission probability, 0.0350) which is equilibrated with ^{214}Pb and ^{214}Bi (Table 1) does not interfere with the photoelectric peak of 185.72 keV γ-rays from ^{235}U. The ratios of photoelectric peaks of γ-rays from ^{235}U to those of γ-rays from ^{234}Th and ^{234m}Pa in depleted uranium reagent were relatively smaller than those in natural uranium reagent (Fig. 1(b), (b′), (c) and (c′)).

Samples were measured at 10 cm from the detector end cap to minimize true coincidence summing. When a sample containing 4.0 g of uranium was measured at 10 cm from the detector (live time, 18,000 s; dead time, 0.77%), no peaks were detected upon summing two kinds of γ-rays from the same nuclide listed on the left-hand side of Table 2. On the other hand, when the same sample was measured on top of the detector (live time, 1800 s; dead time, 7.6%), a sum peak, of which the counting rate corresponded to about 2% of each peak, was detected in the position of the sum of 163.33 and 205.31 keV γ-rays from ^{235}U (data not shown).

A curve for a uranium reagent that was confirmed to be natural based on its label and history is shown in Fig. 2. Points for γ-rays from ^{234}Th, ^{235}U and ^{234m}Pa were plotted on the same smooth curve. An example of a curve for a sample determined to be depleted is shown in Fig. 3, and points for γ-rays from ^{235}U were under the curve fitted to the points for ^{234}Th and ^{234m}Pa.

The discrimination limit of this analysis was calculated in the following way: (1) $R/B(\mathrm{N})_\mathrm{u}$ denotes the R/B value in the position of 185.72 keV calculated from the equation of the curve fitted to the plot of $(R+\sigma)/B$ (σ is a unit standard deviation of R) for ^{234}Th and ^{234m}Pa against γ-ray energy; (2) $R/B(\mathrm{N})_\mathrm{l}$ denotes the R/B value in the position of 185.72 keV calculated from the equation of the curve fitted to the plot of $(R-\sigma)/B$ for ^{234}Th and ^{234m}Pa; (3) $R/B(\mathrm{N})_\mathrm{u}$ was regarded as the upper limit of the 21.72-fold R/B value for 185.72 keV γ-rays from ^{235}U in case of natural uranium (^{235}U isotopic composition of 0.72%); (4) a uranium reagent could be demonstrated to be depleted when its $(R/B(\mathrm{S})+s)$ value was below $R/B(\mathrm{N})_1$. In the above manner, depleted

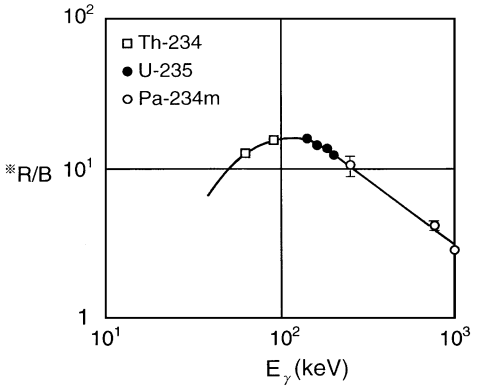

Fig. 2. A curve for a uranium sample of reagent grade confirmed to be natural. R/B value means counting rate (R) of a photoelectric peak of γ-rays divided by its emission probability (B). R/B values for ^{235}U were derived from 21.72-fold counting rates of photoelectric peaks. The knee of the curve was at 180 keV. Equations describing the curve were $\ln(R/B) = -17.9098 + 8.7758\ln(E_\gamma) - 0.92915\{\ln(E_\gamma)\}^2$ below the knee, and $\ln(R/B) = 7.1462 - 0.87419\ln(E_\gamma)$ above the knee. E_γ is γ-ray energy (keV).

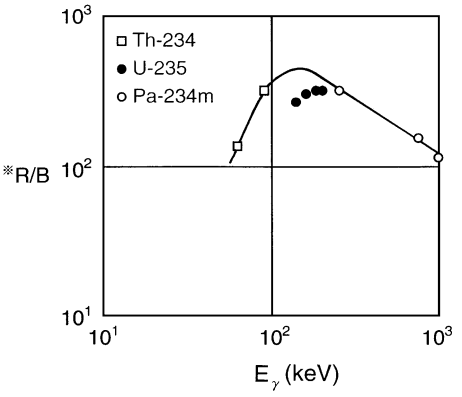

Fig. 3. A curve for a uranium sample of reagent grade determined to be depleted. R/B value means counting rate (R) of a photoelectric peak of γ-rays divided by its emission probability (B). R/B values for ^{235}U were derived from 21.72-fold counting rates of photoelectric peaks. The knee of the curve was at 180 keV. Equations describing the curve were $\ln(R/B) = -37.2734 + 17.4178\ln(E_\gamma) - 1.7482\{\ln(E_\gamma)\}^2$ below the knee, and $\ln(R/B) = 9.8709 - 0.73924\ln(E_\gamma)$ above the knee. E_γ is γ-ray energy (keV).

uranium reagent with less than 0.68% of ^{235}U isotopic composition could be discriminated from natural uranium in the case of a reagent containing 4.0 g of uranium with 18,000 s measuring time.

Three among 16 samples of uranium of reagent grade were determined to be natural in our laboratory. Using this method, depleted uranium of which the isotopic composition is close to that of natural uranium may be identified as natural. However, this method appears to be a useful and a convenient method for discriminating between natural and depleted uranium of reagent grade.

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