

DETERMINATION OF TRANSURANIUM ELEMENTS IN A SO-CALLED "BIKINI ASH" SAMPLE AND IN MARINE SEDIMENT SAMPLES COLLECTED NEAR BIKINI ATOLL

SHUN'ICHI HISAMATSU

School of Medicine, Akita University, Hondo 1-1-1 Akita 010

and

MASANOBU SAKANOUÉ

Faculty of Science, Kanazawa University, Marunouchi 1-1, Kanazawa 920, Japan

(Received 3 May 1977; accepted 9 December 1977)

Abstract—The concentrations of $^{239+240}\text{Pu}$ and ^{241}Am in the debris from the second thermonuclear test detonation of the USA (Bravo) were determined. This debris, called "Bikini Ash", was collected in 1954 on the deck of the Japanese fisherboat "5th Fukuryu-Maru" which was located some 150 km to the east of Bikini Atoll at the time of the thermonuclear test. A portion of the 1954 sample was subjected to analytical analysis in 1974. Accordingly, the concentrations of $^{239+240}\text{Pu}$ and ^{241}Am in the sample were determined to be 25.9 ± 1.7 and 12.9 ± 0.9 dis/min/mg, respectively. From these values, the ratio of $^{241}\text{Pu}/^{239+240}\text{Pu}$ at time zero was calculated to be 26 ± 3 , and this ratio was almost the same as the "Mike" thermonuclear debris. Furthermore, $^{239+240}\text{Pu}$ and ^{241}Am contents of the marine sediment samples collected near Bikini Atoll were also analyzed, and it was found that a significant contamination with these nuclides was found to be still remaining in this area.

INTRODUCTION

ON 1 MARCH 1954, the second thermonuclear test of the USA was carried out at Bikini Atoll (Bravo). The Japanese fisherboat "5th Fukuryu-Maru" was exposed to the nuclear debris from this test. The highly radioactive debris collected on the boat, called "Bikini Ash" in Japan, has become an urgent subject of many investigators (JA54). It was found that this debris was coral reef having a composition of CaO 55.2%, MgO 7.0% and CO₂ 11.8% and contaminated with a large amount of fission products and induced radioactive nuclides, such as ^{237}U . The "Bikini Ash" has been subjected to only a few studies on transuranium elements, although the presence of ^{239}Pu was supposed from one track on nuclear emulsion exposed for many days to a radiochemically separated fraction. In this present study, the objective

was to determine the $^{239+240}\text{Pu}$ and ^{241}Am contents of both the "Bikini Ash" sample and several marine sediment samples collected near Bikini Atoll, as accurately as possible by radiochemical techniques. Just recently, the 59.6 keV gamma ray from ^{241}Am in the "Bikini Ash" has been detected by gamma ray spectrometry with a Ge(Li) detector (OK74). These transuranium elements in the debris might be produced, as shown in Fig. 1a, by the rapid, successive neutron capture of ^{238}U exposed to the unusually high neutron flux generated by the thermonuclear explosion and the following beta-decays. In Fig. 1a, the nuclear reaction sequences for the production of heavy nuclides in a reactor are also shown by the broken line. The radiochemical studies (Di60) made soon after the first thermonuclear explosion test ("Mike") revealed the relative abundance and

the alpha-activity ratio of these nuclides in the debris, as shown in Fig. 1b. For mass number 241, the calculated activity of ^{241}Am is shown as a daughter nuclide of ^{241}Pu . Furthermore, the values on the upper abscissa show the weight of a sample required to detect 1 dis/min of other nuclides in the sample which contains 10 dis/min/mg of ^{239}Pu .

MATERIALS

A 6-mg sample of "Bikini Ash" was obtained from the 70-mg sample stored in the Institute of Physical and Chemical Research, Japan. In this present study, made in 1974~1975, 2 mg of the sample was submitted for analysis of $^{239+240}\text{Pu}$ and ^{241}Am , and 4 mg of the sample was used for low energy photon spectroscopy. It was found by its spectrum, shown in Fig. 2, that $^{239+240}\text{Pu}$, ^{241}Am , ^{155}Eu , ^{137}Cs and ^{125}Sb were contained in this sample.

The position where the "5th Fukuryu-Maru" was exposed to this explosion debris in 1954 is plotted in Fig. 3. Marine sediment samples analyzed in this study were collected in 1973 by a marine research vessel, the "Tokai II" of Tokai University. Accurate latitudes and longitudes of these locations are given in Table 1 together with water depths, topographies of sea bottom, and the characteristics of the sediments. All sediment samples were collected with a dredger. The samples are identified as 73105, 73108, 73109 and 73113 as shown in Table 1. One gram of each sample was dried at 110°C and used for plutonium and americium analyses. Sample No. 73113 contained manganese nodules, which were removed before analysis.

METHODS

An aliquot of ^{236}Pu and ^{148}Gd solution was added to the samples as yield tracers for

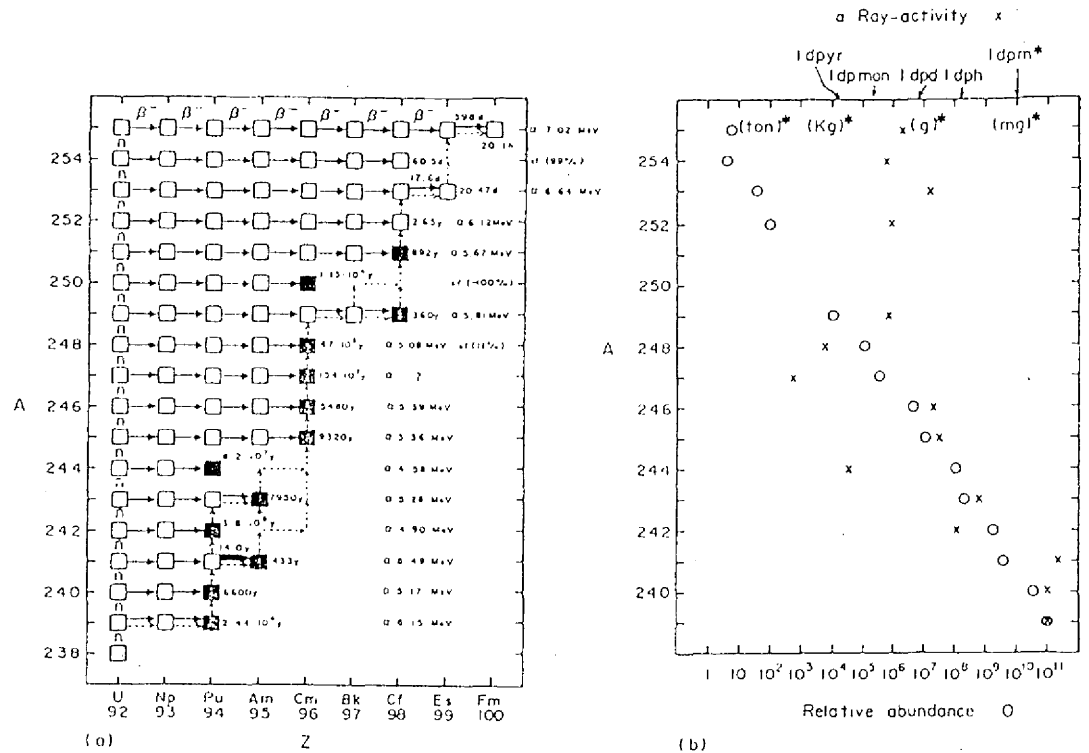


FIG. 1a. Nuclear reaction sequences for the production of heavy nuclides by thermonuclear explosion. b. Relative abundance and alpha-activity ratio of heavy nuclides in the immediate debris of the "Mike".

19773

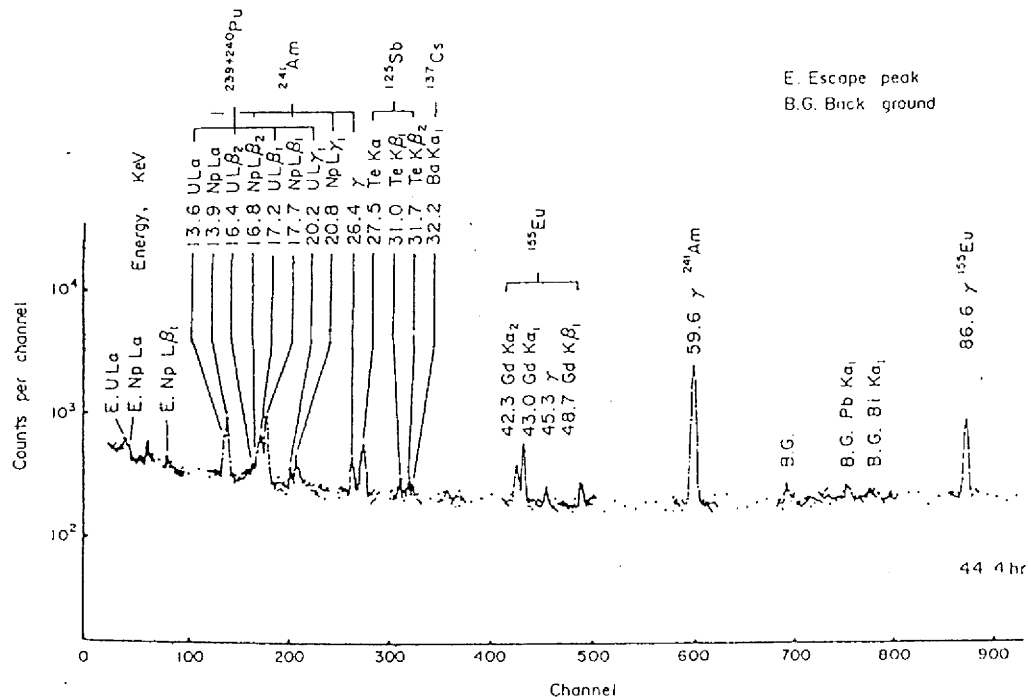


FIG. 2. Low-energy gamma- and X-ray spectrum on "Bikini Ash".

plutonium isotopes and ^{241}Am , respectively. One of these tracers, ^{148}Gd , a 3.18-MeV alpha-emitter, was prepared by the reaction of $^{151}\text{Eu}(p, 4n)^{148}\text{Gd}$, and it was confirmed that the Gd/Am ratio did not change during the same radiochemical procedure as used in the present work. Details of the carrier-free ^{148}Gd preparation (Ko76) and the usefulness of ^{148}Gd as tracer were previously reported elsewhere (Sa72). The other tracer nuclide, ^{216}Pu , was produced by the reaction of $^{237}\text{Np}(\gamma, n)^{236}\text{Np} \xrightarrow{\beta^-} ^{236}\text{Pu}$ (Is69). The concentration of the ^{216}Pu tracer was calibrated with a standard ^{239}Pu solution supplied from the Radioactivity Centre, Amersham, England.

Each sample was treated with 8 M hot hydrochloric acid. By adding aqueous ammonia to the supernatant, the coprecipitation of plutonium and other elements with hydroxide precipitates (iron hydroxide, etc.) was carried out. When only a little amount of precipitate was obtained, it was spiked with about 5 mg Fe^{3+} carrier. The precipitate was

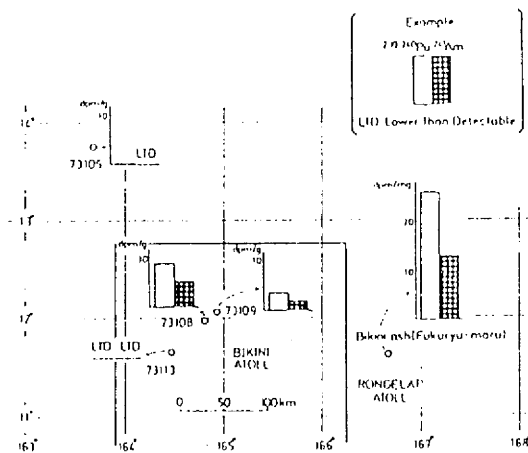


FIG. 3. Analytical results for $^{239+240}\text{Pu}$ and ^{241}Am in "Bikini Ash" and marine sediment samples. The open circles indicate sampling points and the exposure point of the "5th Fukuryu-Maru." The bold line, set by the U.S. Navy, was the boundary of the area prohibited for navigation at the time of the nuclear bomb test in 1954.

Table 1. Sampling Data on marine sediment samples

Sample	Latitude	Longitude	Water depth (m)	Topography of sea bottom	Characteristics of sample
73105	13°43.6'	163°44.3'	2000	The top of Guyot	Globigerina sand
73108	11°56.0'	164°44.8'	1320	The top of Guyot	Globigerina sand
73109	12°02.8'	164°51.7'	1690	The shoulder of Guyot	Globigerina sand
73113	11°39.0'	164°22.6'	4660	Ocean floor	Red clay

then dissolved with hydrochloric acid and the coprecipitation was repeated by adding a sodium hydroxide solution. After removing iron by the solvent extraction with di-isobutylketone, plutonium was extracted with 10% (v/v) tri-*n*-octylamine (TOA) xylene solution from 8 M nitric acid solution. The organic phase was washed successively with 8 M nitric acid to remove the uranium, and with 10 M hydrochloric acid to remove the thorium. Plutonium was stripped with 6 M hydrochloric acid containing 0.2 M hydrofluoric acid (Sa71).

The aqueous phase of the TOA extraction, containing americium and gadolinium, was evaporated to dryness. The americium was then extracted, together with ^{148}Gd , into 50% (v/v) di(2-ethylhexyl) phosphoric acid (HDEHP) toluene solution from the hydrochloric acid solution adjusted to pH 1.2, and stripped with 8 M hydrochloric acid.

For alpha spectrometry, americium and plutonium fractions were subjected, respectively, to electrodeposition on 18-8 stainless steel disks having diameters of 2.7 cm. The electrolytic solution containing 0.5 ml of 0.1 M hydrochloric acid, 0.5 ml of 0.5 M oxalic acid, 0.75 ml of 2 M ammonium formate, 5 ml of sodium chloride and 3 ml of distilled water. The electrodeposition was carried out for 2 hr at 500 mA, using a platinum wire as an anode.

Americium and plutonium were determined by alpha-spectrometry using a Si(Au) surface barrier detector and a 200-channel pulse height analyzer.

Concurrent with these analyses, the intercalibration sample, plutonium standard soil No. 3, prepared by the US Energy Research and Development Administrations Health Service Laboratory in Idaho was also analyzed by the above-mentioned method. The validity of our calibration of ^{239}Pu tracer was confirmed by the agreement of our data with those from the Health Service Laboratory.

RESULTS AND DISCUSSION

The alpha-spectra of plutonium and americium fractions of all samples are shown in Figs. 4a and b, respectively. In the alpha-spectra of the americium fraction of the sample 73113, the contamination with ^{227}Ac , the daughter nuclide of ^{235}U , is shown by the existence of the alpha-emitting daughter nuclides of ^{227}Ac . Since actinium in a 3+ oxidation state is the most stable in an aqueous solution and the chemical properties of actinium resemble americium and lanthanides, actinium may behave as similarly as americium and lanthanide in the present analytical procedure for americium. As the energies of alpha rays from the daughters of ^{227}Ac are higher than that from ^{241}Am , the peaks due to these nuclides did not interfere with the determination of ^{241}Am in samples which had no high ^{227}Ac content.

The contents of $^{239+240}\text{Pu}$ and ^{241}Am are shown in Table 2 and Fig. 3. The overall chemical yields of ^{236}Pu and ^{148}Gd varied from 12 to 42%. The ^{241}Am in the "Bikini Ash" sample was found to be 12.9 ± 0.9 dis/min/mg. The $^{241}\text{Am}/^{239+240}\text{Pu}$ ratios for the "Bikini Ash" sample and the sediment samples were found to be nearly the same, within the statistical counting error of the samples.

There are a few reports on the $^{239+240}\text{Pu}$ contamination of deep sea sediments due to the worldwide fallout. Noshkin and Bowen analyzed six sediment profiles collected from the Atlantic Ocean and the Mediterranean Sea in 1969-1971 (No73). Among these samples three had been collected in the northern hemisphere. The contents of $^{239+240}\text{Pu}$ in ocean floor sediment samples, collected from about 1000 and 5000 m depths, were around 0.02 and 0.005 dis/min/cm³ of bulk sediment, respectively. Livingston *et al.* reported the value of 0.16 dis/min/g for the top-of-core samples collected from the 1000-m depth in the Atlantic Ocean in 1972 (Li75). The present values for samples 73108 and

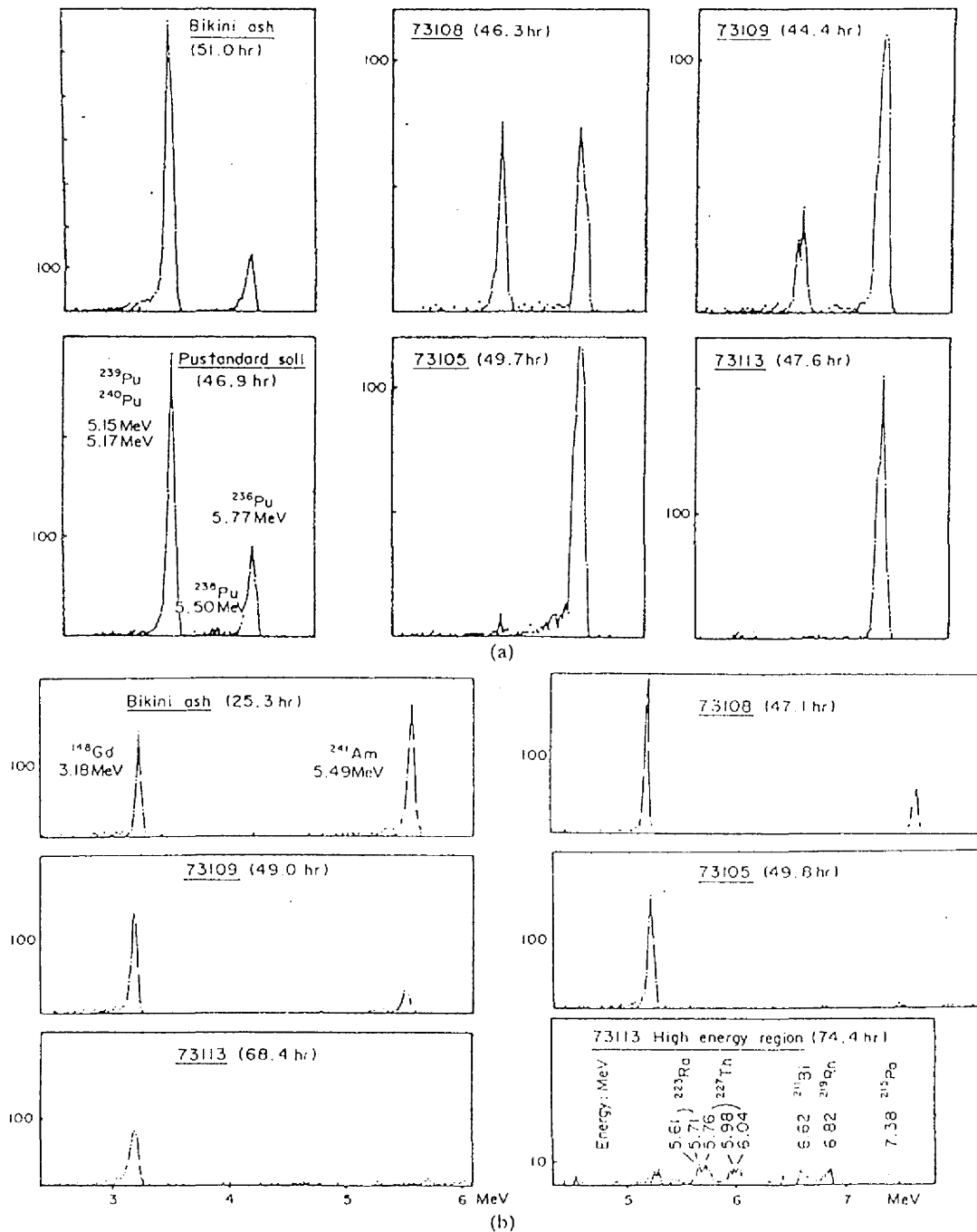


FIG. 4a. Alpha spectra of plutonium fraction from "Bikini Ash" sample and marine sediment samples. b. Alpha spectra of americium fraction from "Bikini Ash" sample and marine sediment samples.

5013229

Table 2. Analytical results for plutonium and ^{241}Am in "Bikini Ash" and marine sediment samples*

Sample	$^{239+240}\text{Pu}$ (dis/min/gram)	^{238}Pu (dis/min/gram)	^{241}Am	$^{241}\text{Am}/^{239+240}\text{Pu}$	Chemical yield (%) Pu	Am
"Bikini Ash"	25.9 ± 1.71	LTD	12.9 ± 0.941	0.50 ± 0.05	31 ± 3	34 ± 3
73105	0.14 ± 0.05	LTD	<0.2	--	34 ± 2	21 ± 2
73108	8.89 ± 0.81	LTD	5.37 ± 0.42	0.60 ± 0.07	18 ± 1	27 ± 2
73109	3.68 ± 0.32	LTD	2.11 ± 0.22	0.55 ± 0.07	30 ± 2	21 ± 2
73113	<0.05	LTD	<0.2	--	42 ± 3	12 ± 1

*The analyses were carried out in February, 1974.
dis/min/mg.

73109 are one-to-two orders of magnitude higher than those quoted above. The $^{239+240}\text{Pu}$ detected in sample 73105 is the same level as that of worldwide fallout. It is notable that $^{239+240}\text{Pu}$ was not detected in sample 73113. It may be caused by the water depth of the sampling site, since this sample was collected from the deepest site among the four samples, along with the effects of the winds and current at the time of the nuclear testing. Recently, Nevisse and Schell reported $^{239+240}\text{Pu}$ and ^{241}Am contents in sediments collected in Bikini Atoll lagoon (Ne75). They determined the ^{241}Am contents by gamma-ray spectrometry. According to their data, the contents of plutonium and americium in 31 samples, including two samples collected outside the atoll, varied from 0.9 to 270 dis/min/g for $^{239+240}\text{Pu}$, and from 0.7 to 170 dis/min/g for ^{241}Am , respectively. The ratio of $^{241}\text{Am}/^{239+240}\text{Pu}$ varied from 0.2 to 0.8, and the average value was 0.53. Compared with those values, the results of marine sediments in this study have reasonable values.

Since ^{241}Am is a daughter nuclide of ^{241}Pu , it seemed interesting to calculate the ^{241}Pu content in the "Bikini Ash" sample by assuming the ^{241}Am originally present in the bomb was negligible. By considering the growth of ^{241}Am from ^{241}Pu in the sample during the 20 yr, the content of ^{241}Pu in the "Bikini Ash" is estimated to have the value of 666 ± 49 dis/min/mg just after the time of detonation. The half-life values of 14.9 yr for ^{241}Pu and 458 yr for ^{241}Am are used in these estimates. The ratio of $^{241}\text{Pu}/^{239+240}\text{Pu}$ was calculated to be 26 ± 3 at the time of nuclear testing. According to the data reported by Diamond *et al.* (Di60), the ratio in the "Mike" debris is 27 ± 3 , almost the same as the present value. For sediment samples, the

above-mentioned calculations may not be valid because the sediments were contaminated with various debris from many other explosion tests carried out since 1946. It is important from the environmental point of view that the growth of ^{241}Am from ^{241}Pu should be taken into account to evaluate the future radioactive contamination of the environment with long life alpha-emitting radionuclides.

CONCLUSIONS

By using our new radiochemical determination technique with ^{148}Gd and ^{236}Pu tracers, the americium and plutonium contents in the so-called "Bikini Ash" sample were accurately determined together with the contents of these nuclides in several marine sediment samples collected near Bikini Atoll. This new technique may be applied to the environmental americium determination in the future, and this information on the environmental contamination with transuranium elements in this region may be useful for the estimation of local environmental radioactivity due to alpha-emitting radionuclides. The ratio of $^{241}\text{Pu}/^{239+240}\text{Pu}$ for the "Bikini Ash" sample at time zero was calculated to be 26 ± 3 , and was almost the same with that in the "Mike" thermonuclear debris.

REFERENCES

- Di60 Diamond H., Fields P. R., Stevens C. S., Studier M. H., Fried S. M., Inghram M. G., Hess D. C., Pyle G. L., Meach J. F., Manning W. R., Ghiorso A., Thompson S. G., Higgins G. H., Seaborg G. T., Browne C. I., Smith H. L. and Spence R. W., 1960, "Heavy isotope abundances in 'Mike' thermonuclear device", *Phys. Rev.* **119**, 2000.
Is69 Ishimori T. and Akatsu E., 1969, "Preparation of ^{236}Pu ", *J. Nucl. Sci. Technol.* **6**, 480.
JA54 The Japan Society of Analytical Chemistry,

- 1954, *Bunseki Kagaku (Japan Analyst)* 3, 333-367.
- Ko76 Komura K., Tanaka S., Uesugi M. and Sakanoué M., 1976, "Proton-induced reactions of ^{151}Eu and ^{153}Eu up to $E_p = 52 \text{ MeV}$ ", *J. inorg. nucl. Chem.* 38, 2157.
- Li75 Livingston H. D., Schneider D. L. and Bowen V. T., 1975, " ^{241}Pu in the marine environment by a radiochemical procedure", *Earth Planet. Sci. Lett.* 25, 361.
- Ne75 Nevisse A. and Schell W. R., 1975, "Distribution of plutonium and americium in Bikini Atoll Lagoon," *Health Phys.* 28, 539.
- No73 Noshkin V. E. and Bowen V. T., 1973, "Concentrations and distributions of long-lived fallout radionuclides in open ocean sediments", *Proc. IAEA Symp. Interaction of Radioactive Contaminants with the Constituents of the Marine Environment*, pp. 671.
- Ok74 Okano S., 1974, private communication.
- Sa71 Sakanoué M., Nakaura M. and Imai T., 1971, "Determination of Plutonium in environmental samples", *Proc. IAEA Symp. Rapid methods for Measuring Radioactivity in the Environment* pp. 171.
- Sa72 Sakanoué M., Imai T., Uesugi M. and Nomura T., 1972, "Sequential radiochemical analysis of alpha radioactive actinide nuclides and radium-228", *IUPAC Int. Congr. Analyt. Chem. Kyoto C2614* (Abstract, pp. 539).