546.211

The Radiochemical Analysis of Radio-Nuclides in Sea Water Collected near Bikini Atoll

by

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(Received May 28, 1955)

Abstract

A radiochemical analysis of sea water containing fission materials collected near Bikini Atoll in June, 1954, was performed. The sea water was boiled with hydrochloric acid, iron and lanthanum salts (each 5 mg as Fe and La) were added to it. They were precipitated as hydroxide, which was dissolved in hydrochloric acid and ferric chloride was extracted with ethyl ether. The remaining solution was evaporated to dryness and the residue was dissolved in hydrochloric acid. Using the latter solution the group separation was done with cation exchanger resins. To the filtrate separated from hydroxide precipitate, ammonium oxalate was added to produce the oxalate of alkaline earths. Strontium was separated by the use of fuming nitric acid. Analytical result shows the presence of Y-91, Ce-141, 144, Ru-103, 106, Rh-106, Zr-95 (Nb-95) and Sr-89 in which the most part was fractions of Y and Ce.

1. Introduction

As a result of the large-scale scattering of fission materials by H-bomb tests at Bikini Atoll carried out during the period from March to May, 1954, radioactive contamination was brought about around the Atoll. By the observation accomplished by Japanese oceanographers aboard the "Shunkotsu-maru", a considerably higher level of activity was detected even in the area as far as several thousand miles from Bikini, mainly flowing in the direction of the North Equatorial Current. As to the distribution of the radioactivity, the readers are referred to another paper written by the present authors [1]. In this paper, we intend to report on the results of radiochemical analysis of radioactive constituents in sea water. The sample used for the analysis was collected at 12°18′N, 161°03.5′E on 20th June, 1954, about 450 km northeast of Bikini Atoll.

Sea water of 16.5 l was used for the analysis, while the precipitate that adhered to the inner wall of a glass container was washed with hydrochloric acid (1 : 1) and subjected to analysis too. The total activity of sea water was 1830 *cpm*/*l* measured aboard the "Shunkotsu-maru" immediately after sampling.

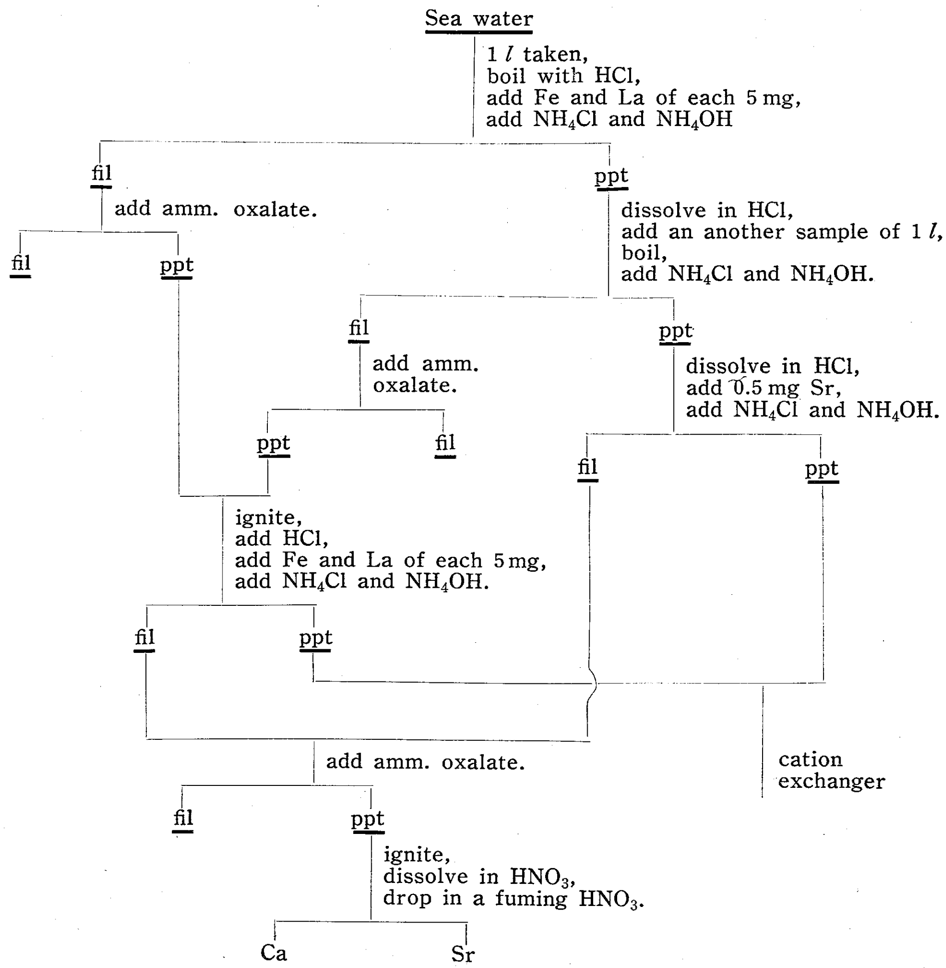
Later, by 12th Aug. in 1954, it decayed to 320 *cpm*/*l*. It was found that the decay rate of radioactivities of the sea water collected near Bikini Atoll is approximately expressed in the next formula. $A(t)=ct^{-1.5}$ where $A(t)$ is the activity, c, a constant and t, time that has elapsed since the date of detonation. Assuming that the last experiment at Bikini was carried out on 5th May, the activity on 1st December on which the analysis was started should be about 190 *cpm/l*. Therefore, the total activity of the sea water used for analysis might be about 3100 *cpm*.

2. The method of analysis

In the analysis of radioactive materials in sea water, they must first be separated from a larger amount of salt. As shown in Table 1, most of the radioactive materials were collected in precipitates of hydroxide and oxalate by coprecipitation with carriers, leaving the main part of salt in filtrates.

At first, sea water of about 1*l* was boiled with hydrochloric acid to drive off the dissolved carbonate. Then, iron and lanthanum salts (respectively, each 5 mg as Fe and La) were added. They were precipitated by adding ammonium chloride and ammonium hydroxide solution. The precipitate was dissolved again in hydrochloric acid. In the latter solution another sample of sea water of 1*l* was

Table 1. The scheme of the radiochemical analysis of sea water.



poured and boiled again. Then, ammonium chloride and ammonium hydroxide solution were added. Such a procedure was repeated until all of the samples were used. The precipitate containing iron and lanthanum hydroxide was dissolved in hydrochloric acid, to which strontium salt (equivalent to 5 mg Sr) was added as a holdback carrier. The precipitate was obtained by adding ammonium hydroxide solution and dissolved again in hydrochloric acid. Then, ferric chloride was extracted from the acidic solution using ether. The remaining acidic solution was evaporated nearly to dryness and the residue was dissolved in 0.2 N hydrochloric acid and poured into a cation exchanger column. Thereafter, group analysis was made by the ordinary process.

On the other hand, to the filtrate already separated from the precipitate containing iron and lanthanum was added ammonium oxalate to obtain the precipitate of alkaline earths. After igniting the precipitate it was dissolved in hydrochloric acid to which iron and lanthanum salts were added as scavengers and precipitated with ammonium hydroxide solution. After filtering out the latter precipitate, oxalate was changed into oxide by ignition and dissolved in a concentrated nitric acid. Then, a fuming nitric acid was dropped in. Thus, strontium nitrate was obtained as precipitate while calcium nitrate remained in a solution. Strontium nitrate was dissolved on a glass filter pad in warm diluted nitric acid and transferred into a planchet for measurement of radioactivity by a G-M counter.

Next, the analysis of the precipitate that adhered on the glass wall of the original container was made. In this case there was only a little amount of salt matter, and therefore, the solution in hydrochloric acid was directly passed through a cation exchanger column to make the group separation.

As the cation exchanger, Amberlite IR-120 was used under the following conditions: (1) Inner diameter of the column was about 20 mm and its height, 50 mm. The grain size was between 100 to 150 meshes. The flow rate of effluent was about 0.8 ml/min. (2) Inner diameter of the column was about 7 mm and its height, 560 mm. Particles of grain size 100 to 150 meshes and of about 50 meshes were mixed together. The flow rate was about 0.3 ml/min.

Ordinary group analysis was carried out under the first condition and for the separation of yttrium and cerium the second condition was employed.

3. Results of radiochemical analysis

In Table 2 the results of analysis are shown. Each nuclide was identified by the shape in elution curves and the β ray energy absorption curves with aluminum. Fig. 1 shows the elution curves obtained for the supernatant sea water sample. The first peak of activity appeared in the effluent from 0.2 N hydrochloric acid. It is considered to be attributable to Ru-103 and Rh-106 (a daughter of Ru-106) according to the β ray energy absorption curves shown

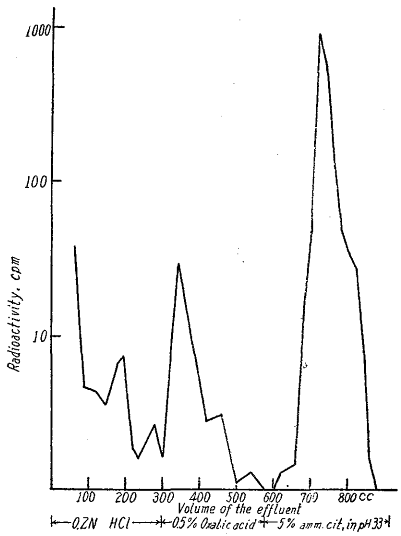


Fig. 1. The elution curves for the sea water sample.

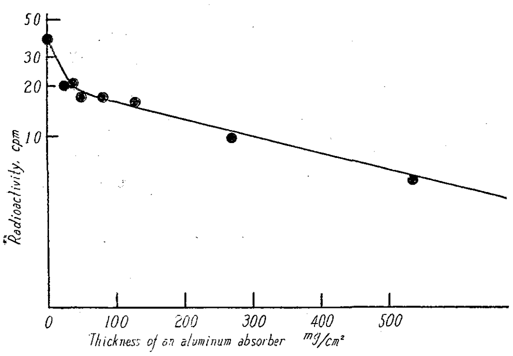


Fig. 2. The β ray energy absorption curves for the effluent from 0.2 N hydrochloric acid.

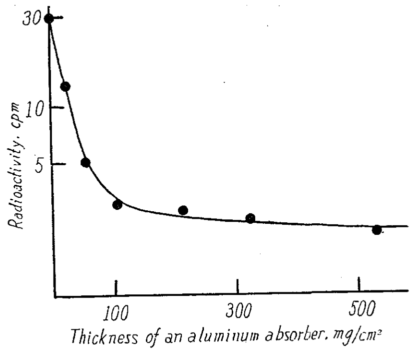


Fig. 3. The β ray energy absorption curves for the effluent from 0.5% oxalic acid.

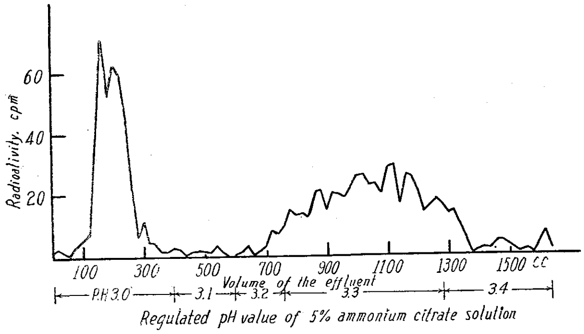


Fig. 4. The elution curves for the effluent from 5% ammonium citrate solution in Fig. 1.

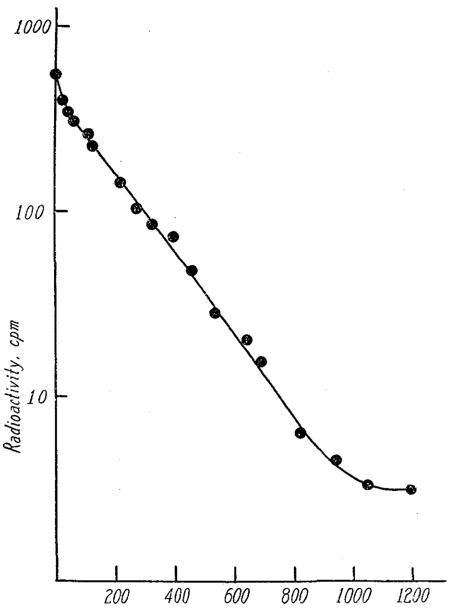


Fig. 5. The β ray energy absorption curves for the effluent from 5% ammonium citrate.

in Fig. 2. The second peak appeared in the effluent from 0.5% oxalic acid. This may be attributed to Zr-95 estimating from the β ray energy absorption curves shown in Fig. 3. Though Nb-95 was not identified, yet its existence was probable. The third peak appeared in the effluent (5% ammonium citrate) of which pH was adjusted with hydrochloric acid to be 3.3. This fraction was separated into two parts by passing through a long column of the resins (56 cm), as shown in Fig. 4. Fig. 5 shows an absorption curve of a fraction of the effluent of the ammonium citrate solution in which the existence of Y and rare earth elements were expected. As seen in Fig. 5, it seems that there are two kinds of β rays of different energies. The soft part may be attributed to Ce-141, 144 while the hard one to Y-91 only.

According to Table 2, it can undoubtedly be said that the contributions of yttrium and cerium are dominant. Activities from nuclides other than Y and Ce are too weak to make possible a detailed discussion. According to Hunter-Ballou's calculation, the contributions of each radionuclide obtained by bombarding slow neutron to U-235 on 210th day after fission are given in the last column in Table 2.

Table 2. The results of radiochemical analysis of sea water near Bikini.

Nuclide	1*			2**			210 day activity (%) in fission materials [U-235 (slow neutron)]
	Activity *cpm*	%	Date of measurement	Activity *cpm*	%	Date of measurement	
Y-91	750	37	Dec. 22, 1954	850	93	Mar. 29	10
Ce-141, 144	1100	55	Dec. 22				15.0
Ru-103, 106 Rh-106	75	3.8	Dec. 1	34	3.7	Mar. 28	8.2
Zr-95 (Nb-95)	45	2.2	Dec. 3	30.5	3.3	Mar. 28	39
Sr-89, (90)	40	2.0	Dec. 20	—	—	Mar. 29	7.5

* Sea water.

** The precipitate that adhered on the glass wall of the original container.

Analytical results show that the contribution in activity of Zr-95 is much lower than the calculation by HUNTER-BALLOU, Y and Ce, on the contrary, much higher. The cause of this discrepancy is not clear. Studies are now in progress to clarify it.

Acknowledgements———The authors wish to express their hearty thanks to Dr. K. KIMURA, Dr. E. MINAMI and members of their laboratories in the University of Tokyo for their valuable suggestions and discussions.

Reference

[1] MIYAKE, Y., SUGIURA, Y. and KAMEDA, K., 1955: On the Distribution of Radioactivity in the Sea around Bikini Atoll in June, 1954. Pap. Met. Geophys., 5, p. 253.