Detection of ^{103m}Rh in the "Bikini Ashes"

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Introduction

The radiochemical analysis of the so-called "Bikini Ashes" which fell on a Japanese fishing boat, the No. 5 Fukuryu Maru on March 1, 1954, was carried out in our laboratory[1] and in several other university laboratories[2]. In the course of their studies, scientists detected ^{103}Ru (half-life: 39.8 d.) in the ashes together with ^{106}Ru (half-life: 1.0 y.) and its daughter ^{106}Rh (half-life: 30 s.). As is well known, ^{103}Ru decays into ^{103m}Rh (half-life: 57 m.) which successively disintegrates into stable ^{103}Rh by isomeric transition. The half-life of ^{103m}Rh is rather short and the energy of the converison electron of ^{103m} Rh is so low (0.034 Mev) that it has been still remained undetected in the ashes. The present authors tried to separate ^{103m}Rh from its parent ^{103}Ru in the carrier-free form by the ion exchange resin method in a short time and to detect the weak radioactivity by the use of the windowless gas flow counter.

Experimental

1. Materials and Apparatus

Materials.—The sample ashes are so-called "Bikini Ashes" which fell on board No. 5 Fukuryu Maru sailing near the Bikini Atoll on March 1, 1954. The chemical and radiochemical compositions of the ashes were already reported in the previous paper[1]. The ashes used in this experiment were collected on board the boat and contained fairly large amounts of dust.

Apparatus for Activity Measurements.—The Geiger-Müller counter model TGC-2 made by Tracerlab Inc. was used for the general activity counting. The thickness of the mica window of the counter tube is 1.4 mg./cm^2 and counting efficiency is about 10%. For the measurement of the weak activity of rhodium fraction, 2π Q-gas flow counter model D42A made by Nuclar Instrument and Chemical Corporation was used.

2. Separation of Ruthenium from "Bikini Ashes"

At first, ruthenium fraction was separated from the ashes by the procedure written below. The sample of some ten million cpm. was taken and ignited to burn away all combustible substances. Then, it was dissolved with 6 N hydrochloric acid, and the insolubles were filtered off. The activity of a small aliquot of the filtrate was measured on the second shelf of the Geiger-Müller counter. Total activity was estimated about 10^6 cpm., 10 mg. of ruthenium was added to the filtrate as a carrier, the acidity of the solution was adjusted

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[1] K. Kimura, E. Minami et al. *Japan Analyst*, 3, 335 (1954). (in Japanese).

[2] T. Shiokawa, et al, ibid., 349; H. Yamatera, et al., ibid., 356.

to 2 N, and then hydrogen sulfide was passed through to precipitate ruthenium as sulfide. The precipitate was dissolved with nitric acid. The solution thus obtained was then treated according to the D. N. Hume's procedure[3]; to the ruthenium solution were added an appropriate amount of water, potassium permanganate and concentrated sulfric acid, then ruthenium was distilled off as ruthenium tetroxide. The distillate was caught in a small volume of water containing a small amount of hydrogen proxide.

The appropriate aliquot portion of the distillate was taken in a counting dish, evaporated up to dryness and the activity was measured under the same measuring condition as in the case of the starting sample solution. The total activity of the distillate was considered to be 1.5×10^5cpm.

The absorption curve of the distillate for aluminum foil was also investigated. The result is shown in Fig. 1. The activity is considered to be composed of two parts; rather high energy β-ray of some 3.9 MeV and low energy β-ray of less than 0.3 MeV. The former is considered to correspond to that of ^{106}Rh (3.55 MeV), the daughter of ^{106}Ru, and the latter to that of ^{103}Ru (0.22 MeV).

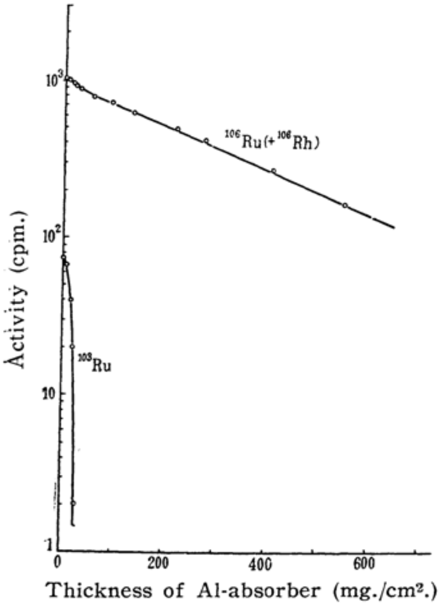

Fig. 1. Absorption curve of Ru*+Rh* fraction (Apr. 5, 1955).

3. Separation of Rhodium from Ruthenium and Detection of ^{103m}Rh

The separation of rhodium from ruthenium for the purpose of detecting ^{103m}Rh includes two essential problems; (1) the half-life of ^{103m}Rh is very short (57 m.), so that the separation must be finished in a short time, (2) the energy of internal conversion electron of ^{103m}Rh is very low (0.034 MeV). Therefore, it is desirable for it to be separated in as high a specific activity as possible to minimize the effect of self-absorption.

P. C. Stevenson, et al.[4] reported that rhodium adhers to the cation exchange resin, Dowex-50, and it is easily eluted out by passing 2 N hydrochloric acid. The workers thus succeeded in the separation of rhodium from such platinum group elements as platinum, palladium and iridium. On the other hand, it is known that ruthenium in 0.2 N hydrochloric acid solution passes through Dowex-50 resin without adhering. The procedure for the separation of rhodium and ruthenium which the present authors used in this experiment is based in principle on this difference of the properties of these elements against resin.

The resin used in this experiment was a cation exchange resin, Dowex-50 in HR-type, 50–100 mesh, ane 1.0 cm. $\phi\times6.0$ cm. in dimension. The flow rate of the solution was 1 ml./min.

The appropriate aliquot of the above mentioned ruthenium distillate was evaporated up to dryness and the residue was dissolved in a small amount of hydrochloric acid. The evaporation and dissolution processes were repeated several times; then, the acidity and total volume of the hydrochloric acid solution were adjusted to 0.2 N and 10 ml., respectively. The solution thus obtained was allowed to flow through the resin bed. After the resin bed was washed with a small quantity of 0.2 N hydrochloric acid, 2 N hydrochloric acid was passed through as the elutriant for rhodium. The effluent was collected and evaporated up to dryness in a counting dish. The activity of the residue was then measured with the 2π Q-gas flow counter, and its decay curve was observed.

The result is shown graphically in Fig. 2-I

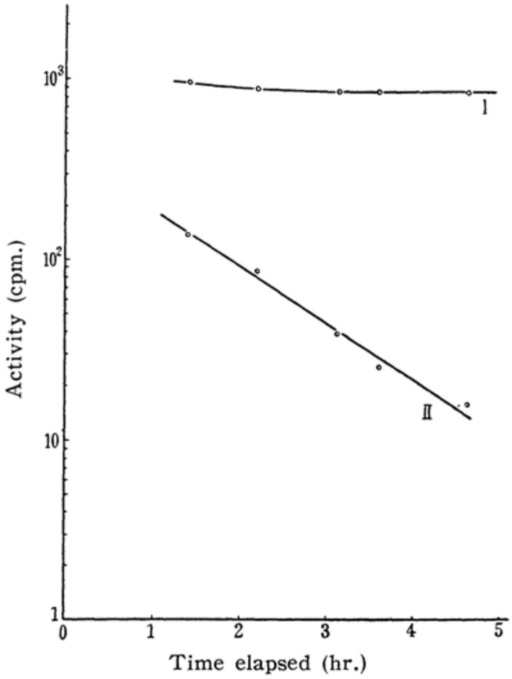

Fig. 2. Decay curve of Rh-fraction (Apr. 14, 1955).

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[3] D.N. Hume, *NNES-PPR*, 9, 1557 (1951).

[4] P.C. Stevenson, et al., *J. Am. Chem. Soc.*, 75, 4876 (1953).

representing the logarithm of the radioactivity against the time which has elapsed. The activity decreases rather considerably for the first several hours[5], and then it becomes approximately constant. In order to analyse this decay curve, the above-mentioned approximately constant value of the later period was subtracted from the activity values for the earlier period, and the differences were again plotted against time. Then, a virtually straight line is obtained as shown in Fig. 2-II. As its inclination coincides with that corresponding to the half-life fifty-seven minutes, the activity can be attributed to that of ^{103m}Rh. Judging from its absorption curve for aluminum foil, the radioactivity which still remains after the decay of ^{103m}Rh is attributed to the radioactivites of ^{103}Ru and ^{106}Ru+^{106}Rh. It is shown that rhodium separated by the above-mentioned method is still accompanied with considerable amounts of radioactive ruthenium.

The ruthenium fraction which passed through the resin bed was set aside and let stand over several hours to allow the growth of its daughter ^{103m}Rh and used for the next separation of ^{103m}Rh. Thus, the separation experiment of ^{103m}Rh was repeated three times in the above-mentioned way, and always observed the radioactivity which should be assigned to ^{103m}Rh.

As to the energy of the internal conversion electron of ^{103m}Rh, it was rather difficult to measure directly in the 2π Q-gas flow counter for its short half-life and low activity. Therefore, the authors applied the following conventional method; after the rhodium fraction was separated and collected in the counting dish in the way mentioned above, the dish was wrapped with the aluminum foil of 4.75 mg./cm^2 thickness[6] and its activity decay was measured. The result is shown in Fig, 3, indicating no decrease in activity. It seems to be concluded deservedly that the radioactivity of the shorter half-life observed in this fraction in the former experiments is perfectly absorbed by the alumium foil of 4.75 mg./cm^2 thickness, and this low energy activity shoud be attributed to the internal conversion electron of ^{103m}Rh whose energy is described 0.034 MeV.

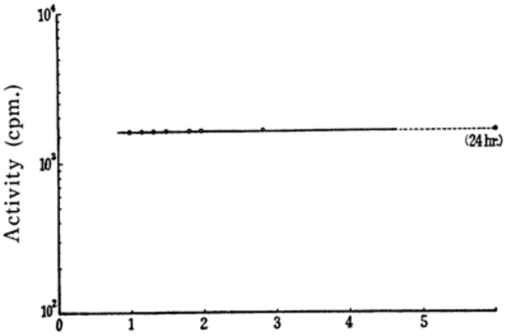

Fig. 3. Masking of ^{103m}Rh decay by 4.75 mg./cm^2 Al-foil (Apr. 21, 1955).

Conclusion

It can be now concluded that ^{103m}Rh is directly detected in the "Bikini Ashes" in the above mentioned way.

As the separation of rhodium must be done in as short a time as possible because of the short half-life of ^{103m}Rh, the efficiency of separation of rhodium from ruthenium in this experiment is by no means satisfactory from the analytical point of view. The rapid and clean-cut separation of ruthenium and rhodium from each other is the problem still remaining to be solved.

The radionuclides detected in the ashes are summarized in Table I including newly

TABLE I

RADIONUCLIDES DETECTED IN THE "BIKINI ASHES"

Nuclides detected	Half-life	Activity percentage of each nuclide (on March 26, 1954) (%)
^{32}P	14.30 d	—
^{35}S	87.1 d	0.1±0.05
^{45}Ca	152 d	0.2±0.1
^{89}Sr	53 d	1±0.5
^{90}Sr	19.9 y	0.02±0.01
^{90}Y	61 h	0.02±0.01
^{91}Y	61 d	8±3
^{95}Zr	65 d	5±2
^{95m}Nb	90 h	—
^{95}Nb	35 d	3±1
^{103}Ru	39.8 d	8±5
^{103m}Rh	57 m	
^{106}Ru	1.0 y	0.9±0.2
^{106}Rh	30 s	
^{125}Sb	2.7 y	—
^{129m}Te	33.5 d	—
^{129}Te	72 m	—
^{132}Te	77.7 h	—
^{131}I	8.141 d	—
^{132}I	2.4 h	—
^{137}Cs	33 y	—
^{140}Ba	12.80 d	5±1
^{140}La	40.0 h	6±1
^{141}Ce	33.1 d	7±5
^{144}Ce	282 d	2±1
^{143}Pr	13.7 d	16±5
^{144}Pr	17.5 m	2±1
^{147}Nd	11.3 d	9±4
^{147}Pm	2.6 y	—
^{237}U	6.75 d	20±10
^{239}Pu	24360 y	α: $(4\pm2)\times10^{-4}$

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[5] The initial time ($t=0$) corresponds to the middle time when the sample solution starts and finishes passing through the resin bed.

[6] The aluminum foil of 4.75 mg/cm^2 thickness corresponds to the maximum range of β-ray of 0.05 MeV energy.

detected ^{103m}Rh as well as ^{35}S[7], ^{125}Sb[8] and ^{137}Cs[8] which are also detected after the issue of the previous paper. In addition, the contribution of each nuclide to the total activity is tabulated in Table I. These numerical values are all expressed by the percentage contribution of activity on March 26, 1954 —twenty-five days after detonation of the Bikini bomb—when the quantitative measurements of activity of the ashes were started.

Summary

^{103m}Rh having very short half-life (57 m) and very low energy in electron conversion (0.034 MeV) was searched for and detected in the "Bikini Ashes". It was separated from the ashes by the method using the cation exchange resin, Dowex-50, and its activity was measured by the 2π Q-gas flow counter.

The radionuclides detected in the ashes are briefly summarized in a table.

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[7] K. Kimura, N. Ikeda and M. Inarida, Read before the Annual Meeting of the Japan Society for Analytical Chemistry, Oct. 1954 Osaka.

[8] M. Honda, Y. Sasaki, Read before the Annual Meeting of the Chemical Society of Japan, Apr. 1955, Tokyo.