

## RUTHENIUM-106 IN THE ADJACENT SEA OF JAPAN

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### Abstract

Ruthenium-106 was concentrated from large volume of sea water by co-precipitation with magnesium hydroxide, and then separated from other interfering nuclides by oxidation to Ru(VII) in alkali medium and by solvent extraction of  $\text{RuO}_4$  to carbontetrachloride. The analyzed values of radioactivity were increased by oxidation-reduction pretreatment. This increase was discussed using Ru-106 tracer of several chemical forms. The mean value of Ru-106 in the Japan Sea is about three times as large as that in the Kuroshio region. The concentration of Ru-106 in surface water increased after the reopening of nuclear explosion tests, reached its maximum in 1963 and decreased exponentially thereafter. The half-lives of Ru-106 and Ce-144 in surface layer were calculated, and are compared each other.

### 1. Introduction

The determinations of radioactive nuclides in sea water have been conducted by many workers, and almost all of them were those of long lived nuclides, such as Sr-90 or Cs-137 (MIYAKE et al. 1958, 1960, 1961, HIGANO et al. 1960, 1962), but comparatively short lived nuclides have scarcely been determined except for Ce-144 (HIGANO et al. 1961).

Ru-106 is also one of the fission products and its proportion in fission products can not be neglected (IWASHIMA and WATARI 1963). However, the complicated chemical behavior and many oxidation states of ruthenium make the determination of Ru-106 difficult, therefore, only a few determinations of Ru-106 in marine environment have been reported.

TSURUGA (1962, 1963) determined the Ru-106 and concentration factors in seaweeds from Hiroshima Bay, and discussed on the mechanism of uptake of radoruthenium by seaweeds. YAMAGATA (1963) reported Ru-106 in coastal water, but the concentration of Ru-106 in the adjacent sea of Japan has never been reported.

Therefore, the measurements of Ru-106 were conducted to investigate the geochemical behavior of Ru-106 in the sea and to evaluate the contamination level in the adjacent sea of Japan.

### 2. Experimental

*Sample* 20~40 liters of sea water was used for each determination. Sea water was acidified by adding concentrated hydrochloric acid at the rate of 2 ml. per liter of sea water immediately after the sea water was collected.

*Reagents* Antiformin. Commercial antiformin which contains 6% of active chlorine was used without further purification. The blank test of the

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reagent proved the radioactivity to be negligible.

Ru-carrier. Commercial ruthenium trichloride was used as carrier.

All other reagents used in this experiments were guaranteed reagent quality.

*Procedure* (Table 1)

10mg. of yttrium, 10mg. of cerium, 10mg. of zirconium and 10mg. of ruthenium were added to the sample as carriers. After the sample was neutralized with 10M-NaOH soln., and excess NaOH soln. was added until a portion of magnesium was precipitated as hydroxide, 6% antiformin was added at the rate of 1.2 ml. per liter of sea water, and the sample was stood for 30 min. to make the oxidation of Ru (III) to Ru (VII) complete. The oxidized ruthenium was reduced by adding 4 g. of NaHSO<sub>3</sub> and 12 ml. of ethanol. After the sample was heated to about 70°C., it was stood aside until almost all precipitates settled. Clear supernatant was filtered through a Buchner funnel. Residual precipitate and that on the filter paper were dissolved in minimum amount of hydrochloric acid (about 10 ml.). The solution was neutralized with 10M-NaOH soln. and 1 ml. was added in excess. 10 drops of 6% antiformin was added to re-oxidize Ru to Ru (VI) or (VII), and the mixture was centrifuged. The supernatant was transferred to other clean beaker. The precipitate was dissolved in minimum amount of hydrochloric acid, and then the oxidation and centrifugation were repeated. The precipitate was used for the analyses of Zr-95 and Ce-144. The supernatants were combined and 2 ml. of ethanol was added. After heating on a water bath until the supernatant become colorless, the precipitate of ruthenium mixed oxides was filtered and dissolved in hydrochloric acid. The solution was condensed to about 1 ml. on the water bath and then diluted to 10 ml. by distilled water. Further radiochemical purification of ruthenium was done by using solvent extraction method devised by MEADOWS et al. (1962) : Ruthenium was oxidized to tetroxide by antiformin, extracted by carbontetrachloride and back-extracted by 3M-NaOH soln. containing 3 drops of 1M-NaHSO<sub>3</sub>. Ruthenium was precipitated as mixed oxides of Ru (III) and (IV) by adding ethanol and by heating. The ruthenium mixed oxides was filtered on filter paper, washed by ethanol and ethyl ether and dried in vacuum desiccator.

Ru-106—Rh-106 was counted by 4 pi gas flow low-background counter. Counting efficiency was about 70%. The radioactivity was corrected for the decay since the date of collection. Chemical yield of ruthenium was determined by colorimetric method of Ru (IV) devised by WATERBURY et al. (1960). The chemical yield was 71.4% (mean).

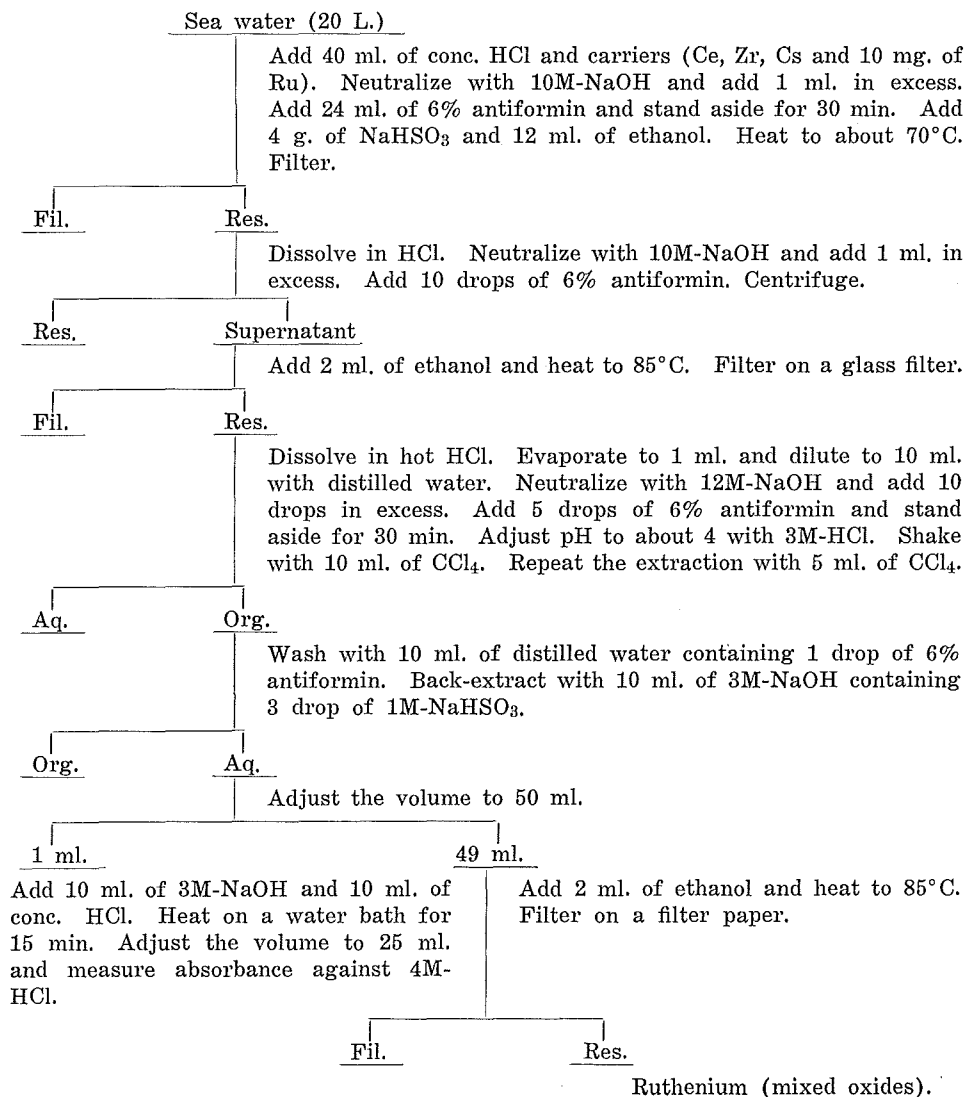
### 3. Horizontal Distribution

The analytical results of Ru-106 in surface sea water are shown in Table 2. The yearly mean values of Ru-106 and Ru-106/Sr-90 in the Kuroshio region and the Japan Sea are shown in Table 3. Though the increase of Sr-90 in surface sea water are not significant after the reopening of nuclear explosion

tests in 1961 (NAGAYA, 1964), Ru-106 in surface sea water increases abruptly like Ce-144 and reaches maximum in 1963 ( $1.68 \mu\mu\text{c/L}$  in the Kuroshio region and  $5.82 \mu\mu\text{c/L}$  in the Japan Sea). The radioactivity of Ru-106 in the northern part of the Japan Sea agrees well with that of the Oyashio region and they are three-fold of those of the Kuroshio region and the southern part of the Japan Sea. This result agrees with that obtained from the horizontal distributions of Sr-90 and Ce-144 (NAGAYA, 1964). These high values in the northern part of the Japan Sea and the Oyashio region are explained as follows.

In the Kuroshio region, the radioactivity in the surface layer is diluted with sea water coming from the south where the amount of fallout was very little compared with the area near Japan. On the contrary, in the

TABLE 1. ANALYTICAL SCHEME OF Ru-106 IN SEA WATER



northern part of the Japan Sea and the Oyasio region, the current are relatively stagnant and the surface sea water is supplied from the north where the amount of fallout is large.

The values of Ru-106/Sr-90 in the Kuroshio region and the Japan Sea in 1963 (3.1 and 5.2 respectively) and in 1964 (1.09 and 1.78 respectively) are very large when compared with values from Hunter Ballou taking into consideration the amount of Sr-90 that had been present already in sea water before the reopening of the nuclear explosion tests in 1961 ( $0.3 \mu\mu\text{c/L}$ , HIGANO et al. 1962). These results are explained as follows.

The fission yields of Sr-90 and Ru-106 are significantly influenced by the types of fission and these high values of Ru-106/Sr-90 are considered to be due to the fission processes other than U-235 (Table 4).

#### 4. Secular Variations

The secular variations of Ru-106 and Ce-144 (NAGAYA, 1964) in the Kuroshio region and in the Japan Sea are shown in Fig. 1.

The radioactivity of Ru-106 increased rapidly from 1962 owing to the reopening of the nuclear explosion tests, reached maximum in 1963 and then gradually decreased owing to the absence of large scale nuclear explosion test in air thereafter.

The effects of the tests conducted by Red China in 1964 and 1965 on the radioactivity of the ocean water are too small to produce a significant contribution to the total activity in sea water.

Fig. 1 shows that the Ru-106 in surface layer decreases exponentially after the maxima in March 1963 in the Kuroshio and in July 1963 in the Japan Sea. The half-lives of Ru-106 and Ce-144 in the surface layer were calculated from Fig. 1 by least squares method and shown in Table 5.

The correction were made for radioactive decay since the maxima in 1963 to compensate the difference of the nuclear physical half-lives of Ru-106 (1 y.) and Ce-144 (285 d.) and resulted half-lives are also included in Table 5 (half-life corrected).

In the Kuroshio region, the half-life and corrected half-life of Ru-106 in surface layer are 0.70 y. and 1.8 y. respectively. On the other hand, in the Japan Sea, they are 0.44 and 0.77 y. respectively. There are difference between the half-lives of Ru-106 in the Japan Sea and those in the Kuroshio region, and the former is about twice of the latter. This result means that the mixing in the vertical direction is considerably more violent in the Japan Sea than in the Kuroshio region, and agrees well with the results which have been obtained by the oceanographical observations.

In the case of Ce-144, the nuclear physical half-life (285 d.) is short compared with that of Ru-106, therefore, the half-life in surface layer is also short, but the corrected half-life of Ce-144 in the Kuroshio region (1.6 y.) agrees well with that of Ru-106 (1.8 y.), but in the Japan Sea, a little difference was observed between Ru-106 and Ce-144. This may be due to the difference of adsorbability to the particulate matter of Ce-144 and Ru-106 owing to the

presence of Ce (IV) (SUGIHARA 1962, GOLDBERG 1963) in the Japan Sea where the suspensoid is rich. On the other hand, in the Kuroshio region, the decrease of the radioactivity in the surface layer are influenced by the

TABLE 2. ANALYTICAL RESULTS OF Ru-106 IN SURFACE SEA WATER.

Location	Sampling Date	Depth (m)	Ru-106 $\mu\text{c/L}$ .	Ru-106/Sr-90
Kuroshio region.				
31° 59' N., 135° 43' E.	Jul. 17th, 62	0	1.02±0.18	2.6±0.6
32° 01' N., 138° 48' E.*	Mar. 22nd, 63	0	1.68±0.06	4.3±0.2
33° 28' N., 138° 35' E.*	Nov. 16th, 63	0	0.66±0.04	1.8±0.2
32° 55' N., 138° 52' E.*	Mar. 13th, 64	0	0.66±0.03	0.9±0.1
33° 32' N., 141° 02' E.	Mar. 19th, 64	0	0.28±0.02	1.0±0.1
33° 58' N., 140° 42' E.	Mar. 19th, 64	0	0.32±0.02	0.8±0.1
33° 05' N., 136° 05' E.*	Apr. 16th, 64	0	0.52±0.03	1.2±0.1
33° 30' N., 137° 00' E.	May 17th, 64	0	0.32±0.02	0.8±0.1
33° 01' N., 137° 03' E.*	May 17th, 64	0	0.34±0.02	0.9±0.1
32° 01' N., 137° 01' E.	May 17th, 64	0	0.53±0.02	1.3±0.1
34° 50' N., 142° 09' E.*	Jun. 30th, 64	0	0.56±0.04	1.5±0.2
32° 45' N., 135° 12' E.*	Jul. 13th, 64	0	0.36±0.02	1.3±0.1
33° 59' N., 138° 30' E.	Aug. 15th, 64	0	0.67±0.03	1.7±0.2
34° 10' N., 142° 06' E.	Sept. 8th, 64	0	0.42±0.02	1.2±0.1
32° 49' N., 140° 01' E.	Sept. 16th, 64	0	0.48±0.02	1.1±0.1
33° 01' N., 135° 46' E.*	Nov. 15th, 64	0	0.27±0.02	0.7±0.1
33° 29' N., 139° 12' E.*	Dec. 11th, 64	0	0.29±0.02	0.9±0.1
33° 10' N., 135° 54' E.*	Feb. 15th, 65	0	0.19±0.02	0.6±0.1
33° 27' N., 138° 43' E.*	Mar. 18th, 65	0	0.16±0.01	0.5±0.1
33° 24' N., 136° 09' E.*	Apr. 27th, 65	0	0.21±0.02	0.8±0.1
33° 28' N., 138° 28' E.*	May 20th, 65	0	0.18±0.01	0.7±0.1
* Samples collected in the Kuroshio current.				
Northern part of the Japan Sea.				
38° 43' N., 136° 35' E.	Nov. 8th, 61	0	0.55±0.07	1.7±0.2
44° 03' N., 150° 08' E.	May 10th, 62	0	2.78±0.11	9.5±1.1
45° 40' N., 150° 48' E.	May 10th, 62	0	2.09±0.08	7.5±0.9
38° 04' N., 133° 57' E.	May 1st, 63	0	2.64±0.10	.....
39° 35' N., 135° 07' E.	Aug. 6th, 63	0	4.72±0.13	5.1±0.2
40° 30' N., 135° 53' E.	Aug. 6th, 63	0	5.82±0.11	5.3±0.2
45° 46' N., 139° 32' E.	May 19th, 64	0	0.80±0.03	1.3±0.1
45° 46' N., 138° 47' E.	May 19th, 64	0	0.90±0.04	1.7±0.1
43° 42' N., 136° 31' E.	May 21st, 64	0	1.24±0.04	2.2±0.1
41° 11' N., 137° 01' E.	May 27th, 64	0	1.20±0.04	2.0±0.1
40° 01' N., 132° 31' E.	May 29th, 64	0	1.81±0.05	2.6±0.1
40° 01' N., 137° 49' E.	May 30th, 64	0	1.22±0.04	2.1±0.1
41° 15' N., 139° 34' E.	Aug. 7th, 64	0	0.88±0.03	1.4±0.1
39° 27' N., 135° 17' E.	Aug. 9th, 64	0	1.15±0.03	1.8±0.1
37° 54' N., 137° 44' E.	Aug. 20th, 64	0	1.27±0.03	1.8±0.1
42° 00' N., 138° 20' E.	Nov. 9th, 64	0	0.92±0.03	1.4±0.1

TABLE 2. ANALYTICAL RESULTS OF Ru-106 IN SURFACE SEA WATER. (CONTINUED)

Location	Sampling date	Depth (m)	Ru-106 $\mu\mu\text{c/L}$ .	Ru-106/Sr-90
40° 54' N., 139° 27' E.	Nov. 10th, 64	0	0.73±0.03	1.3±0.1
37° 30' N., 138° 10' E.	Mar. 18th, 65	0	0.47±0.02	0.9±0.1
39° 20' N., 136° 00' E.	Mar. 19th, 65	0	0.31±0.02	0.7±0.1
Southern part of the Japan Sea.				
35° 55' N., 132° 48' E.	Aug. 26th, 61	0	0.44±0.05	1.0±0.1
36° 39' N., 132° 00' E.	Nov. 8th, 61	0	0.61±0.06	1.9±0.2
36° 39' N., 132° 00' E.	Oct. 30th, 63	0	1.10±0.05	2.1±0.2
38° 42' N., 136° 36' E.	Mar. 24th, 64	0	0.44±0.02	0.8±0.1
36° 39' N., 132° 00' E.	May 10th, 64	0	0.56±0.02	1.1±0.1
36° 37' N., 132° 04' E.	Aug. 21st, 64	0	0.48±0.02	0.5±0.0
36° 39' N., 132° 00' E.	Oct. 31st, 64	0	0.34±0.02	0.7±0.1
36° 08' N., 132° 00' E.	Mar. 30th, 65	0	0.20±0.01	0.6±0.1
36° 19' N., 134° 58' E.	May 9th, 65	0	0.24±0.01	0.8±0.1
Oyasio region.				
39° 13' N., 144° 11' E.	Jul. 7th, 63	0	2.44±0.06	4.4±0.3
41° 47' N., 146° 15' E.	Jul. 16th, 63	0	3.56±0.07	6.1±0.3
40° 20' N., 143° 39' E.	Jul. 19th, 64	0	1.60±0.05	2.3±0.1
39° 00' N., 144° 31' E.	Jul. 20th, 64	0	0.80±0.03	1.7±0.1

TABLE 3. YEARLY MEAN VALUES OF Ru-106 AND Ru-106/Sr-90 IN SURFACE SEA WATER.

	Kuroshio		Oyasio	
	Ru-106 $\mu\mu\text{c/L}$ .	Ru-106/Sr-90	Ru-106 $\mu\mu\text{c/L}$ .	Ru-106/Sr-90
1962	1.02±0.09 (1)	2.6±0.6 (1)		
1963	1.26±0.04 (2)	3.1±0.1 (2)	3.00±0.05 (2)	5.3±0.2 (2)
1964	0.43±0.01 (14)	1.09±0.03 (14)	1.20±0.03 (2)	2.00±0.07 (2)
1965	0.19±0.01 (4)	0.65±0.05 (4)		
N. Japan Sea.		S. Japan Sea.		
1961	0.55±0.07 (1)	1.7±0.2 (1)	0.53±0.07 (2)	1.5±0.1 (2)
1962	2.44±0.07 (2)	8.5±0.7 (2)	0.63±0.13 (1)	
1963	4.39±0.02 (3)	5.2±0.1 (2)	1.10±0.05 (1)	2.1±0.2 (1)
1964	1.10±0.01 (11)	1.78±0.03 (11)	0.46±0.01 (4)	0.77±0.04 (4)
1965	0.39±0.01 (2)	0.80±0.07 (2)	0.22±0.01 (2)	0.70±0.07 (2)

TABLE 4. FISSION YIELDS OF SEVERAL SORTS OF FISSION REACTIONS.

Time after nuclear fission	Ru-106/Sr-90		
	1 year	2 year	3 year
Pu-239 (Thermal neutron)	34	18	9.1
U-238 (Fast neutron)	11	5.8	3.1
U-235 (Thermal neutron)	1.6	0.8	0.4

TABLE 5. HALF-LIVES OF Ru-106 AND Ce-144 IN SURFACE SEA WATER.

Current region	Ru-106		Ce-144	
	Half-life in surface layer (year)	Half-life corrected (year)	Half-life in surface layer (year)	Half-life corrected (year)
Kurosio	0.70±0.05	1.8±0.4	0.60±0.06	1.6±0.3
N. Japan Sea.	0.44±0.04	0.77±0.12	0.29±0.03	0.47±0.10

TABLE 6. ADSORPTION OF Ru-106 IN SITU. TO POLYETHYLENE CONTAINER.

Sample number	Rucarrier and HCl were added in situ.	Only HCl was added in situ.
1.	0.18±0.01 $\mu\mu\text{c/L}$ .	0.17±0.01 $\mu\mu\text{c/L}$ .
2.	0.32±0.02 $\mu\mu\text{c/L}$ .	0.30±0.02 $\mu\mu\text{c/L}$ .

TABLE 7. THE RESULTS OF THE METHODS WITH AND WITHOUT OX-RED PRETREATMENT.

Current region	Ox-Red method $\mu\mu\text{c/L}$ .	Hydr. method $\mu\mu\text{c/L}$ .
Kurosio	0.66±0.03	0.33±0.02
	0.17±0.01	0.14±0.01
Japan Sea	0.80±0.03	0.69±0.03
	1.20±0.04	0.96±0.04

TABLE 8. THE RESULTS OF TRACER EXPERIMENTS.

Sample number	Tracer (Ru-106) added	The analyzed values by this method
1.	83.4 d. p. m.	81.8±2.6 d. p. m.
2.		81.6±2.6
3.		85.3±2.5
4.		82.2±2.3
5.		80.6±2.3

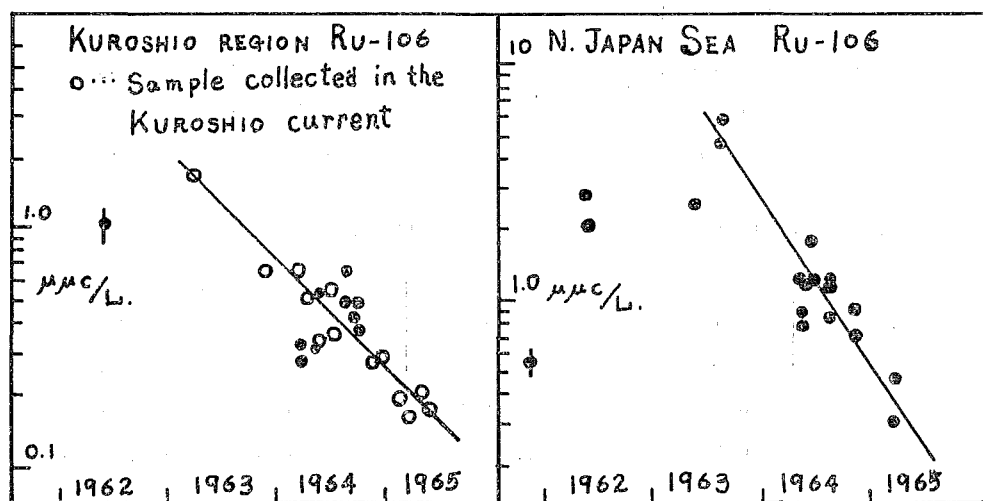


Fig. 1-a. Secular variation of Ru-106 in surface sea water.

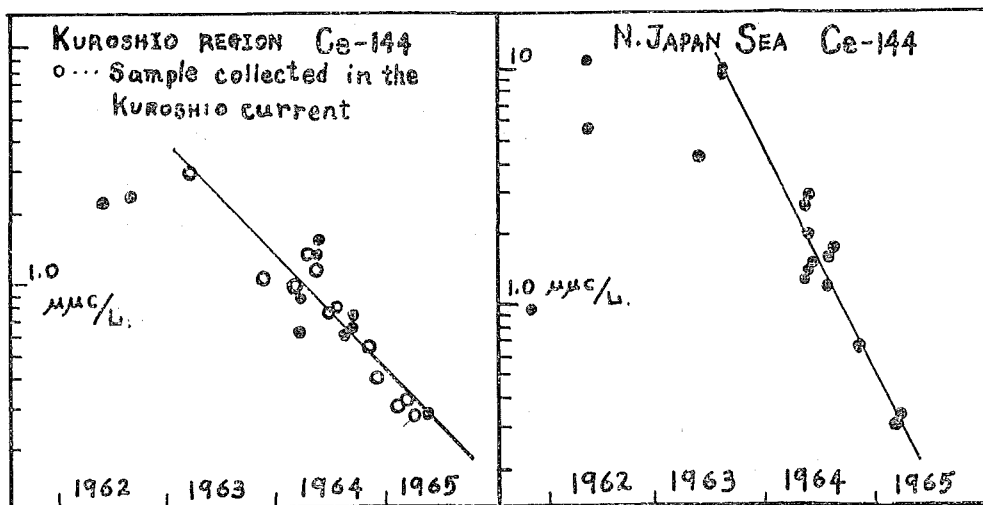


Fig. 1-b. Secular variation of Ce-144 in surface sea water.



horizontal mixing with the sea water of lower radioactivity coming from low latitude area rather than vertical mixing. Therefore, there are no difference between the corrected half-life of Ru-106 and that of Ce-144.

## 5. Discussion of the Analytical Method

### *Adsorption of Ru-106 to the container*

The adsorption of Ru-106 to the polyethylene container was investigated by adding Ru-106 tracer to two 500 ml. portions of sea water that were contained in 500 ml. polyethylene bottles, and adjusting pH to 1.5 and 6 respectively. They were stood aside for 2 days. After carrier was added, Ru was precipitated as hydroxide, dissolved in hydrochloric acid, adjusted to 5 ml., and counted by a well type scintillation counter. When the sea water sample was acidified to pH 1.5 by adding 2 ml. of conc. HCl per liter of sea water, 95% of added Ru-106 was recovered, but when pH was adjusted to about 6, only 56% of Ru-106 was recovered.

As for Ru-106 in sea water in situ., Ru carrier and conc. HCl was added immediately after sampling. After standing aside for 10 days, Ru-106 was analyzed. Results are shown in Table 6. There are no difference in the results between the sample in which only HCl was added and that in which HCl and Ru carrier was added. These results indicate that the adsorption of Ru-106 to polyethylene was negligible when the sample was adjusted to pH 1.5 by adding HCl.

### *Oxidation and reduction pretreatments*

The values of Ru-106 were increased by preliminary oxidation with antiformin and by reduction with sodium bisulphite and ethanol before the concentration of Ru from large volume of sea water. The results are shown in Table 7. This difference will be discussed later.

### *Radiochemical purification of Ru-106*

To concentrate Ru-106 from large volume of sea water (20-40 L.), the co-precipitation method with magnesium hydroxide which has been used for concentration of yttrium was applied (SHIOZAKI, et al. 1964). For the purpose of separation of ruthenium from rare earth nuclides, zirconium and great amount of magnesium in sea water, ruthenium was oxidized to Ru (VII) and made into solution by adding antiformin in alkali media. In this step, ruthenium was purified considerably, however, for further purification, solvent extraction method was used which consists of the extraction of ruthenium tetroxide oxidized by antiformin to carbontetrachloride and back-extraction to aqueous layer by reducing tetroxide to Ru (VI) by sodium bisulphite. The absorption spectrum of Ru (IV) which was used for chemical yield determination is shown in Fig. 2. This spectrum agrees very well with that reported by WATERBURY et al (1960), and shows good reproducibilities. The beta ray energy absorption curves and decay curves of samples are shown in Figs. 3 and 4. These curves agree with those of standard Ru-106—Rh-106. In any decay curves of sample, the effects of Ru-103 are negligible. This may be due to marked lowness of beta energy of Ru-103 compared with that of Rh-106.



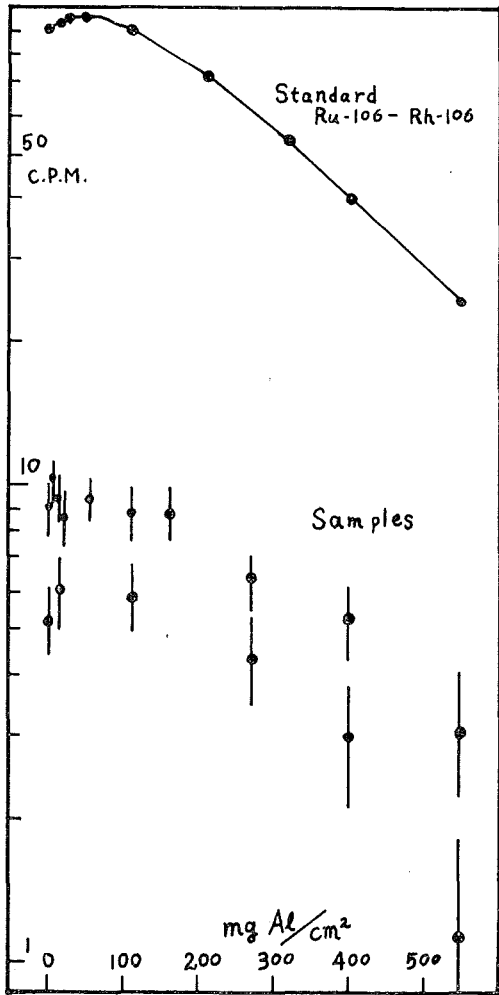


Fig. 3. Energy absorption curves of Ru-fraction of Samples.

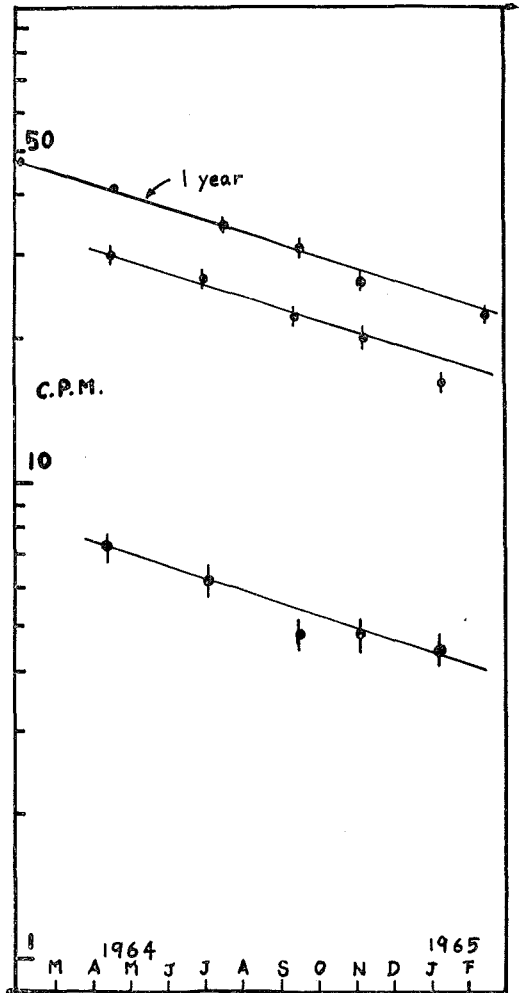


Fig. 4. Decay curves of Ru-fraction of samples.

results are shown in Table 9. When Ru (VI) is present in sea water as high oxidation state ruthenium, there is difference between the results of Ox-Red method and Hydr. method. However, Ru (VI) is oxidizing agent and very easily reduced to  $\text{RuO}_2$  by organic matter, therefore, it is difficult to think that high oxidation state ruthenium is present stably in sea water. As the nitrosyl complex compound is considered to be the most important inorganic complex of ruthenium, the tracer of the chemical form of nitrosyl ruthenium chloride was added, but there was no difference between Ox-Red method and Hydr. method. As the chemical form other than nitrosyl ruthenium chloride, nitrosyl ruthenium nitrocomplex can be considered to be present in sea water. Nitro complex is formed by  $\text{NO}_2^-$  ion in sea water. To investigate the effect of  $\text{NO}_2^-$  on the formation of nitrosyl ruthenium nitro complex, Hydr. method was conducted using artificial sea water containing known amount of  $\text{NO}_2^-$  ion and Ru-106. Results are shown in Table 10. It is proved that the presence of  $1 \mu\text{g-atom/L.}$  of  $\text{NO}_2^-$  in sea water produces the considerable difference between them. These results may indicate that nitrosyl ruthenium nitro complex may have been produced when the acidified sample was stood aside for several days from sampling to analysis.

TABLE 9. THE RESULTS OF TRACER EXPERIMENTS OF NITROSYL RUTHENIUM COMPLEX COMPOUND AND HIGH OXIDATION RUTHENIUM.

Chemical form of tracer	Non-radioactive Ru	Tracer added	Ox-Red	Hydr.
Nitrosyl ruthenium	40 $\mu\text{g./L.}$	764 c. p. m.	759 c. p. m.	746 c. p. m.
Pottasium ruthenate	80 $\mu\text{g./L.}$	1258 c. p. m.	1259 c. p. m.	989 c. p. m.

TABLE 10. THE EFFECT OF  $\text{NO}_2^-$  CONCENTRATION IN SEA WATER TO THE NITROSYL RUTHENIUM NITRO COMPLEX FORMATION.

$\text{NO}_2^-$ concentration in sea water	Tracer added	Hydr.	Recovery
0 $\mu\text{g-atom./L.}$	1996 $\pm$ 10	1964 $\pm$ 10	98.5%
1 $\mu\text{g-atom./L.}$		1920 $\pm$ 9	81.3%

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