RADIO CHEMICAL ANALISIS OF STRONTIUME 90 AND CESIUM 137 IN SEA WATER

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Abstract

In order to investigate the contamination of sea water by artificial radioactive materials in adjacent sea of Japan, Sr-90 and Cs-137 are separated from sea water sample of large volume which were collected at 4 stations in the Pacific Ocean, and analysis radiochemically. Sr is analyzed by Nitric acid method. Cs is absorbed to Nickel Ferrocyanide to separate from large volume water and is analyzed by ammonium phosphomolybdate method and by chloroplatinate method.

1. Introduction

Most of the artificial radioactive materials in the adjacent sea of Japan are considered as brought by ocean currents—the North Equatrial Current and the Kuroshio—from the Bikini and Eniwetok atolls, for the fraction of activity in the cause of fall out is very low compared with that of transported by ocean currents (Miyake and Saruhashi, 1958); and the main spot of contaminated water mass will arrive to the adjacent sea of Japan 6—9 months after nuclear explosions at the Bikini and Eniwetok atolls.

On the other hand, mixing of the radioactive materials in the Kuroshio with the waters near the current is very distinguished, as the Kuroshio is very intricate locally (e. g. Yoshida, 1959). Then, it might be supposed that the more the atomic explosions are tested near the Bikini and Eniwetok atolls, the higher the concentration of long-life nuclides of fission—for instances Sr-90 and Cs-137—will be.

But, the concentration of Sr-90 and Cs-137 are very small compared with the maximum permisible concentration and also the biological concentration factor in the sea is not very large for these elements, therefore the distribution of Sr-90 and Cs-137 should be made to confirm experimentaly as to its variation in space and its time change and these results could be available for study of the radioactive waste disposal into the sea.

Recently the method of analysis of Sr-90 in large volume sea water has progressed by use of chelate complex (Sugihara and Bowen, 1959; Miyake and Saruhashi, 1959) and Cs-137 has been analysed using sodium-cobaltinitrite (Sugihara and Bowen, 1959).

N. Yamagata and S. Matsuda(1958) estimated Cs-137 concentration in coastal waters from the analysis of Cs-137 in bittern and carnallite.

Difficulty in this analysis is that, the concentrations of these nuclides are very small, therefore, these nuclides must be condensed from large volume sea water sample at the first step of the analysis.

The authers proved that a Nickel Ferrocyanide is useful in analysis Cs-137 in large volume sea water and this method is now adapted to actual analysis of Cs-137 in the Pacific Waters.

In our analysis of Sr-90, expensive chelete reagent is not used but ordinary Nitrate-method, using Nitric acid, is adapted to the analysis.

The apparatus used in the present analysis are listed below.

Used Counter : G. M. Counter(Model 100) and Scintillation Counter(Well Type) by Scientific Research Institute Ltd. Tokyo, Japan.
Used Reagents : Analytical grade in Japanese Industrial Engineering Table.
Used Standard of Radiation:
Ra D. E. F. : dpm. standardized by the Electro technical Laboratory of the Ministry of International Trade and Industry.
Sr-90 : dpm standardized in comparison with Ra D. E .F.
Cs-137 : dpm standardized in comparison with Ra D. E .F.

2. Condensation of Cs-137 from Sea Water

T. Takaya(1959) made an experiment in detail on the absorption of Cs to Ferrocyanide in aqueous solution and found that Nickel Ferrocyanide is very effective for the decontamination of Cs-137 in aqueous solution.

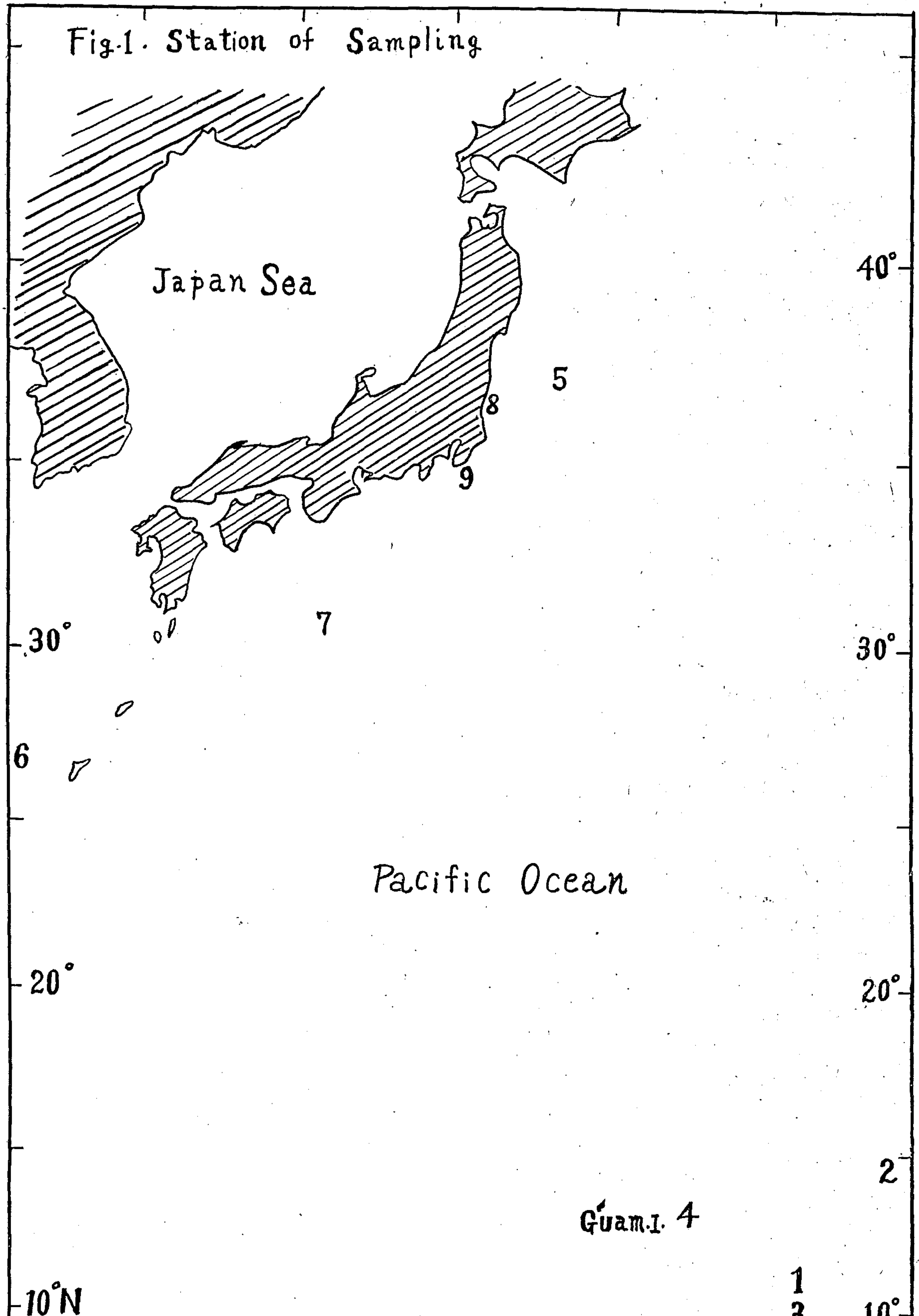
The authers adapted this method to the condensation of Cs-137 from sea water. Take each 100 ml of sea water to 5 beakers, and 2×10^5 cpm of Cs-137 to each beaker. Stir and pick up 5 ml of sea water into test tubes and count radioactivity using well type Scintillation counter (see Table 1). Then add 25 mg of $K_4Fe(CN)_63H_2O$ and $NiCl_2$ soln.(15 mg as Ni) to sea water

TABLE 1. CONDENSATION OF CS IN SEA WATER

Sample Sea Water: 100 ml added 2×10^5 cpm of Cs^{137}

Sample No.	Carrier and precipitate	Activity of Solution (1) cpm/5 ml	Activity of Supernate (11) cpm/5 ml	$\frac{(1)-(11)}{(1)}\times 100$
1	10 mg of Cs $Ni_2Fe(CN)_6$	9360±44	93±6	99.1
2	$Ni_2Fe(CN)_6$	9836±45	62±7	99.4
3	$Ni_2Fe(CN)_6$ $Fe(OH)_3$	9787±45	91±7	99.1
4	10 mg of Cs $Ni_2Fe(CN)_6$ $CaCO_3$	9731±44	10±6	99.9
5	$Ni_2Fe(CN)_6$ $CaCO_3$	9349±44	3±6	100.0

Fig.1. Station of Sampling



sample in these beakers, stir and let the precipitate settle over night. Pick up each 5ml of supernate in these beakers into test tubes and count radioactivity (see Table 1).

As a results the decontamination of Cs-137 in sea water sample is very sufficient, that is the efficiency of fixation for Cs ion is very high especially when $Ni_2Fe(CN)_6$ coprecipitates with $CaCO_3$.

3. Analysis of Sea Water

For this purpose 100 liters of sea water were collected at each of four stations in the Pacific Ocean and these locations are shown in Fig. 1 and 6 samples have been analyzed up to the present. All numerical values are shown in Table 2.

TABLE 2. Sr 90 AND Cs 137 IN SEA WATER

Sample No. volume (*l*)	2 100.0	4 101.5	5 100.0	6 39.1
Date of Sampling	14 July 58	11 Mar 59	2 July 59	4 June 59
Location	14°30′ N 153°53′ E	13°04′ N 147°31′ E	37°10′ N 143°14′ E	26°46′ N 126°01′ E
Sr–90 $\mu\mu$ c/*l*	0.29 ± 0.10	$0.4_6\pm0.0_4$	$0.5_5\pm0.0_4$	$0.8_7\pm0.03$
Cs–137 $\mu\mu$ c/*l*	——	$0.4_9\pm0.0_9$	——	$0.3_0\pm0.1_5$ ~~$1.6_3\pm0.1_4$~~
Rare-Earth	45 ± 0.6	$1.5_9\pm0.0_6$	$2.9_8\pm0.0_8$	$2.6_8\pm0.1_1$
Date of Counting	9 Oct. 58	12 Aug. 59	28 Sep. 59	20 Oct. 59

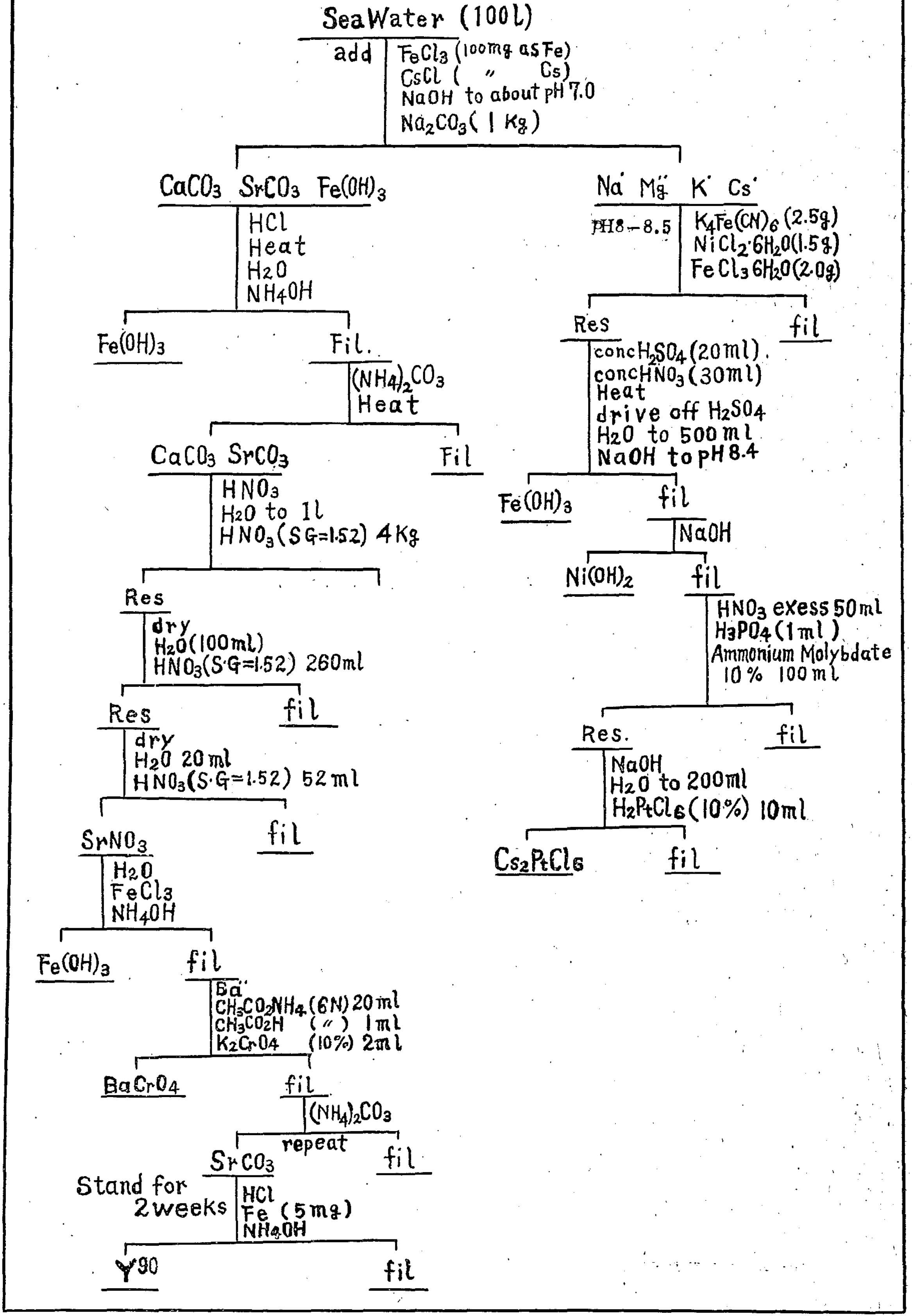
4. Procedure

Add 100 ml of HCl(12N) to sea water sample(100 L) on boad. As shown in Table 3, add the following carrier 100 mg of Fe as $FeCl_3$ soln., 100 mg of Cs as CsCl soln. and mix well. Add NaOH(6N) soln. to pH 7.0, add Na_2CO_3 soln.(1 kg of Na_2CO_3) and stir 2 hours. Let the precipitate settle a week. Siphon off the almost supernate and filiter this residue on 7.5 cm Toyo No. 5 C paper in a Büchner funnel. These supernate and filtrate constitute Cs-137 fraction. Separate Fe from the precipitate and count radioactivity of rare earth in $Fe(OH)_3$ using well type Scintillation counter.

Sr-90

Sea water contains about 40 g of Ca in 100 liters. So about 3 liters of HNO_3(S.G. = 1.45) is necessary to dissolve $Ca(NO_3)_2$. Use 4 kg of HNO_3 (S.G. = 1.52) at the first separation of Sr and Ca and at this step the contamination of Ca reduces to less than 1/10 of the former Ca concentration. Add very slowly 260 ml of HNO_3(S.G. = 1.52) at the 2nd separation and 52 ml of HNO_3(S.G. = 1.52) at 3rd separation.

TABLE 3 THE SCHEME OF ANALYSIS



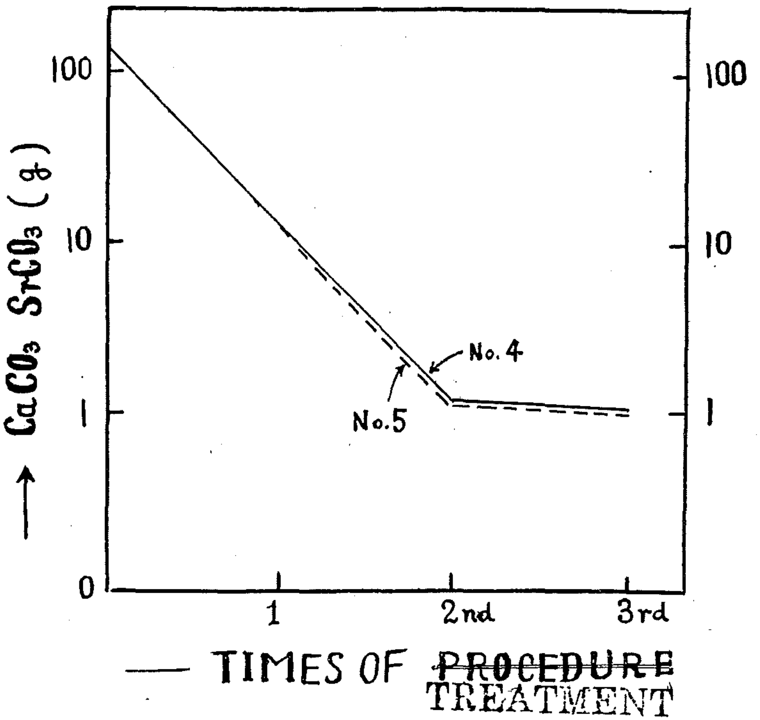


Fig.2 Separation of Ca and Sr

As shown in Fig. 2, purification of Sr is successful. Dissolve the dried $Sr(NO_3)_2$ in 200 ml of distilled water, add 10 mg of $Ba^{\cdot\cdot}$, 10 ml of CH_3COONH_4 (6N) and 1 ml of CH_3CO_2H(6N). Heat and add 2 ml of K_2CrO_4(10%). Filter off $BaCrO_4$ on a glass filter(No. 4) and add $(NH_4)_2CO_3$(6N) to the filtrate and then precipitate $SrCO_3$. Settle it 4 hours, filter this $SrCO_3$ on a glass filter(No. 4). Repeat these treatments of precipitation of $SrCO_3$.

Dry $SrCO_3$ 3 hours at 110°C and weigh it. Chemical yield of Sr is about 75%. Let $SrCO_3$ sample stand 2 weeks. Dissolve $SrCO_3$ by adding HCl(6N) in a 200 ml beaker on which covered with glass pan. Heat and drive off CO_2 from the solution, and dilute to 100 ml with distilled water and add 5 mg of $Fe^{\cdots}$. Precipitate Y-90 with $Fe(OH)_3$ at pH 8.4 and filter on a glass filter. Wash the precipitate with hot NH_4Cl(1%). Dissolve $Fe(OH)_3$ adding minimum volume of HCl(6N) and dry on a steam bath. Dissolve $FeCl_3$ with distilled water and transfer it in a stainless sample cylinder. Dry it on a steam bath and count radioactivity of Y-90.

Cs-137

It is difficult to filter directly $Ni_2Fe(CN)_6$ in separation of Cs, for this precipitate is very fine. Then add $FeCl_3$ soln. and coprecipitate with $Fe(OH)_3$. Siphon off the supernate and filter the residue on 7.5 cm Toyo No. 50 paper in a Büchner funnel. Wash with hot NH_4Cl(1%) soln. Transfer the precipitate with a filter paper into a beaker. Add 20 ml of conc. H_2SO_4 and 30 ml of conc. HNO_3 little by little and heat it. Decompose $Ni_2Fe(CN)_6$ and paper perfectly, drive off excess of H_2SO_4, and dissolve the residue in 500 ml of distilled water. Add NaOH soln. to pH 8.4, heat and leave it, then filter off $Fe(OH)_3$. Add NaOH(6N) to precipitate $Ni(OH)_2$ and filter it. Neutralize by adding HNO_3, add excess 50 ml of HNO_3(S.G. = 1.4) and 1 ml of conc.H_3PO_4, heat to 60°C, and add slowly 100 ml of ammonium molybdate(10%) while stiring. Let the yellow precipitate settle 4 hours and filter, wash the precipitate with HNO_3 (1N), and dissolve the precipitate adding minimum volume of hot NaOH(6N). Dilute to 200 ml with distilled water, add 10 ml of H_2PtCl_6(10%), and let the precipitate settle over night. Filter on 35 mm Toyo No. 5 C weighed paper, dry the precipitate of Cs_2PtCl_6 with filter paper at 110°C, and weigh it. Transfer Cs_2PtCl_6 with filter paper into test tube and count its radioactivity. Chemical yield is about 76%.

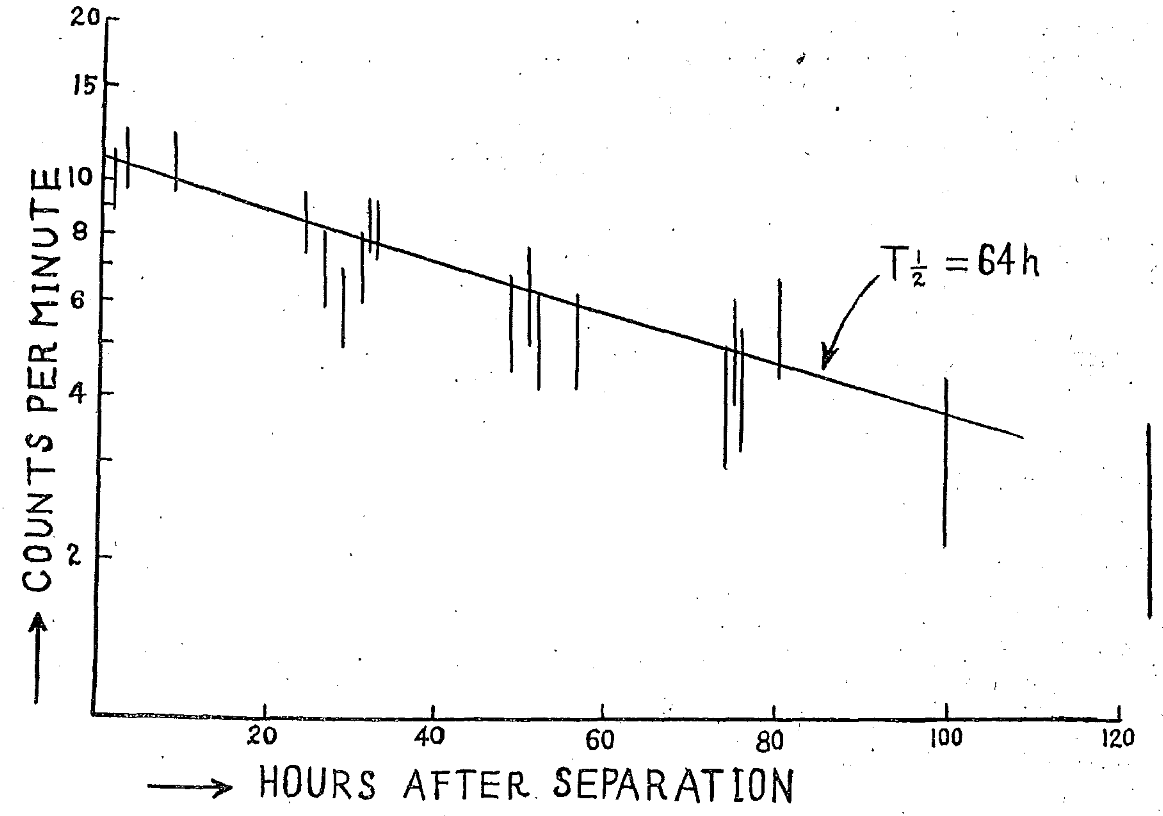


Fig. 3 Decay Curve for Y90 Fraction

5. Discussions

We found that our values in Table 2 are smaller compared with those obtained by Y. Miyake and his coworkers (1959). If this is due to the difference of assay techniques, we can consider two questions as follows.

(1) Separation of Sr from Ca may not be complete in our method.

(2) True counting efficiency for Y-90 might be somewhat lower than

obtained from our standard.

On the question (1), we hardly believe that Sr are contaminated with Ca because we performed with great care the separation of Sr from Ca with HNO_3 and also repeated the procedure three times as shown in Fig. 3.

We intend to make further check on this point by using flame spectrum method. On the question (2), we measured radioactivity of 5 mg of Fe (containing Y-90) which is mounted directly on the sample cylinder for lack of suitable sized filter-stick. That is, we precipitated the ferric ions as hydroxide, filtered it off, dissolved the precipitate in small volume of HC1, evapolated excess HC1 on the steam bath, transfered it to the sample cylinder, and counted its radioactivity by G. M counter.

We took into consideration the corrections for thickness of mica window and of intermediate air mass which are due to the energy difference between sample and standard, however, if we discuss difference of efficiencies more strictly, we have to take into consideration the effect of the back scattering that is due to the difference between silver and stainless-steel, because Ra D. E. F is mounted on the silver plate, but samples are mounted on the stainless-steel. But, the difference is at most about 10%, and seems to have almost no correction to final values.

Therefore, we considered as follows; movement of the water mass in the sea is too complicated to draw out a definite conclusion and we have to have more observed data. As for rare earth elements, we intend to separate Ce from other elements and investigate the ratio of Ce-144 to Sr-90 or Cs-137.

6. Conclusions

Though the variations of the motion of water mass are so complicated that we cannot draw a definite conclusion from these few data, we can presume from these analytical data that the concentrations of Sr-90 and Cs-137 in the surface sea water of the Western Pacific Ocean in 1959 are about 1 $\mu\mu c/L$. Analysis of sea water samples which were collected from different regions is now going on in our laboratory and more definite picture of long-life radioactivities in the Western Pacific is expected to be present in near future.

Acknowledgements

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References

Miyake, Y. etal 1958, Distributions of Artificial Radioactivity in the Pacific Ocean. Read at the Annual Meeting of the Oceanogr. Soc. of Japan in April, 1958.

Miyake, Y. and Saruhashi, K. 1959, Sr-90 in Sea Water. Read at the first Meeting of the Japan Radiation Research, in Oct., 1958.

Sugihara, T. and Bowen, V. 1959, Analytical Chemistry, 31, 44-49.

Takaya, T. 1959, Collected Abstracts of the third Symposium on Atomic Energy sponsored by Science Council of Japan, P. 23.

Yamagata, N. and Matsuda, S. 1958, Cs-137 Concentration in the Coastal waters of Japan. Read at the Annual Meeting of the Oceanogr. Soc. of Japan, in Nov., 1958.

Yoshida, S. 1959, Short Period Fluctuations of the Kuroshio. Read at the Annual Meeting of the Oceanogr. Soc. of Japan in Oct., 1959.