Cesium-137 in the Coastal Waters of Japan

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The levels of radioactive cesium-137 in various materials have been analyzed by the authors and their colleagues since May 1957. A part of the results was compiled by Hiyama and presented to the Scientific Committee on the Effects of Atomic Radiation[1]; the full report is to be published in near future. The analytical data from other countries for cesium-137 in various materials are also available in the U.N. Report[2]. However, we have received no information on the level of cesium-137 in sea-water although that of strontium-90 was presented by Bowen in 1957[3]. It is necessary to know the level of the concentration of cesium-137 in oceanic water caused by nuclear fission explosions and also to guess a tolerable discharge rate of radioactive waste, especially for the Japanese people for whom marine products are the principal sources of proteins.

The cumulative ground deposit in Japan of strontium-90 has been shown by Miyake to be about 8 mc/km^2 in June 1957[4], and perhaps this value is also valid for cesium-137, of which the fission yield and the half-life are almost the same. If we consider temporarily that the sea-water is uniformly mixed to the depth of 100 m., then about 80 $\mu\mu$c of cesium-137 is expected to be present in one kilo-liter of sea-water. The sensitivity for cesium-137 measurement was about 100 $\mu\mu$c, and so it was a matter of actual difficulty to deal with kilo-liters of sea-water in the laboratory. Fortunately, domestic salt is commonly produced directly from sea-water in Japan; hence bittern or carnallite of industrial origin could be chosen as the starting material.

The Behavior of Cesium during the Evaporation of Sea-water.— It is a well known fact that cesium and rubidium are enriched in carnallite as compared in sea-water. Jander and Busch found 0.0002% of cesium chloride in Stassfurt carnallite on the average[5]. In the manufacturing process by solar and vacuum evaporation, cesium and rubidium have also been expected to be enriched in bittern and carnallite. The authors performed several experiments by the use of radioactive tracers ^{86}Rb and ^{137}Cs. Small fractions of sodium chloride and potassium chloride were crystallized respectively from their saturated aqueous solution by the isothermal evaporation. Both the activities of the crystal and of the evaporation residue of the initial solution were measured and the logarithmic distribution coefficient λ was calculated from the equation:

$$\lambda \log \frac{\text{NaCl (Total)}}{\text{NaCl(Total)-NaCl(Crystal)}} = \frac{{}^{137}\text{Cs (Total)}}{{}^{137}\text{Cs(Total)-}{}^{137}\text{Cs(Crystal)}}$$

In case of carnallite crystallization, activities were measured for both the initial solution and the mother liquor. The

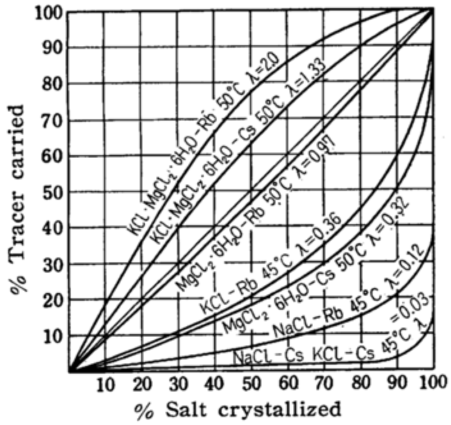

Fig. 1. Efficiency with which the traces of cesium and rubidium are carried by crystallization of several oceanic salts.

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1) "Radiological Data in Japan II", edited by Y. Hiyama, Government of Japan, Sept. 1957; U. N. General Assembly A/AC. 82/G/R. 30 (1958).

2) "The Effects of Atomic Radiation", U. N. Report Annex D, A/AC. 82/R. 65/Add. 3 (1958).

3) V. T. Bowen, "Some Geochemical Studies at the Air-Water Interface", presented to the N. R. C. Meteorology Panel, Sept. 25, 1957.

4) Y. Miyake and K. Saruhashi, *Papers in Meteorology and Geophysics*, 8, 242 (1957); U. N. General Assembly, A/AC. 82/R.R. 65/Add. 3 Table XIV (1958).

5) G. Jander and F. Busch, *Z. anorg. u. allg. Chem.*, 187, 165 (1930).

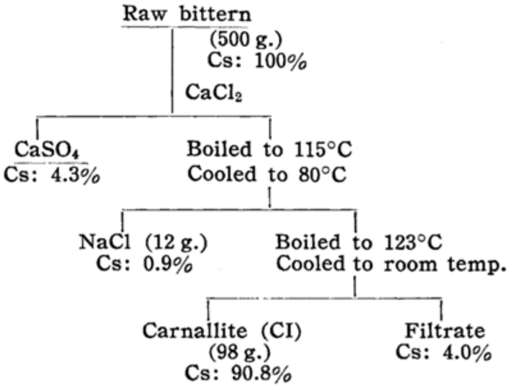

Fig. 2. Loss of cesium in the process of crystallization of carnallite from bittern.

results summarized in Fig. 1⁶⁾ are in accord with the fact that cesium and rubidium have been naturally enriched in carnallite, and this nature will be useful for the practical concentration aimed at cesium-137 determination in sea-water. However, as the industrial conditions of carnallite formation greatly differ from the natural, the authors attempted to check the concentration procedure for cesium with a tracer experiment. The procedure and the loss of cesium is schematically shown in Fig. 2; the recovery of cesium is satisfactory.

Recrystallization of Carnallite.—Further enrichment of cesium can be accomplished by fractional recrystallization of carnallite. Halperin and Sambursky applied this method to the determination of rubidium in Dead-Sea carnallites⁷⁾. As easily conceivable from the well-known phase diagram of the system $KCl-MgCl_2-H_2O$, on evaporation of the solution of artificial carnallite which contains a few per cent of sodium chloride, first only sodium and potassium chloride are deposited until the so-called "carnallite point" is reached, where the deposition of carnallite begins. The authors have modified this method for the practical convenience as described below.

A quantity of hot water less than that sufficient for complete dissolving is added to the primary carnallite (CI) and the suspension is cooled with vigorous agitation. Undissolved sodium and potassium chloride are filtered off and the filtrate is boiled until the boiling point reaches 123°C and then cooled to room temperature. The second carnallite (CII) thus obtained is only about one fourth the weight of the primary carnallite and contained 92.6% of the original cesium, so that a fourfold enrichment in concentration of this element can be obtained (Fig. 3).

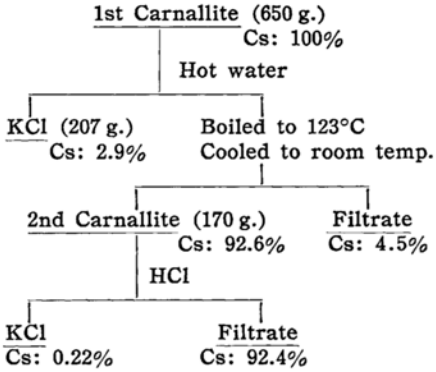

Fig. 3. Loss of cesium in the process of recrystallization of carnallite.

Another recrystallization of CII resulted in the formation of the third carnallite (CIII) weighing about 600~800 g. which was expected to contain 70~80% of the total cesium originally existing in 50 kg. of bittern. When started from 2.5 kg. of the industrial carnallite sample, only one recrystallization was required to make the mass suitable for the further treatment of cesium separation. The chemical composition of several samples of bittern and carnallite is shown in Table I. An early experiment revealed that only 20 kg. of bittern or 1 kg. of carnallite was sufficient for cesium-137 determination and the later determination were made on this scale.

Separation and Determination of Cesium in Carnallite.—An aliquot of the saturated solution of the final carnallite was reserved for the flame photometric determination of natural cesium and the remainder was made 2.5 N acid with hydrochloric acid after the addition of carrier cesium chloride (100 mg. as Cs). Precipitated potassium chloride was filtered off and to the filtrate was added sodium silicomolybdate solution*⁾ at 60~70°C with constant agitation. After cooling, the precipitate of cesium silicomolybdate was filtered off and washed with 2.5 N hydrochloric acid and then with water. The precipitate was dissolved with the least possible amount of hot 10% solution of sodium hydroxide. The undissolved silica was filtered off and

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6) S. Matsuda, *J. Mineral. Soc. Japan* (*Kôbutsugaku-Zasshi*), 3, 523 (1958).

7) A. Halperin and S. Sambursky, *Bull. Research Council of Israel*, 2, 107 (1952).

* Prepared by the method of Jander and Busch, loc. cited.

TABLE I. CHEMICAL COMPOSITION OF BITTERN AND CARNALLITE

(g./100 g.)

Location	Sample	KCl	NaCl	$MgCl_2$	$MgSO_4$	Total
Onahama	Bittern	3.84	4.03	19.1	6.43	33.4
	CII	18.6	10.7	31.2	0.24	60.7
	CIII	20.7	8.60	33.0	0.19	62.5
Horobetsu	Bittern	3.28	7.92	16.1	3.56	30.9
	CII	19.0	8.67	31.3	0.45	59.4
	CIII	23.5	5.68	31.2	0.19	60.6
Akao	Carnallite	19.1	14.8	32.7	0.45	67.1
	CII	19.4	7.48	31.7	0.39	59.0
Hōfu	Carnallite	23.9	15.5	31.4	0.67	71.5
	CII	20.6	6.87	31.5	0.16	59.1
Tōji	Carnallite	16.4	5.95	30.9	4.95	58.2
	CII	20.5	5.07	32.2	0.42	58.2
Theor. Carnallite $KCl\cdot MgCl_2\cdot 6H_2O$		26.8	0	34.3	0	61.1

TABLE II. CESIUM-137 CONCENTRATION IN BITTERN AND CARNALLITE

Loc. No.	Location	Sample No.*	Date of Manufacture	^{137}Cs Conc.	$\mu\mu c$**
1	Horobetsu, Hokkaidō	B-1	Oct. 1957	500	± 21
		B-14	Mar. 1958	200	24
2	Watanoha, Miyagi Pref.	B-13	Mar. 1958	1800	46
3	Onahama, Fukushima Pref.	B-2	Aug. 1957	430	17
		B-3	June 1957	290	33
		B-4	Mar. 1958	270	33
4	Asahi, Chiba Pref.	B-8	Mar. 1958	4950	50
5	Kurobe, Toyama Pref.	B-15	Apr. 1958	220	48
6	Kira, Aichi Pref.	B-12	Mar. 1958	2600	60
7	Akao, Hyōgo Pref.	C-3	Oct. 1957	680	20
		C-6	Mar. 1958	450	15
		B-6	Mar. 1958	1300	40
8	Tōji, Okayama Pref.	C-2	Sept. 1957	1450	58
		C-5	Mar. 1958	1650	46
		B-5	Mar. 1958	1500	52
9	Matsunaga, Hiroshima Pref.	B-7	Mar. 1958	1700	48
		C-4	Mar. 1958	1400	31
10	Hōfu, Yamaguchi Pref.	C-1	June 1956	800	40
11	Naruto, Tokushima Pref.	B-10	Mar. 1958	2100	44
12	Takuma, Kagawa Pref.	C-7	Aug. 1957	1800	46
		C-8	Mar. 1958	1200	83
		B-9	Mar. 1958	1500	55
13	Takada, Ōita Pref.	B-11	Mar. 1958	2500	45

* B indicates bittern and C indicates carnallite sample.

** Computed for the basis of 50 kg. bittern.

after the filtrate was made up to about 300 ml. with water, 10% aqueous solution of chloroplatinic acid was added to precipitate the cesium. The precipitate was washed with water and then with ethyl alcohol, dried at 110°C, weighed and mounted for counting.

Radioassay was performed by β-counting by the use of a shielded GM-tube of the mica end-window type and the result was corrected for the absorption and the scattering of cesium chloroplatinate and the chemical yield. Details of the later steps of separation and radiochemical determination have already been described[8,9]. Contamination of the final precipitate of cesium chloroplatinate with other fission activities, potassium-40, and rubidium-87 is negligibly small[9].

In the determination of natural cesium, it is necessary to take care, not to introduce contamination resulting from the reagents to be used. As there is no evidence of the absence of a trace of cesium in sodium salt, the dipicrylamine has been chosen as the precipitant for potassium. The reagent can easily be purified and a tracer experiment has proved that potassium dipicrylaminate effectively carries down traces of cesium.

An aliquot of the saturated solution of the final carnallite containing approximately 0.1 g. of potassium was diluted to about 50 ml. and treated with magnesium dipicrylaminate solution. The separation of potassium and cesium from the precipitated dipicrylaminate was accomplished in the simple way by the methyl isobutyl ketone extraction, of which the principle was previously reported[10]. The intensity of cesium 852.1 mμ line was measured in the usual way.

Materials and Results

Fifteen samples of bittern and eight samples of carnallite manufactured during June 1956 and April 1958 were collected around Japan. The location and the date of manufacture are shown in Table II and Fig. 4. The outline of manufacture of salt in Japan must be described to serve for the later discussion. The modern system of manufacture is entirely artificial, driven by electric power. Sea-water is pumped up directly into a vacuum evaporator and is never exposed to the open air, so the consideration about atmospheric contamination during the whole production process is unnecessary. The samples of bittern manufactured by this system are B-1, 2, 3, 4, 14 and 15 in Table II. On the other hand, the other samples have been manufactured by the usual salt-field system. In this case, sea-water is exposed to the open air, so that, we must consider the influence of fall-out during production.

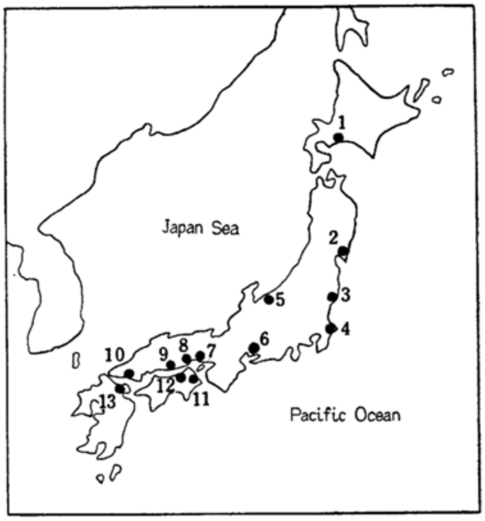

Fig. 4. Locations materials obtained.

The results are shown in Table II. Four kilo-liters of sea-water will produce about 50 kg. of bittern which are equivalent to about 2.7 kg. of carnallite. Values in Table II have been computed on the basis of 50 kg. of bittern. The analytical data for the natural cesium content of several samples are shown in Table III in which the isotopic ratios of cesium-137 and -133 have also been calculated.

The Natural Cesium Content of Sea-water.—Several authors have given surprisingly different values for the cesium content of sea-water. The maximum value is 4.3 μg. whereas the minimum is only 0.002 μg. per liter. The earliest estimate was given by Goldschmidt et al. as 2 μg.[11], although it was not based on actual determination in sea-water. Harada reported values from 0.002 to 0.01 μg.[12] Minami et al. started from about 50 ml. of

TABLE III. ISOTOPIC RATIO OF CESIUM-137 TO -133 IN BITTERN AND CARNALLITE

Sample No.	^{133}Cs mg.	^{137}Cs μμc	^{137}Cs/^{133}Cs $\times 10^9$
B-3	0.21	130	7.7
B-5	0.33	590	22
B-7	0.52	650	16
B-10	0.30	960	40
B-11	0.56	1060	24
B-14	0.26	85	4.1
C-4	0.25	1200	60
C-5	0.22	610	35
C-7	0.33	670	25

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[8] N. Yamagata et al., *Japan Analyst* (*Bunseki Kagaku*), 7, 433 (1958).

[9] N. Yamagata and T. Yamagata, This Bulletin, **31**, 1063 (1958).

[10] N. Yamagata and S. Watanabe, ibid. **30**, 580 (1957).

[11] V. M. Goldschmidt et al., *Nachr. Ges. Wiss. Göttingen, Math.-Physik. Klasse*, **1933**, 235.

[12] Y. Harada, *J. Chem. Soc. Japan* (*Nippon Kwagaku Kwaisi*), **64**, 1049 (1943); Those values were apparently misabstracted as 2∼10 μg./l. in the *Chem. Abstr.*, **41**, 3394 (1947).

sea-water, by use of the cathode layer emission spectroscopy and gave the value of 0.1~1 μg. per liter(13). Ishibashi and Hara reported values from 3.4 to 4.3 μg.(14) Recently, the most sensitive radioactivation analysis was applied by Smales and Salmon and the value of 0.5 μg. (±10%) per liter was reported(15). The relative proportions of the major constituents in sea-water are practically constant, although some of the micro-elements of biological activities may fluctuate with time and space. On account of the strongly ionic nature of this element and its biological insignificancy, we can not guess any proper reason for real fluctuations of the concentration of cesium in the open oceans. In fact, the levels of cesium given by Smales and Salmon have been fixed within narrow limits for sea-water from the Atlantic Ocean including a sample of coastal water. The circumstance is considered also valid for the Pacific Ocean and the coastal waters of Japan. On the assumption that the value of 0.5 μg. is correct for the sea waters around Japan, we should like to proceed with the discussions in the following section.

Discussion

The concentration of cesium-137 in samples other than Location No. 1, 3 and 5 is considerably higher by factors of 5 to 10 or more than that in the latter locations; the trend is clear also in the isotopic ratio. The difference may be attributed principally to the contamination by fall-out during production. We can guess the possible contamination as follows. One of the salt-field systems of obtaining the brine from sea-water is the oldest, called the "Irihama" system and the evaporation is effected principally by the sun. For instance, in March 1958 ,at Watanoha, Miyagi Prefecture (Loc. No. 2), 12 kl. of brine of specific gravity ($d_4^{15}=1.125$) 16.0° Bé was produced per hectare in two days. Another plan to obtain the brine is a combination of the system of evaporation by the sun and air called the " flowing-down " system. For instance, 120 kl. of sea water is treated per day per hectare by this system. From these figures we can guess the possible contamination of 50 kg. of bittern approximately as 0.3~6 mμc when the fall-out rate of cesium is temporarily assumed to be 0.03~0.3 mc/km²/month in early 1958.

The above computation indicates that the bittern and the carnallite obtained at the locations other than No. 1, 3 and 5 where salt is produced by the salt-field system are possibly contaminated by fall-out during production to a great extent. Only the results obtained for the bitterns from the locations No. 1, 3 and 5 are reliable to enable us to guess the levels of concentration of cesium-137 in sea-water. On the basis of the approximate figure of the weight of bittern equivalent to the volume of sea water, viz., 50 kg. to 4kl. and of 70% of the over-all yield of cesium, we can compute the concentration of cesium-137 in sea-water approximately to be 70~150 μμc/kl. The values of 160 and 310 μμc/kl. are also derived on the basis that the isotopic ratio of cesium-137 to -133 is 4.1 and 7.7×10^{-9} (Table III) and the cesium-133 content of sea-water is 0.5 μg./l.

The greater part of the domestic salt consumed in Japan comes from sea-salt and an average person takes approximately 15 g. of sodium chloride every day. The average daily intake of cesium-137 by a Japanese in the period from Aug. 1957 to Aug. 1958 is determined by the authors to be 22~56 μμc. The contribution of sea-salt to the total intake of cesium-137 by a person may be roughly computed if the assumption is admitted that the cesium in sea-water moves into the salt during manufacture following the distribution law by the coefficient of 0.03 (Fig. 1). Thus, the weight ratio of Cs/Na in the salt shall be 1.5×10^{-9} as compared with the ratio of 5×10^{-8} in sea-water (calculated from the values, 0.5 μg. of cesium and 10 g. of sodium in one liter). When we take the ratio of cesium-137 to -133 in sea water approximately to be 10^{-8} or 1 mμc of cesium-137 per 1 mg. of cesium-133, 15 g. of sodium chloride shall contain 0.01 μμc of cesium-137. It means that the contribution of sea-salt to the total intake of radioactive cesium-137 by a person is only 10^{-3} or less.

The β-counting equipment used by the authors was a usual mica end-window type GM-counter shielded by lead blocks. Natural background was 10~12 c.p.m. and counting efficiency was 5.3% for cesium-137 by our experimental conditions. About 100 μμc was the minimum amount of cesium-137 to be measured with a standard error of ±10%. Our present program includes the arrangement of a low-level β-counting equipment. With this, only 50~100 liters of sea-water

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13) E. Minami, N. Yamagata et al., Read at the Symposium, held by the Chemical Society of Japan for Geochemistry at Nagoya Univ. (1947). Not published.

14) M. Ishibashi and T. Hara, *Bull. Inst. Chem. Res., Kyoto Univ.*, **32**, 248 (1954).

15) A. A. Smales and L. Salmon, *Analyst*, **80**, 37 (1955).

are sufficient for cesium-137 determination. With a slight modification of the separation method direct separation from sea-water will be possible.

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