On the Amount of Cesium Dissolved in Sea-water*

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The amount of cesium dissolved in sea-water was determined by the new colorimetric method using $HBiI_4$ reagent, and it was found to be 0.4~1.3 μg/liter. Moreover, a correlation of the amounts of alkali elements dissolved in sea-water was sought by using the mean values of those elements as found by the author. As a result, the amounts of sodium, potassium, rubidium and cesium in sea-water were found to obey the following linear equation, $y=-0.203x+4.8$.

INTRODUCTION

The amount of cesium dissolved in sea-water seems to be very small, and its determination is especially difficult since a large number of similar elements such as potassium and rubidium are also present. Several reports concerning the amount of cesium dissolved in sea-water have already been made. The value which was presumed by Goldschmidt[1] based on the report[2] that the ratio of rubidium to cesium is 100 : 1, has been adopted as the amount of cesium dissolved in sea-water, that is to say, 2 μg/liter[3]. Thereafter, Ishibashi and Harada[4] were the first to estimate the amount of cesium starting from 285 liters of brine and the amount of cesium in one liter of sea-water was found to be $2\sim10\times10^{-3}$ μg. Then Ishibashi and Hara[5] reported that one liter of seawater at Suma and at the offing of Shirahama contained 3.4~4.3 μg. However, after a short time these values were corrected to 0.4~1.3 μg because dipicrylamine which had been repeatedly used, was found to contain a considerable amount of cesium. Recently, the amount of cesium in sea-water was determined by the activation analysis and was found to be 0.5 ± 0.05 μg/liter[6].

This paper deals with the determination of cesium dissolved in sea-water through the application of the method for the determination of a small amount of cesium. The recovery of the cesium from sea-water was radiometrically determined by using Cs-137 as a tracer and measuring its radioactivity in the fiinal stage.

REAGENTS

Sodium cobaltinitrite : 50 grams of $Co(NO_3)_3\cdot6H_2O$ and 110 grams of $NaNO_2$ are dissolved in 300 ml. of water and 40 ml. of 50% acetic acid is added. After removal of the nitrogen dioxide gas by suction for 12 hours, the solution is

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filtered.

Dipicrylamine (H_H) : The H_K precipitated in a slightly alkaline solution is dissolved in a minimum amount of acetone. The amine precipitated with nitric acid is digested in hot water, filtered and washed.

Reagent (a) : 9*N*-$NaNO_2$ solution.

Reagent (b) : 20.5 grams of Bi $(NO_3)_3 \cdot 5H_2O$ and 2 grams of $AgNO_3$ are dissolved in 100 ml. of 6*N*-CH_3COOH. The solution is filtered through a glass-filter.

Reagent (c) : A mixture of 3 parts of reagent (a) and 2 parts of reagent (b).

Cs^{137} Standard solution : The Cs^{137} in the from of CsCl solution was obtained as a processed isotope from the U. S. Atomic Energy Commission, Isotopes Division, Oak Ridge, Tenn. 20 mg. of ammonium chloride, excess perchloric acid and ethyl alcohol are added to 50 ml. of the solution which is obtained by dilution of 0.7 ml. of original solution to a liter——here, 1 ml. corresponds to approximately 1 μC. $Cs^{137}ClO_4$ obtained by precipitation with ammonium perchlorate is dissolved in hot water and diluted to 25 ml. with distilled water. One ml. of the solution has nearly the strength of 2 μC. The mass of Cs^{137} which has the strength of 2 μC, is theoretically computed from the following formula :

$$M = 3.7 \times 10^7 \times 1.44T \ (W/N) \times 2 \times 10^{-3} = 0.02828 \ \mu g$$

where, M = mass of the radioactive isotope which has the strength of 2 μC. (μg) ; W = atomic weight ; T = half-life (sec.) ; N = Avogadro's Number (6.02×10^{23}).

This assured us that further experiments would be free from any disturbance due to the mass of Cs^{137}. A measurement of the radioactivity was made by a mica-window GM counter.

EXPERIMEMT

(1) Procedure

To 10 liters of sea-water in a small necked bottle, 1 ml. of the Cs^{137} standard solution and 200 ml. of $Na_3Co(NO_2)_6$ reagent are added. In about three hours, the resulting cobaltinitrites of potassium, rubidium and cesium completely fall down to the bottom and the supernatant liquid is siphoned off as much as possible. It has already been reported that under the above conditions, if the temperature of solution is below 10°C, a small amount of rubidium and cesium in solution is quantitatively precipitated, but that with a rise in temperature the recovery of rubidium and cesium decreases remarkably. The precipitates are transferred into a beaker and dissolved by heating with 4 ml. of conc. H_2SO_4. Then cobalt is removed as the hydroxide, and it is reprecipitated. H_H is added to the hot filtrate and after cooling, H_K, H_{Rb} and H_{Cs} are obtained by means of the conventional method. After removal of H_H, the filtrate is evaporated until a crystal deposits on the vessel wall. Then, the deposited KCl is filtered off and washed with conc. HCl. The filtrate is evaporated to the same volume as before, filtered and washed with HCl-C_2H_5OH (1 : 2) solution. Thus most of the KCl is removed from the rubidium and cesium. The chlorides are converted into the nitrates with nitric acid. The nitrates free from nitric acid are dissolved in 4 ml. of water, and 3 ml. of reagent (a) and 2 ml. of reagent (b) are added. After ice-cooling for two hours, the precipitates are washed five to six times with 0.8 ml. of the ice-cooled reagent (c) each time. The precipitates are recrystallized and dissolved with dil. HNO_3. Though the separation of rubidium and cesium from potassium can be done quantitatively by these operations, the details of procedure are not reported in this paper. With a few drops of 6 *N*-HCl and hydrogen sulfide gas, silver and bismuth are precipitated. After vaporization of the filtrate to dryness, the sum of rubidium and cesium is found by using 0.1 *N*-H_{Ca} reagent. The filtrate which is obtained by removal of the amine, is diluted to the mark of the vessel used in the previous study and the activity of the solution is measured by a GM counter. By comparison with that of the Cs^{137} standard solution under the same conditions, the recovery of cesium is found to be efficient. After measurement of the cesium by the previously mentioned procedure, the true amount of cesium dissolved in sea-water is obtained with a correction based upon the recovery. Thereafter, as 30 μg of cesium was found to have been contained in a definite amount of H_H which had been used for the precipitation of the dipicrylaminates of K, Rb and Cs, the values of cesium found in sea-water were further corrected.

Table 1. Analysis of sea-water at the offing of Suma.

Exp. No.	1	2	3
Sea-water (*l*)	10	10	10
Chlorinity (‰)	17.64	17.64	17.64
Soln temp. (°C)	11	11	11
H_{Rb+Cs} (mg.)	13.65	14.28	12.80
Rb found (μg/*l*)	223	232	209
Cs found (μg/10*l*)	36	33	30
Cs corrected (μg/10*l*)	(41-30)	(36-30)	(35-30)
Cs (μg/*l*)	1.1	0.6	0.5

Table 2. Analysis of sea-water at the offing of Shirahama and at Koganoura.

		Shirahama			Koganoura
	place	1	2	3	
Sea-water	volume (*l*)	10	10	10	10
	depth (m.)	5	10	45	5
	chlorinity (‰)	18.48	18.61	18.99	18.2
	soln temp. (°C)	13.5	13.5	13.5	13.5
H_{Rb+Cs} (mg.)		16.91	18.60	14.53	14.01
Rb found (μg./*l*)		276	304	273	229
Cs found (μg./10*l*)		27	32	35	30
Recovery (%)		72.3	73.0	75.1	82.5
Cs corrected (μg./10*l*)		(34-30)	(41-30)	(43-30)	(35-30)
Cs (μg./*l*)		0.4	1.1	1.3	0.5

The results are shown in Tables 1 and 2 respectively. In these experiments, the recovery was a little low due to the fact that the sea-water was treated immediately and the solution temperature was higher than 10°C. So the amounts found for rubidium were lower than the true values. Here the mean values of rubidium and cesium in one liter of sea-water were found to be 244 μg and 0.8 μg respectively.

(2) Determination of Cesium Dissolved in Brine

Rubidium and cesium were directly precipitated with an excess of H_H from two liters of brine, and their amounts were found by the same procedure as before. Table 3 shows the results obtained. It has already been reported by Ishibashi and Harada[7] that a linear relationships is found between the logarithmic millimole of the amount of sodium, potassium, rubidium and cesium in sea-water and their atomic number. Therefore the newly obtained data was applied to this regularity and their relation is shown in Table 4 and Fig. 2. As seen from Fig. 2, the cesium deviates considerably from the straight line. However, if (3N/2-W/4) is taken as the abscissa instead of the atomic number —here, N means the atomic number and W the atomic weight, the all points except those for lithium will be found to lie nearly on a straight line (Fig. 2). The straight line is represented by the following equation if the ordinate and the abscissa are replaced by y and x respectivery.

Table 3. Analysis of brine.

Brine taken	2 *l*
H_{Rb+Cs}	9900 μg
Rb found	1620 μg
Recovery	77 %
Cs in Brine	8.8μg/*l*
Cs corrected	2.8μg/*l*

Table 4. Data on the amount of alkali elements dissolved in sea-water.

Element	At. No.	At. Wt.	Amount (mg./kg.)	milli-mole	log	3N/2-W/4
Li	3	6.940	0.117*	0.01685	−1.77	2.76
Na	11	22.997	10470**	455.2	2.66	10.75
K	19	39.100	377.2	9.74	0.99	18.73
Rb	37	85.48	0.238	0.00278	−2.56	34.13
Cs	55	132.91	0.00076	0.00000571	−5.24	49.27
Fr	87	[223]	?	—	—	74.75

N : Atomic number.
W : Atomic Weight.
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$$y = -0.204x + 4.8$$

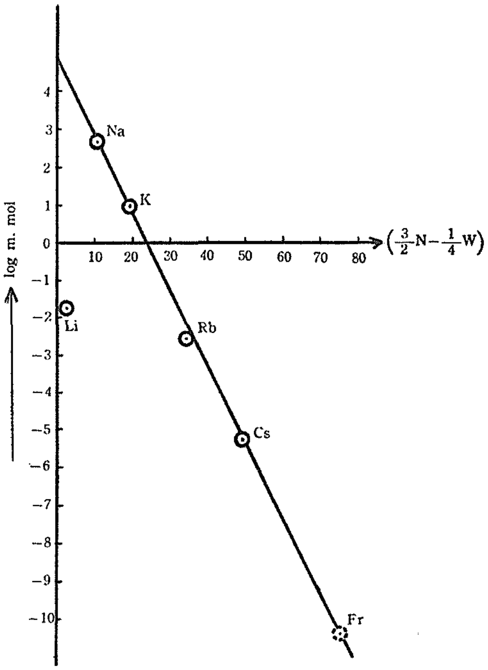

Fig. 1.

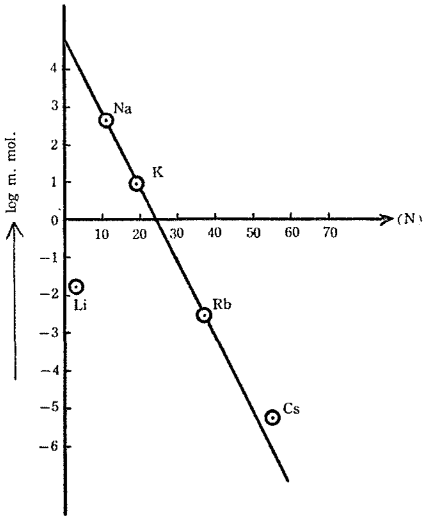

Fig. 2.

SUMMARY

To sum up,

(1) The amount of cesium dissolved in sea-water was found to be 0.8 μg/liter.

(2) The relationship between the amount of sodium, potassium, rubidium and cesium in sea-water is represented by the following eqation, $y=-0.204x+4.8$

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