

## On the Amount of Beryllium in Sea Water

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Investigation was made in order to determine the amount of beryllium in sea water. Beryllium was concentrated with ferric hydroxide as carrier. The ferric hydroxide was fused with sodium hydroxide. After cooling, the fused mass was treated with water and the solution was filtered. Beryllium in the filtrate was determined fluorometrically with morin. The recovery of beryllium in this procedure was about 86 per cent. Three hundredths and  $0.4 \mu\text{g}$  of beryllium have been found, respectively in one liter of sea water sampled at Shirahama and Uno.

The presence of beryllium in sea water has not yet been decided. Previously, Ishibashi and Shigematsu<sup>1)</sup> presumed that the amount of beryllium dissolved in sea water would be about  $0.006 \mu\text{g}$  per liter, from the regular relation between the ratio of the amount of an element dissolved in sea water and that dissolved in earth's crust and its ionic potential.

In this paper, the authors have quantified the amount of beryllium in sea water by the use of a fluorometric method with morin, and  $0.03$  and  $0.38 \mu\text{g}$  of beryllium was found in a liter of sea waters sampled at Shirahama and Uno, respectively.

### FLUOROMETRIC DETERMINATION OF BERYLLIUM WITH MORIN

In the previous investigation<sup>2)</sup>, the authors studied on the fluorometric method for the determination of beryllium with morin, and established the following procedure applicable to the sample containing  $\mu\text{g}$  quantity of beryllium.

Procedure: A sodium hydroxide solution of beryllium was taken into a 50 ml volumetric flask and neutralized with 5 N hydrochloric acid. One ml of 0.1 per cent (weight by volume) solution of morin in ethanol and 2 ml of 0.5 N sodium hydroxide solution (and 1 ml of 1 per cent potassium cyanide solution, if necessary) were added. To this solution, 1) ml (or 30 ml) of ethanol was added, and the solution was diluted to the volume. After standing for 30 minutes, the intensity of yellowish fluorescence was measured with photoelectric fluorophotometer as shown elsewhere<sup>3)</sup>.

Interfering elements: At the same time, it was found that the presence of magnesium, manganese, copper, vanadium and zinc interfere. Under the conditions described here zinc ion gives a fluorescence similar to that of beryllium, but zinc

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fluorescence can be destroyed completely by adding 1 ml of 1 per cent potassium cyanide solution.

In this procedure, the sensitivity is about 0.1  $\mu\text{g}$  of beryllium. Beryllium in the range of 1~7  $\mu\text{g}$  in 50 ml of 20 per cent alcoholic solution and 0.2 to 1  $\mu\text{g}$  in 50 ml of 60 per cent alcoholic solution can be quantitatively determined with in the error of  $\pm 10$  per cent.

### ENRICHMENT OF BERYLLIUM IN SEA WATER

The minuteness of beryllium content in sea water makes its direct determination difficult. In order to concentrate and separate beryllium from the major constituents of sea water such as chloride, sulfate, sodium, calcium and magnesium by coprecipitation method with aluminum hydroxide or ferric hydroxide as collector, the authors conducted the experiments as follows.

The definite amount of standard beryllium solution was added to a beaker containing a known amount of aluminum or ferric iron solution, and diluted to about 100 ml. Ammonium hydroxide was added until the solution became slightly alkaline, then it was allowed to stand over night to settle the precipitate. The precipitate was filtered, dried and ashed in a nickel crucible at as low temperature as possible in burning off the filter paper. The residue was fused with 1 g of sodium hydroxide for 30 minutes. After cooling, the mass was treated with ice cold water and then filtered through the filter (Toyo filter paper No. 5c) into a 100 ml volumetric flask. The content of the flask was diluted to the mark. A 5 ml aliquot of this solution was taken and the beryllium was determined according to the procedure mentioned above.

The results are shown in Table 1.

These data indicate that beryllium is almost completely coprecipitated with

Table 1. Coprecipitation of beryllium with aluminum hydroxide and ferric hydroxide.

	Collector added (mg)	Be added ( $\mu\text{g}$ )	Be found ( $\mu\text{g}$ )	Recovery of Be (%)
Al	10	100	98	98
	10	50	46	92
	10	50	48	96
	10	20	20	100
	10	20	18	90
	10	10	10	98
	10	10	11	110
	5	20	21	105
	5	5	4.5	90
	Fe	40	100	86
20		100	84	84
10		100	86	86
10		100	86	86
5		100	90	90

aluminum hydroxide. At this time, however, if the large quantities of aluminum is used as carrier, the concentration-quenching action of aluminum may occur. On the other hand, when ferric hydroxide is used as collector, the recovery efficiency of beryllium is about 86 per cent, slightly less than that of aluminum hydroxide. But in this case ferric iron can be separated from beryllium by sodium hydroxide treatment, evidently no interference of ferric hydroxide being involved. For this reason, ferric hydroxide is preferred as collector of beryllium.

#### DETERMINATION OF BERYLLIUM IN SEA WATER

In order to determine the applicability of the following procedure for the analysis of beryllium in sea water, recovery studies were made by adding definite amounts of beryllium to an artificial sea water (prepared by Lyman and Fleming<sup>4</sup>).

Analytical Procedure: To an artificial sea water 50~100 mg of ferric ion as ferric chloride solution and 10 ml of hydrochloric acid were added. Then 20 ml of ammonium hydroxide was added dropwise under constant stirring, and it was allowed to stand overnight to settle the precipitate. The precipitate was filtered through the filter by decantation, then dried and ashed in a nickel crucible. The residue was fused with 1~3 g of sodium hydroxide, treated with cold water and the amount of beryllium was determined as similarly as described in the forgoing sections.

The results are presented in Table 2. The recovery of beryllium in this procedure was more than about 85 per cent.

Table 2. Recovery of Beryllium in Sea Water.

Artificial Sea Water Taken (l)	Fe Added (mg)	Be Added ( $\mu$ g)	Be Found ( $\mu$ g)
5	100	0	0.0
5	50	100	95
5	100	100	95
20	100	50	42
20	100	100	85
20	100	100	80

#### RESULTS OF ANALYSIS OF SEA WATER

The analyzed sea waters were sampled, (A) at offshore of Uno, Okayama, on November 22th, 1953 and (B) at offshore of Shirahama, Wakayama, Japan on August 29th, 1955. The results of analysis are shown in Table 3.

The beryllium content of inland sea water (sample A) and open ocean water (sample B) were found to be 0.38 and 0.03  $\mu$ g per liter, respectively.

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Table 3. Beryllium in Sea Water.

No.	Chlorinity	Sample Taken (1)	Found ( $\mu\text{g}$ )	Be $\mu\text{g}/\text{l}$
A	16.00	80	31	0.38
B	18.61	80	2.5	0.03

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