Fluorometric Microdetermination of Uranium. V. The Uranium Content of Sea Water

By Masaki NAKANISHI

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Experimental

A sample of 200 ml. of sea water is enough to determine the uranium content by the present fluorometric method.

The sample water is treated in the way as described in the foregoing papers. For fear that the organic substances are present in the original sample, the residue of the first evaporation is dealt with nitric acid and evaporated again. Then the residue is dissolved in dilute hydrochloric acid and the insoluble matters are separated.

The iron hydroxide precipitate obtained as the carrier of uranium must be re-precipitated, because it probably includes a certain amount of sodium chloride.

Even in the case when the treatments are carried out along the normal course as given before, almost no noticeable interference of impurities comes about. Consequently no special procedures of removing impurities are required in the analysis of sea water. For this reason the particulars of the processes are omitted here to avoid the repetition.

Results

The uranium content of sea water obtained in several samples are given in Table 1 and 2.

Table 1

No.	Location	Depth, m.	Content of U, 10^{-6}g./l.	Salinity, ‰
(1)	Mutsu-wan (Aomori Prefecture)	0	0.46	28.8
(2)	Sagami-nada (Shizuoka Prefecture)	29	1.36, 1.04 1.20, 1.30 1.06, 1.12 mean: 1.18	34.7

Table 2

	(3) 32°39.1′ N 135°27.0′ E		(4) 31°49.0′ N 135°23.7′ E	
Depth, m.	Content of U, 10^{-6}g./l.	Salinity, ‰	Content of U, 10^{-6}g./l.	Salinity, ‰
0	—	—	1.96	34.72
500	3.37	34.33	2.98	34.61
1000	2.65	34.31	—	—
1500	2.76	34.40	2.55	34.54
2000	2.79	34.52	2.44	34.58
3000	3.06	34.60	—	—
4000	2.70	34.61	—	—

	(5) 31°50.0′ N 133°08.2′ E	
Depth, m.	Content of U, 10^{-6} g./l.	Salinity, ‰
0	1.75	34.45

The sample (1) was taken from the surface water in Mutsu Bay one kilometer off Asamushi (Aomori Prefecture) on April 27, 1946, and the determination was carried out several weeks after the sampling.

The sample (2) was obtained at the mouth of Ito Bay (eastern side of the Izu Peninsula, Shizuoka Prefecture) at the depth of 29 m. from the surface, close to the sea-bottom. This was sampled on April 29, 1947, and the treatment followed soon after.

The samples (3), (4) and (5) were examined in the attempt to find the uranium content of the ocean water, which is less affected by the influences of land. For using these materials as analytical samples the present writer is much obliged to the Hydrographical Department, Ministry of Transportation. Sampling was performed on December 5, 1947, and the treatment came off in June (1948), in

January (1949) and in June (1949) for the sample (3), (4) and (5) respectively. All these samples were kept preserved in the glass bottles.

Discussion

On the uranium content of sea water several reports have been published in foreign countries. Among them Hernegger and Karlik⁽¹⁾ first applied the fluorometric method to this purpose. The results they obtained are given in Table 3.

Table 3

Location	Depth, m.	Content of U, 10^{-6} g./l.	Salinity, ‰
Gullmar Fjord	0	0.36	23.9
〃	60	0.98	34.1
〃	100	1.17	34.3
Skagerak	500	1.90	35.2

The sample water for analysis was taken near the western coast of Sweden. According to their later report,⁽²⁾ they obtained the values from 2.0 to 2.2×10^{-6} g.U per l. for the uranium content of coast and ocean water.

Later on Föyn and others⁽³⁾ reported 1.5×10^{-6} g./l., and this value was approved by Wattenberg.⁽⁴⁾

The present writer intends to compare his results with those given in Table 3.

The sample (1) taken from the surface water close to the coast of a bay is an example of those which are much affected by the inland water. Therefore it is of little importance from the geochemical point of view to discuss in detail on the uranium content of sea water from this result. In this sample of sea water, the uranium content was found to be considerably small just as it was expected, and in the same degree of magnitude as reported previously by Hernegger (Table 3). The only conclusion is that the uranium content will probably be higher in sea water than in common inland water.

Similarly the sample (2) was subject to the influences of land, though a less degree, and can not be looked on as the typical sea water. But the result obtained from this sample shows a fairly large value, which nearly corresponds to that of Hernegger's which was collected at 100 m. depth. In the present case the depth (29 m.) of sampling is of no great importance, because it is also the depth of the sea-bottom. The value obtained will be equivalent to that of the deeper layer of the open sea.

Quite different from these two, the samples (3), (4) and (5) are the true sea water, belonging to the Kuroshio Current, and are supposed to give the uranium content of sea water in various depths.

In these samples the values obtained are in general somewhat larger than expected, except that taken at the depth of 0 m. (surface). The blank test was carried out and the standard fluorescent beads of known content were examined on the correctness. Moreover the relatively high values obtained above are not attributed to the substance contaminated from the glass bottles, though Hoffmann⁽⁵⁾ told about the unexpectedly large uranium content of some sorts of glass and porcelain. This is because the uranium in the sample (4), which was treated about half a year later after the sample (3) had been treated, shows no increase in content during the interval.

The concentration of uranium in the surface water is evidently lower than that in the deeper layer. In order to search into the biological concentration of this element, the sample (5) was first filtered through a filter paper, and the remaining residue was ignited to ash. Then the ash was treated by the fluorometric method. But no trace of uranium was found in it, and this fact means that the remains of the dead micro-organisms stayed by the filter paper do not play any important part to concentrate the element. The smaller value in the sample (5) is also consistent with that of the sample (4), though the reason why the sea water is poorer in uranium in the surface layer is not yet finally given.

Even though there comes out a peak at the depth of 500 m., the uranium content of deeper layers seems to be approximately constant, as the determination method involves the error amounting to 10%. Provided that uranium finds itself in the same concentration throughout the deeper layers, the average value comes up to 2.82×10^{-6} g.U/l., and this is the most probable value for the deep ocean water.

This result will be contributive to the problem of the radioactive elements in sea water.

Evans and others⁽⁶⁾ made an investigation

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(1) F. Hernegger and B. Karlik, *Sitz. Akad. Wiss. Wien*, Abt. IIa, **144**, 217 (1935).

(2) F. Hernegger and B. Karlik, *Göteborgs K. Vetensk-Samh. Handl.*, V. B. 4, No. 12.

(3) E. Föyn, B. Karlik, H. Petterson and E. Rona, *Medd. Oceanogr. Inst. Göteborg*, Nr. 2, (1939).

(4) H. Wattenberg, *Z. anorg. allgem. Chem.*, **251**, 86 (1943).

(5) J. Hoffmann, *Sprechsaal*, **75**, 214 (1942).

(6) R. D. Evans, A. F. Kip and E. G. Moberg, *Am. J. Sci.*, **36**, 241 (1938).

on the radium content of sea water at the western coast of North America, and gave the information of the variation in depth shown in the first column in Table 4.

Table 4

Depth, m.	(I) Content of Ra, 10^{-13} g./l.	(II) Equilibrium amount of U (calc.), 10^{-6} g./l.	(III) $\frac{\text{U (obs.)}}{\text{U (calc.)}}$ (approximate)
0	0.3 ± 0.1	0.09	20
600	1.5 ± 0.1	0.44	7
1300	3.2 ± 0.2	0.94	3

The amount of uranium which is in the radioactive equilibrium to radium is calculated in the second column. And the last column represents the ratios of the observed values given in Table 2 to the corresponding calculated values. As shown clearly in the table the ratios rapidly decrease with the depth; in other words, it is obviously sure that radium is gradually precipitated in some mechanism,(7) for the concentration of uranium is approximately constant to the depth.

In regard to the thorium content of sea water, several reports have been published, among which the values $<2\gamma$/l.(8), $\leqq 0.5\gamma$/l.(9), 0.5γ/l.(4) and 0.66γ/l.(10) were displayed. The last one was determined with the surface water of the Seto Inland Sea, and this is no more than one third of the corresponding uranium amount. Therefore the relation between uranium and thorium in sea water is in direct opposition to that in common igneous rocks.

Other investigations of the writer show that the largest uranium content of the inland waters ever found in Japan belongs to the water of Shin-arima hot spring (Hyogo Prefecture) amounting to 0.95×10^{-6} g.U/l., which has also the largest content of radium (381.14×10^{-12} g. Ra/l.).

Simple springs generally have less contents, for example, less than 2×10^{-9} g.U/l. for Shuzenji hot spring (Shizuoka Prefecture).

Even Masutomi springs (Yamanashi Prefecture), which are told to be the most radioactive spring group in this country, contain rather a small amount of uranium, that is, from 0.4 to 0.04×10^{-6} g.U/l. as far as the writer has examined.

He also failed to find any noticeable amount of uranium in the analyses of some sorts of river and underground waters.

Although we have received some papers(11) from abroad reporting of finding more uranium in some mineral springs than in sea water, we may conclusively maintain that the sea water in generel has the greatest concentration of uranium in the hydrosphere.

Summary

Coast and ocean water sample were analysed on their uranium contents by the fluorometric method.

The variation to the depth of 4000 m. was also examined in the ocean water sample. The content is likely to be constant even to the deep, though a little decrease appears in the surface water.

The obtained values in the deeper layer (average 2.8×10^{-6} g.U/l.) are somewhat higher than those by foreign investigators.

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Chemical Institute, Faculty of Science,
the University of Tokyo, Tokyo
Laboratory of Chemistry, Faculty of Science,
Ochanomizu University, Tokyo

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(7) C. S. Piggot and Wm. D. Urry, *Am. J. Sci.*, **239**, 81 (1941); H. Hamaguchi, *J. Chem. Soc. Japan*, **62**, 839, (1941).

(8) H. Wattenberg, *Z. anorg. allgem. Chem.*, **236**, 339 (1938).

(9) E. Föyn, D. Karlik, H. Petterson and E. Rona, *Nature*, **143** 275 (1939).

(10) M. Ishibashi and S. Azuma, *Chemistry and Chemical Industry*, **2**, 14 (1949).

(11) J. Hoffman, *Monatsh.*, **74**, 38 (1941).