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# THE DETERMINATION AND OCCURRENCE OF ALUMINUM IN SEA WATER

BY

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The presence of aluminum ions in sea water has long been an accepted fact, but there are few figures available on the concentrations in which the element exists and in particular under varying conditions. Thompson and Robinson (7) report certain results of analyses in which no attempt was made to prevent contamination of the samples with dissolved material from the bottles in which they were stored. The approximate concentration reported was 0.07 milligram atom per liter (1.90 mg.), a figure found to be in excess of the concentrations in samples which had been stored in bottles coated internally with paraffin.

It has been suggested that some of the aluminum in sea water is present in the form of organic complexes, and thus requires decomposition before ordinary analytical methods are adaptable. The variation, however, between values obtained directly and by wet combustion is quite small, indicating that most of the aluminum is probably present in the ionic form. By precipitation with 8-quinolinol (oxine) in neutral or slightly acid solution, interference by other elements in sea water is avoided.

The method employed was a modification of the colorimetric method of Alten, Weiland, and Loofman (1), using a Bausch and Lomb Universal spectrophotometer for the color comparison, thus limiting the error caused by visual peculiarities of the observer. A comparison of several suggested reagents was made before this method was adopted. Alizarin S, first proposed by Atack (2) was unsatisfactory. Cupferron (3) would be better suited to nephelometric analysis, although settling is quite rapid. Aluminon, most commonly used, required too careful control of conditions for use with sea water. Furthermore, iron is a disturbing factor, and the aluminum must be determined by an indirect analysis. Morin (5) might be used in fluorescence analysis but light transmission varies insufficiently. Kolthoff (4) suggests quinalizarin, but standard and sample must be run simultaneously, a process usually unnecessary in spectrophotometric work. There is also considerable tendency for the reagent itself to precipitate.

8-Quinolinol, 8-hydroxyquinoline, or oxine, precipitates aluminum as  $Al(C_9H_7ON)_3$  from solutions of *pH* 4.2-9.8. Calcium and magnesium will

\* Contribution No. 87.

precipitate at a  $pH$  above 8.2, and by regulation of the  $pH$  to 6-7, the interfering effect of these ions is negligible. Moderate amounts of aluminum can be determined by direct weighing of the complex, but for amounts such as are present in sea water, the colorimetric method (1) is better. The precipitated aluminum compound is dissolved in alcohol- $HCl$  mixture and coupled with diazotised sulfanilic acid. The color which is developed with  $NaOH$  solution, follows Beer's Law, is stable for at least four hours, and is readily compared with a blank. As little as 0.002 mg. of aluminum gives a definite color reaction, although the errors involved in analysis of such small samples are much greater than more moderate amounts. It was necessary to use small samples of water as larger amounts give incomplete precipitation, and attempts to concentrate the sea water by radiant surface evaporation, with subsequent removal of the precipitating salts, gave low results. The results were about 0.01 mg. at./1. lower than samples analyzed directly.

## REAGENTS

*Oxine solution.*—1 g. of the oxine is triturated with 1 ml. of glacial acetic acid and poured into 100 ml. boiling water. The solution is kept at boiling temperature with frequent stirring until the reagent has dissolved. The solution is then cooled and filtered.

*Sodium acetate solution.*—A saturated solution is prepared at about 50° and permitted to cool. The solution is kept in contact with excess solid sodium acetate.

*Solvent.*—Equal volumes of 2-normal  $HCl$  and 95% ethyl alcohol.

*Sulfanilic acid.*—8.6 g. are dissolved with warming in 1000 ml. of 30% acetic acid.

*Sodium nitrite.*—2.85 g. per 1000 ml. water.

*Sodium hydroxide.*—80 g. per 950 ml. water.

Impurities in the reagents should, of course, be avoided. Very small amounts can safely be compensated for in the calibration of the spectrophotometer with the standard solution and by comparison with the blank. The solutions are stored in paraffined bottles.

## STANDARD

0.4397 g. of potassium aluminum sulfate is dissolved in water and made up to 1000 ml. 1 ml. of this solution contains 0.025 mg., equivalent to 0.00092 mg. at., of aluminum and is diluted to 5-10 ml. volume for use as standard. The extinction co-efficient of the standard is determined for use in calculating the values of subsequent analyses.

## METHOD

The sea water sample is filtered through a Whatman No. 42 paper, and 10 ml. of the filtrate are pipetted into a Pyrex test tube. The sample is made faintly acid with 1 : 4; acetic acid : water (two drops usually enough), and 0.6 ml. of saturated sodium acetate solution added, followed by 0.25–0.50 ml. of the oxine reagent. The solutions are mixed by inversion and allowed to stand for 12 hours at room temperature. The tube is then placed in a water bath maintained at 70° for 30 minutes, after which the liquid is filtered through a medium-grained filter stick and the precipitate washed with successive small portions of boiling water. After washing, the filter stick is disconnected from the suction, and the sides of the precipitation tube are washed down with 2 ml. of alcohol-*HCl* mixture. The tube and filter stick are heated at 70° until the precipitate has completely dissolved, and the solution is then sucked through the filter stick which has not been removed from the test tube, into a 50 ml. volumetric flask. The test tube and stick are washed thoroughly with hot water which is also sucked through the stick into the flask. To the solution in the flask is added 1 ml. of sulfanilic acid solution and 1 ml. of sodium nitrite solution. The flask is allowed to stand for 10 minutes and 10 ml. of sodium hydroxide solution then added. The solution is made up to volume and after 10 minutes is transferred to the spectrophotometer tube and compared with a blank, prepared from the alcohol mixture, sulfanilic acid, sodium nitrite, and sodium hydroxide. If the aluminum concentration is too high, an aliquot is taken.

The solutions may also be compared on the colorimeter, preferably using a color filter. Nessler tubes are inconvenient as permanent standard solutions are not possible.

## THE OCCURRENCE OF ALUMINUM

During the period of May 5, 1936, to May 5, 1937, surface samples of water were collected for the authors by Dr. Lyman Phifer in paraffined bottles from San Juan Channel from the observation pier of the field laboratories at Friday Harbor, Washington. Samples were taken at high tide every five days. Table I shows the average monthly concentrations of aluminum together with the maximum and minimum values found each month. The monthly averages show the general seasonal trend more accurately than the other data which fluctuates considerably.

There appears to be but a slight variation in the seasonal samples which are somewhat lower than the deep sea samples discussed later. The early spring months seem to give samples containing a larger amount of aluminum, possibly due to the leaching of suspended matter brought down by the rivers during the spring freshets. The wider variation between individual samples at that time of year also appears to support this statement.

The aluminum content of samples taken on August 27, 1936, in the Northeast Pacific Ocean off Cape Flattery from 50-100 miles off the continental shelf, were also determined. The results are shown in Table II.

The values obtained vary, increasing with depth with indications of maximum aluminum at 900 to 1000 meters. Below these depths the concentration decreases and as the bottom is approached increases again. This fact has also been observed in the case of iron as reported by Thompson and Bremner (6) and corresponds to the region of low oxygen values reported by Thompson, Thomas and Barnes (8).

Attempts were made to determine beryllium. The results in general were negative due to the lack of a sufficiently sensitive method.

### SUMMARY

The concentration of aluminum in sea water has been determined.

The concentration of aluminum in sea water averages, for all samples, seasonal and depth, 0.020 mg. at./l., or 0.54 mg.

The monthly averages show a slight tendency to higher values in the early spring months and extending into June.

The concentration of aluminum varies with depth, there being a slight increase in the region approaching 1000 m., that region in which high iron and low oxygen values were also found.

TABLE I  
SEASONAL VARIATIONS IN ALUMINUM CONTENT OF SEA WATER IN  
SAN JUAN CHANNEL

Milligram Atoms per Liter			
1936	Average	Maximum	Minimum
May	0.016	0.021	0.012
June	.014	.024	.009
July	.013	.024	.006
August	.012	.018	.007
September	.009	.011	.007
October	.008	.010	.006
November	.009	.011	.007
December	.008	.012	.006
1937			
January	.009	.011	.006
February	.009	.011	.007
March	.009	.013	.008
April	.012	.016	.008
May	.015	....	....
Mean	.011	.015	.007

TABLE II

CONCENTRATION OF ALUMINUM AT VARIOUS DEPTHS IN THE WATERS OFF THE  
CONTINENTAL SHELF, NORTHEAST PACIFIC OCEAN

Milligram Atoms per Liter

Depth Meters	Lat. 48° 06' Long. 126° 30'	Lat. 48° 06' Long. 127° 00'
0	0.021	0.015
10	.019	.016
25	.016	.023
50	.018	.014
100	....	.012
150	.015	.013
200	.027	.018
300	.050	.024
400	.033	.028
500	.021	.033
600	.022	.047
700	.025	.054
800	.043	.033
900	.053	.061
1000	.055	.042
1100	....	.040
1200	.056	.020
1500	.048	.020
2000	.065	.027

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