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TITANIUM IN SEA WATER

By

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ABSTRACT

Small amounts of titanium have been detected in sea water by a colorimetric procedure using a thymol reagent and also by a spectrographic method. Diatoms and sea muds were found to have larger amounts of titanium than sea water. Thus it would seem that titanium is concentrated by diatoms in their shell structures.

INTRODUCTION

Silicon, an important constituent in the sea whose role is well established, is utilized by diatoms and various marine animals in the building of their shell structures. Titanium is very much like silicon chemically; thus it might be expected to be present in sea water as the titanate ion. Titanium is widespread in the earth's crust and ranks ninth in abundance, but information on the occurrence of titanium in the sea is very meager. Bardet, et al. (1938) reported the spectroscopic detection of titanium in the hydroxide precipitate from 60 l of sea water, and Webb and Fearon (1937) reported the presence of titanium in both land and sea organisms. To date there has been no confirmation of these findings.

In the present investigation an attempt has been made to explore, in a preliminary fashion, the titanium content of sea water. Various water samples, diatoms, and sea muds have been analyzed by a spectrophotometric method with thymol as the reagent. This method, reported by Griel and Robinson (1951), has greater sensitivity than the commonly used hydrogen peroxide method (Lenher and Crawford, 1913). A number of sea water samples have also been analyzed spectrographically for titanium.

SPECTROPHOTOMETRIC INVESTIGATION

Method of Analysis. The method of analysis is essentially the same as that of Chuiko (1940) in which the titanium was concentrated by coprecipitation with aluminium hydroxide. Thirty mg of aluminium as aluminium sulfate were added to 1 liter of filtered sea water; the pH was adjusted to 5.5-6.5. Regulation of the pH is essential, since aluminium hydroxide is known to coagulate at a pH of 4.1 or

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greater and to begin dissolving at a pH of about 9. The mixture was allowed to stand for 12 hours at room temperature; aging on a steam plate made the precipitate easier to filter but it did not increase the recovery of titanium. Precipitation with magnesium hydroxide at pH 9 was also tried as a carrier for titanium in place of aluminium hydroxide. The results were perhaps as good but no better. The precipitate was filtered off by using Whatman paper No. 30, after which it was washed with distilled water and dissolved in about 50 ml of 10% sulfuric acid. The solution was evaporated to fumes of sulfur trioxide, cooled slightly, and then 0.25 ml of 30% hydrogen peroxide was added to remove color due to organic matter. The excess hydrogen peroxide was destroyed by fuming again for 5 minutes. After cooling, 0.25 ml of thymol reagent was added for each 8 ml of sulfuric acid solution. The optical density was obtained on a Beckman DU spectrophotometer at a wavelength of 440 $m\mu$, using a 1 cm Corex cell and a 0.1 mm slit-width. The titanium concentration was obtained from a calibration chart in which concentration had been plotted against optical density.

Reagents and Standard Solutions. Thymol. A 1% solution of thymol was made by adding molten thymol slowly from a medicine dropper to ice-cold concentrated sulfuric acid that was stirred rapidly. *Standard Titanium Solutions.* 3.68 g of air-dried $K_2TiO(C_2O_4)_2 \cdot 2H_2O$ were digested for 10 minutes with 100 ml of concentrated sulfuric acid and 8 g of ammonium sulfate. The resulting solution was diluted to 1 liter with concentrated sulfuric acid and standardized gravimetrically. The titanium was precipitated either with cupferron (Yoe and Sarver, 1941: 145) or ammonium hydroxide (Kolthoff and Sandell, 1943: 704) and ignited to TiO_2 . This stock solution analyzed 10 μg -at Ti/ml of solution; a working standard solution containing 0.1 μg -at Ti/ml was prepared by dilution with concentrated sulfuric acid.

Testing the Method. To test the reliability of the method when applied to natural waters, analyses were made of various waters (shown in Table I) to which known amounts of titanium had been added. The recovery of titanium was satisfactory, particularly in the case of the natural sea water and distilled water media. The results in general were slightly low. It was felt, however, that the method possessed sufficient accuracy to furnish useful information, if titanium is present in sea water in appreciable amounts.

With this method the possibility of interference by fluoride in sea water was considered. Since slightly ionized complexes of the type TiF_6'' are known to be formed by titanium, and since appreciable amounts of fluorides occur in sea water (Thompson and Taylor, 1933),

TABLE I. RECOVERY OF TITANIUM FROM WATER SAMPLES

Water Type	Titanium Content, $\mu\text{g-at Ti/L}$		
	Added	Found	Deviation
Distilled	0.10	0.12	+0.02
	0.15	0.13	-0.02
	0.20	0.20	0.00
	0.40	0.30	-0.10
Artificial Sea Water	0.20	0.14	-0.06
	0.20	0.20	0.00
S = 34.5 ‰	0.30	0.20	-0.10
	0.40	0.30	-0.10
Pacific Ocean	0.10	0.07	-0.03
	0.20	0.17	-0.03
Ocean City, Wash.	0.20	0.23	+0.03
	0.20	0.17	-0.03
Aug. 8, 1949	0.10	0.13	+0.03
S = 30.4 ‰	0.20*	0.17	-0.03

* In addition to the titanium, 5 mg NH_4F were added to 1 liter of the sea water.

there would seem to be a definite possibility that titanium might be held as the complex, in which case it would not be available for estimation by the present method. On the basis of the following evidence it was concluded that this is not the case. First, as shown in Table I, there was satisfactory estimation of titanium when known amounts were added to sea water samples. Second, when additional fluoride was added to sea water along with known amounts of titanium (Table I), satisfactory determination of titanium was still obtained. Third, no significant increase in titanium content was noted when a sea water sample (Table II) was fumed with concentrated sulfuric acid to destroy any possible titanifluoride complex and to expel HF before estimation of titanium. In this experiment, after fuming the sample with sulfuric acid, it was diluted to its original volume with distilled water, and the titanium content was then determined by the usual procedure.

Analysis of Water Samples. Seven surface samples from the Puget Sound area, plus one from the Pacific Ocean, were analyzed for titanium. Most samples showed only trace quantities, though one sample was found to have 0.02 $\mu\text{g-at Ti/l}$, which is the minimum concentration estimable by this method. Analysis of fresh water samples from three streams flowing into Puget Sound indicated the same minimum concentrations.

Analysis of the vertical series of samples from Point Jefferson, Puget Sound gave the results shown in Table II. These results con-

TABLE II. TITANIUM CONTENT OF PUGET SOUND WATER AT VARIOUS DEPTHS

Location: Point Jefferson, Lat. 47° 44' 30" N, Log. 122° 25' 30" W

Date	Depth	Salinity ‰	Titanium Content μg-at Ti/L
June 14, 1951	S	27.5	0.04
	50	29.7	Tr
	100	29.9	Tr
	150	30.1	0.02
	200	30.1	0.02
	275	30.2	0.04
Nov. 8, 1951	S	30.1	Tr
	50	30.7	0.02
	150	30.8	Tr
	250	30.9	0.02
	270	30.9	Tr
Dec. 27, 1951	S	29.4	0.04
	100	30.1	0.02
	200	30.2	0.02
	Composite		0.04
	S*	29.4	0.04

* Water sample fumed with H₂SO₄ to destroy any titanium fluoride complex.

firm previous results that the titanium content is in the neighborhood of the minimum sensitivity of the method. The data in Table II also indicate that there is no significant increase in the titanium content with depth.

Analysis of Diatoms and Sea Muds. From previous results on the analysis of sea water, it appears that titanium, while present in sea water, is found in amounts that are barely detectable by the present method of analysis. Further evidence for the presence of titanium in sea water was sought in the analysis of diatom and sea-bottom mud samples to ascertain whether or not titanium is utilized and concentrated by diatoms in their siliceous structures.

The diatom samples, taken with a No. 20 silk bolting cloth plankton net, were washed with distilled water to remove sea salts and then dried at 95°C. The mud samples, taken with a bottom sampler, were also dried at 95°C.

A 0.3 g sample was weighed into a platinum crucible and the ash content was determined. The ash was mixed with 1.5 g of anhydrous sodium carbonate and fused. The product was leached with water and filtered, and the residue was dissolved in 10% sulfuric acid. The sulfuric acid solution was evaporated to fumes of sulfur trioxide, diluted to three times its volume with water, cooled and filtered; the

filtrate was again evaporated to fumes of sulfur trioxide. The concentrated sulfuric acid was cooled, thymol indicator was added, and the color was measured in the spectrophotometer. Some of the samples gave a color to the sulfuric acid, so portions without indicator were used in the reference cell. Results are shown in Table III. Too few samples were analyzed to attach any significance to the variation in the results obtained; however, it is clear that titanium is present in all samples in appreciable amounts.

TABLE III. TITANIUM CONTENT OF DIATOMS AND SEA MUDS

Location	Date	% Ash	% Titanium	
			On Dried Sample	On Ash
DIATOMS				
Strait of Georgia				
Dodd Narrows, B. C.	April 30, 1930	43	0.052	0.12
San Juan Channel				
Friday Harbor, Wash.	Aug. 19, 1937	58	0.048	0.083
East Sound				
Orcas Island, Wash.	Aug. 16, 1937	72	0.0021	0.0028
Lake Washington				
Seattle, Wash.	April 22, 1935	69	0.0036	0.0052
SEA MUD				
East Sound				
Orcas Island, Wash.	Aug. 10, 1937	86	0.20	0.23
Bering Strait	Aug. 1938	93	0.21	0.23
Lat. 65° 22' N.				
Long. 165° 17' W.				

SPECTROGRAPHIC ANALYSIS OF SEA WATER

With the titanium concentration in sea water at the threshold value of the colorimetric method of analysis, confirmation of its presence in sea water was sought by spectrographic analysis. Mr. Boyd C. Mills made the analyses on a grating spectrograph at the College of Puget Sound, Tacoma, Washington. This instrument had a 3.5 m Perkin-Elmer grating in a modified Rowland mount. The dispersion was 3.58 Å/mm. The aluminium hydroxide coagulants from liter samples of sea water were air-dried and excited in a carbon arc. The electrodes were 1/4" carbon rods; a current of 14 amperes was passed through a 1 cm gap.

Spectrographic analyses were made of: four samples collected at Point Jefferson on December 27, 1951 (Table II); a surface sample collected at Hood Canal on December 19, 1951; a distilled water sample

containing 0.04 $\mu\text{g-at Ti/l}$; and a blank on the reagents. Positive titanium lines in the 3300 Å region, with the 3349 Å line being most prominent, were obtained for the surface samples from Point Jefferson and Hood Canal and for the distilled water containing 0.04 $\mu\text{g-at Ti/l}$; no titanium lines were obtained for the other samples. It is probable that titanium could have been detected spectrographically in all samples if it had been concentrated from larger volumes of sea water, as Bardet, et al. (1938) had done in their work. It should be noted also that these same sea water samples were analyzed colorimetrically for titanium and that minimum quantities were found (Table II). The authors believe that the spectrophotometric method with thymol is somewhat more sensitive than the spectrographic method.

DISCUSSION

It would seem that titanium, though present in sea water samples, is found in extremely small concentrations. It has been detected both spectrographically and spectrophotometrically in certain sea water samples. Apparently it occurs to the extent of about 0.02 $\mu\text{g-at Ti/l}$, which is about the threshold value for the colorimetric thymol method used. The fact that titanium was found in considerable amounts in diatoms and sea-bottom mud samples substantiates the conclusion that titanium is present in sea water. An exact determination of the titanium content of sea water must await the development of a more sensitive method of estimation.

The finding of 0.0021 to 0.032% Ti in diatoms is only about 1/20 of the 0.05 to 1% range reported by Webb and Fearon (1937) for living organisms in general. Possibly this is due in part to the fact that diatoms grow in a medium low in titanium content, whereas land plants are able to extract titanium from the soil where it is present to the extent of about 0.62%.

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