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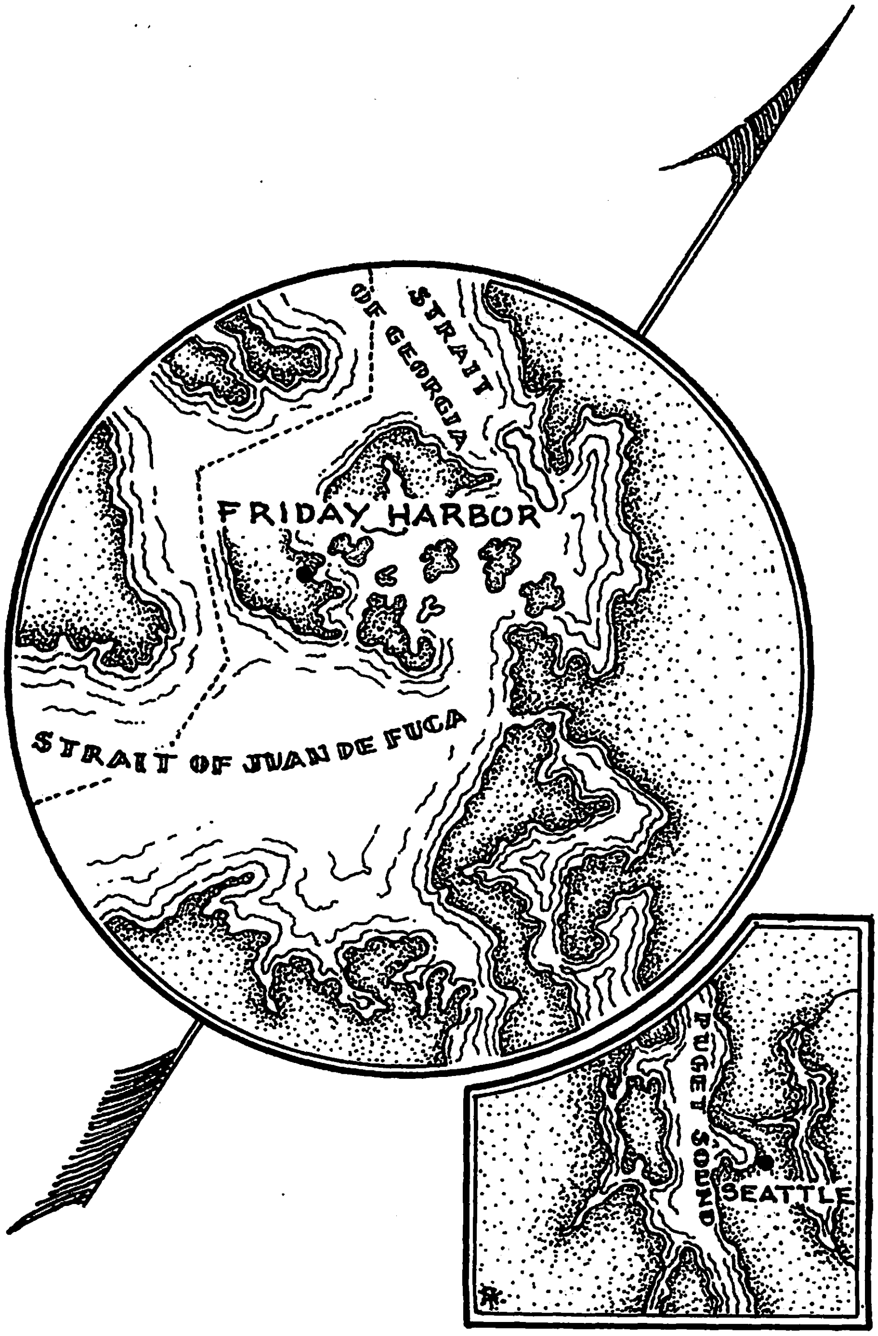
THE FORMS OF SILICATE AVAILABLE FOR COLORIMETRIC DETERMINATION

Technical Report No. 11



Office of Naval Research
Contract N8onr-520/III
Project NR 083 012
August 1952

UNIVERSITY OF WASHINGTON DEPARTMENT OF OCEANOGRAPHY
(Formerly Oceanographic Laboratories)
Seattle, Washington

Reference No. 52-4

THE FORMS OF SILICATE AVAILABLE FOR COLORIMETRIC DETERMINATION

by

Tung-whei Chow and Rex J. Robinson

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RH Fleming

August, 1952

Richard H. Fleming
Executive Officer

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THE FORMS OF SILICATE AVAILABLE FOR COLORIMETRIC DETERMINATION

SUMMARY

A study has been made concerning the availability of silica for colorimetric determination in various silicate compounds.

It has been found that silica in silicates with $Na_2O:SiO_2$ molar ratios greater than one can be determined by the colorimetric method. When the ratio is less than one, in concentrated solutions the available silica decreases with the ratio in a linear manner. In dilute solutions the per cent availability of silica increases with decrease in concentration. Colloidal silicic acid is not determined colorimetrically, upon standing only part of it is transformed into an estimatable form. The color intensity of silicomolybdate in sea water has been determined to be less than in distilled water by a factor of 1.23. It has also been found that in sea water medium all soluble silicate can be determined colorimetrically.

The utility of the silicomolybdate method for the colorimetric estimation of various forms of silicates thus has been defined. The conclusions should apply to both the molybdenum blue and silicomolybdate methods. The work with a sea water medium should be of significance in the estimation of silicate in any saline medium.

THE FORMS OF SILICATE AVAILABLE FOR COLORIMETRIC DETERMINATION

INTRODUCTION

The colorimetric method of Dienert and Wandenbulcke (1923) is now considered as the most convenient for determining silicate in natural waters. Silicate in ionic form, but not colloidal silicic acid, is thought to be determined by this method. Robinson and Kemmerer (1930) reported that all the silica could be determined colorimetrically only when the Na_2O:SiO_2 molar ratio was greater than unity, but Brujewicz and Blinov (1934) and Robinson and Putnam (1940) stated that the disilicate, in which the ratio was 1/2, could also be determined quantitatively. Consequently it is not known what silicate forms can be estimated by this method. The present paper reports the results of an investigation concerning this question.

REAGENTS AND CHEMICALS

All reagents used in this research were of C.P. quality. The various solutions were prepared with distilled water. Several of the different sodium silicates were supplied by the Philadelphia Quartz Co. of California; others were made by fusing silica with appropriate amounts of anhydrous sodium carbonate. Sulfuric acid and ammonium molybdate solutions were kept in glass bottles and showed no contamination of silica from the glass after a long period. All the other solutions were stored in plastic or paraffin-coated glass bottles. Silicate-free synthetic sea water with a chlorinity of 19 $^{o}/oo$ was prepared according to Robinson and Spoor (1936).

STANDARD SILICATE SOLUTIONS

A standard silicate solution was made by fusing pure silica with an excess of anhydrous sodium carbonate in a platinum crucible. The mixture was dissolved in water, diluted to one liter and kept in a plastic bottle. The silica content of this solution was determined by the usual gravimetric method (Scott, 1939). Working standards were prepared by dilution of appropriate amounts of this solution to 50 ml. volume. The silicomolybdate color was developed according to the following procedure.

COLORIMETRIC PROCEDURE

Fifty milliliters of the sample were measured into a flask, 2 ml. of 10% ammonium molybdate solution and 0.2 ml. of 18 N sulfuric acid were added. After five minutes the optical density was determined with the Beckmann spectrophotometer at a wave length of 430 mμ and a slit width of 0.15 mm. Distilled water containing the same concentration of reagents was used as the reference standard. Silicate solutions, too concentrated for colorimetric estimation, were first diluted before the color development. In this case, the reagents were added immediately after the dilution in order to avoid change in available silica.

EXPERIMENTAL

All the optical density readings were obtained with a model DU Beckmann spectrophotometer. Measurements were made with 1 cm. and 10 cm. Corex cells.

I. Validity of Beer's Law and Selection of Wave Length.

The validity of Beer's law in respect to silicomolybdate was examined at various wave lengths. It was found that Beer's law was valid at wave lengths greater than 360 mμ. For wave lengths less than 360 mμ, a negative deviation was observed possibly due to the large slit opening required to keep the galvanometer balanced. Although any wave length greater than 360 mμ could be used to measure the optical density, that of 430 mμ was selected as being most suitable for the range of silicate concentrations involved in this research. The extinction coefficient of silicomolybdate at this wave length was calculated to be 7200 l. $cm.^{-1}$ $mole^{-1}$.

II. The Estimatable Silica in Distilled Water Solutions of Silicates With Different $Na_2O:SiO_2$ Molar Ratios

A number of solutions of silicates were prepared with the $Na_2O:SiO_2$ molar ratios ranging from 5.70/1.00 to 1.00/3.78. The sodium oxide content was determined gravimetrically and acidimetrically (Scott, 1939). The silica content was determined both colorimetrically, by the previously outlined procedure, and gravimetrically (Scott, 1939). The results are shown in Table I.

It is seen that all the silica in silicates with the $Na_2O:SiO_2$ molar ratios greater than one was in a form which could be analyzed by

TABLE I

Analysis of Silicate Solutions with Various $Na_2O:SiO_2$ Molar Ratios

$Na_2O:SiO_2$		Na_2O, mg/l.		SiO_2, mg/l.		
Ratio	Grav.	Acid.[1]	Acid.[2]	Grav.	Color.	%
5.70/1.00	2908	----	----	494	489	99.0
2.07/1.00	2024	2021	1957	944	940	99.6
1.00/1.00	893	890	843	868	860	99.1
1.00/1.25	1494	1484	1408	1832	1775	96.9
1.00/1.54	2216	2193	1984	3307	3020	91.3
1.00/1.97	1056	1050	960	2012	1775	88.2
1.00/2.33	720	710	629	1625	1330	81.8
1.00/2.78	424	426	373	1142	853	74.6
1.00/3.13	348	343	285	1055	735	69.7
1.00/3.78	223	225	192	816	494	60.5

[1] Methyl orange used as indicator.

[2] Phenolphthalein used as indicator.

the colorimetric method. This is in accordance with the conclusions reported by previous investigators (Robinson and Kemmerer, 1930; Robinson and Putnam, 1940). It is probable that the silica in such solutions exists as metasilicate ions, which quantitatively form the yellow silicomolybdate complex with molybdate ions in an acidic solution.

From the data in Table I, it can also be observed that in the silicate solutions with the $Na_2O:SiO_2$ molar ratios less than one, only part of the silica was available for colorimetric determination. With decreasing $Na_2O:SiO_2$ ratio there was decreasing availability of silica; when the ratio was 1.00/3.78, only about 60 per cent of the silica was available. In Figure 1 the per cent availability has been plotted against the molar ratio and the relationship is observed to be linear. These results are in agreement with the work of Robinson and Kemmerer (1930).

Further investigation of solutions with $Na_2O:SiO_2$ molar ratios less than one showed that, for each ratio, there was a rather definite silica concentration above which there was a constant percentage availability, and below which an increasing proportion of the silica became available colorimetrically with decreasing concentration of silica. With sufficient dilution all the silica could be estimated by the colorimetric method. After dilution, equilibrium was attained rather slowly and increasing amounts of silica were obtained colorimetrically for an appreciable period of time. Data in support of these conclusions are given in Tables II and III.

In the case of solutions of the disilicate, in which the $Na_2O:SiO_2$ ratio is 1/2, all the silica was available when the silica

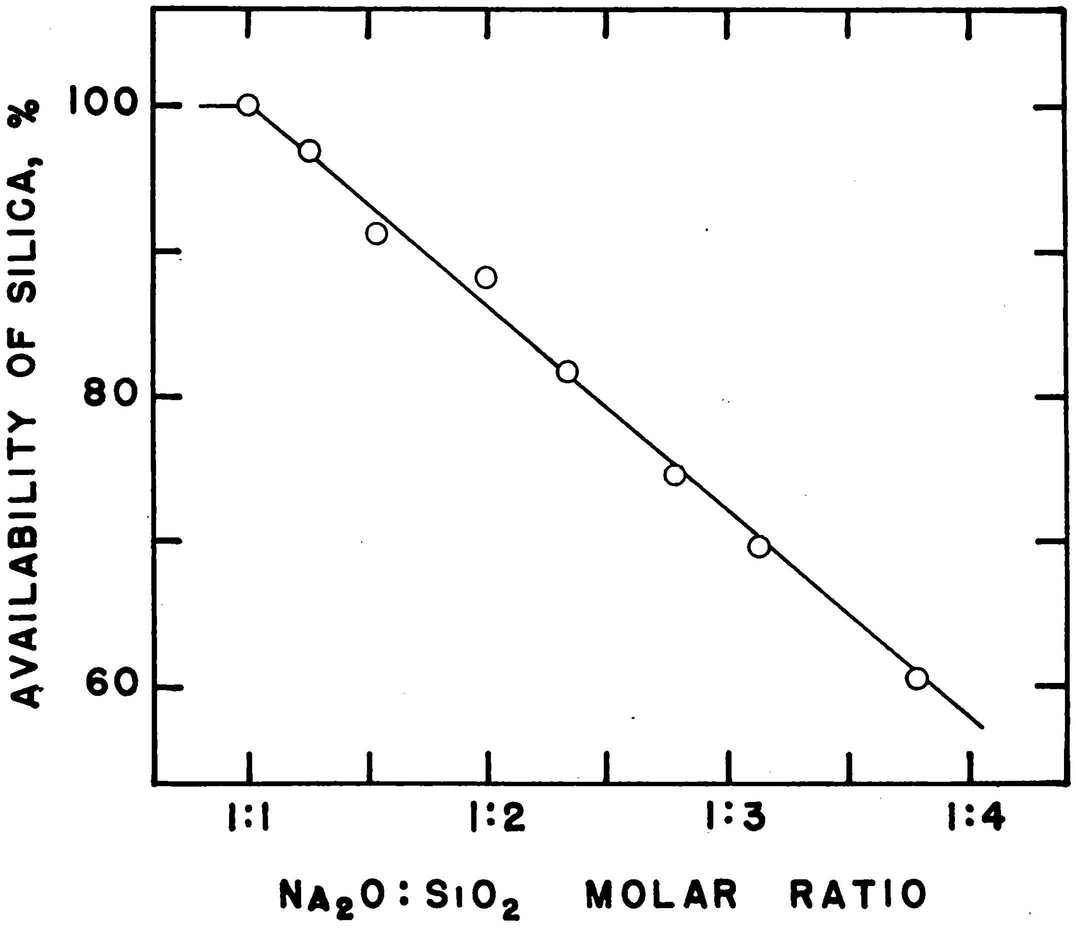

Figure 1. Per Cent Availability of Silica in Silicates with Various $Na_2O:SiO_2$ Molar Ratios

TABLE II

Effect of Time After Dilution on Per Cent Availability of Silica

Time After Dilution (minutes)	SiO_2, mg/l.		%
	Grav.	Color.	
	$Na_2O:SiO_2 = 1.00/1.97$		
0	100.6	88.7	88.2
6		93.5	92.9
12		95.5	94.9
22		96.6	96.0
32		97.8	97.2
45		99.0	98.4
61		100.0	99.4
	$Na_2O:SiO_2 = 1.00/2.78$		
0	57.1	42.6	74.6
4		44.5	77.9
9		46.0	80.6
19		47.6	83.4
40		49.6	86.9
94		52.2	91.4
120		53.3	93.4
240		55.6	97.4

TABLE III

Effect of Concentration on Per Cent Availability of Silica

$Na_2O:SiO_2$ Ratio	SiO_2, mg/l. Grav.	SiO_2, mg/l. Color	%
1.00/1.71	155	152	98.1
1.00/1.90	134	135	100.7
1.00/1.99	360	350	97.2
1.00/1.97	373	360	97.0
	447	425	95.1
	503	472	93.8
	575	517	89.9
	619	546	88.2
	2012	1775	88.2
1.00/3.13	26.4	26.4	100.0
	52.8	49.0	92.8
	105.5	92.2	87.4
	211	176	83.4
	352	250	71.0
	422	294	69.7
	1055	735	69.7
1.00/3.78	34.0	33.0	97.1
	68.0	63.0	92.6
	102.0	90.0	88.2
	204	162	79.4
	340	226	66.5
	453	274	60.5
	816	494	60.5

content was less than 360 mg. per liter whereas only a portion could be determined above this concentration; see Table III. This may explain why Robinson and Putnam (1940) and Brujewicz and Blinov (1934) found that all the silica in sodium disilicate was avilable for colorimetric determination whereas Robinson and Kemmerer (1930) had not. The latter investigators in their work had used a silica concentration of 682 mg. per liter, while Robinson and Putnam used a solution containing only 232 mg. of silica per liter. It is not known what concentration of silica was used by Brujewicz and Blinov.

The existence of colloidal silica in the silicate solutions with $Na_2O:SiO_2$ molar ratios less than one may offer a possible explanation for the change in per cent availability of silica with change in concentration. In the more concentrated solutions, part of the silica is in the colloidal form and thus not available for colorimetric determination. In dilute solutions, the colloidal form tends to be transformed to the ionic state which then can be determined colorimetrically. This explanation is supported by the fact that colloidal silica was found to remain after dialysis of these silicate solutions through a cellophane-membrane. The proportion of the silica in the colloidal form increases with decrease in the $Na_2O:SiO_2$ ratio, resulting in the linear relationship observed between the availability of silica and the molar ratio in Figure 1.

It should also be noted that in the acidimetric determination of sodium oxide in sodium silicate, methyl orange is a better indicator to use than phenolphthalein as recommended by Scott (1939). Since at the equivalence point silicate exists as silicic acid, which has a pK value of 9.7 (Lange, 1949), the solution has a low pH value. As indicated in Table I, if phenolphthalein was used, the titration values for sodium oxide were lower than the gravimetric results, whereas satisfactory agreement was obtained when methyl orange was used.

III. The Estimatable Silica in Various Silicates in Synthetic Sea Water Solution

Silicate solutions of different $Na_2O:SiO_2$ ratios were diluted with synthetic sea water yielding solutions with chlorinities between 17.1 and 18.9 ‰. These solutions were analyzed colorimetrically for their silica contents and the results recorded in Table IV. For those solutions with $Na_2O:SiO_2$ ratios less than one, the colorimetric analyses were made several days after dilution to allow for the establishment of equilibrium.

The data show that, for a given amount of silica, there is developed a lesser color intensity of silicomolybdate in sea water than in distilled water. This is attributed to the effect of the various salts dissolved in sea water. The ratio of the gravimetric silica content to the observed colorimetric value yields a ratio which is a measure of this salt effect and is called the salt factor. From Table IV it is observed that the salt factors were rather constant in value with an average of 1.23 regardless of the ratio of $Na_2O:SiO_2$ in the silicate used. This value is somewhat greater than the 1.16 factor reported by Robinson and Spoor (1936), but lower than the value of 1.66 obtained by Brujewicz and Blinov (1934). The salt factor of 1.25 recently given by Saeki (1950) is in agreement with the value reported here.

TABLE IV

Determination of the Salt Factor in Synthetic Sea Water Solutions

$Na_2O:SiO_2$ Ratio	SiO_2, mg/l. Grav.	SiO_2, mg/l. Color.	Grav./Color. Ratio
5.70/1.00	49.4	39.8	1.24
2.07/1.00	94.4	75.8	1.25
1.27/1.00	81.7	66.9	1.22
1.00/1.02	25.2	21.6	1.23
1.00/1.54	165.4	138.0	1.20
1.00/1.71	15.5	12.5	1.25
1.00/1.97	201.7	159.0	1.26
1.00/1.99	36.0	29.5	1.22
1.00/2.33	162.5	135.0	1.20
1.00/2.78	114.2	92.0	1.24
1.00/3.13	105.5	84.5	1.24
1.00/3.78	81.6	65.0	1.25
	Mean value		1.23 ± 0.02

The salt factor was also determined by comparing the optical densities of silicomolybdate of the same concentration in both distilled and sea water solutions. This was done for a number of concentrations of silicomolybdate and the results are plotted in Figure 2. The ratio of the slopes of the two straight lines in distilled water and sea water solutions gives an average value for the salt factor. By this method a value of 1.24 was found which is in very good agreement with the previously determined factor.

Although the salt factor reported was obtained in synthetic sea water solutions, it is applicable also to natural sea water as will be shown later. Since the dissolved salts depress the color intensity of the silicomolybdate, this factor should always be taken into account when determining silica in saline solutions.

From the results in Table IV, it can be said that all soluble silicates in sea water can be determined colorimetrically, even those with $Na_2O:SiO_2$ ratios less than one. Colloidal silica probably has been converted to the ionic form, thus becoming available for colorimetric determination. It should be pointed out that colloidal silica should be converted to the ionic form even more readily in natural sea water, because of its alkaline nature, than in the synthetic sea water used here.

IV. The Estimatable Silica in Colloidal Silicic Acid in Distilled Water and Sea Water Media

Since colloidal silica was thought to enter into the estimation of silicates with $Na_2O:SiO_2$ ratios less than one as discussed previously, it was considered desirable to study further its colorimetric availability.

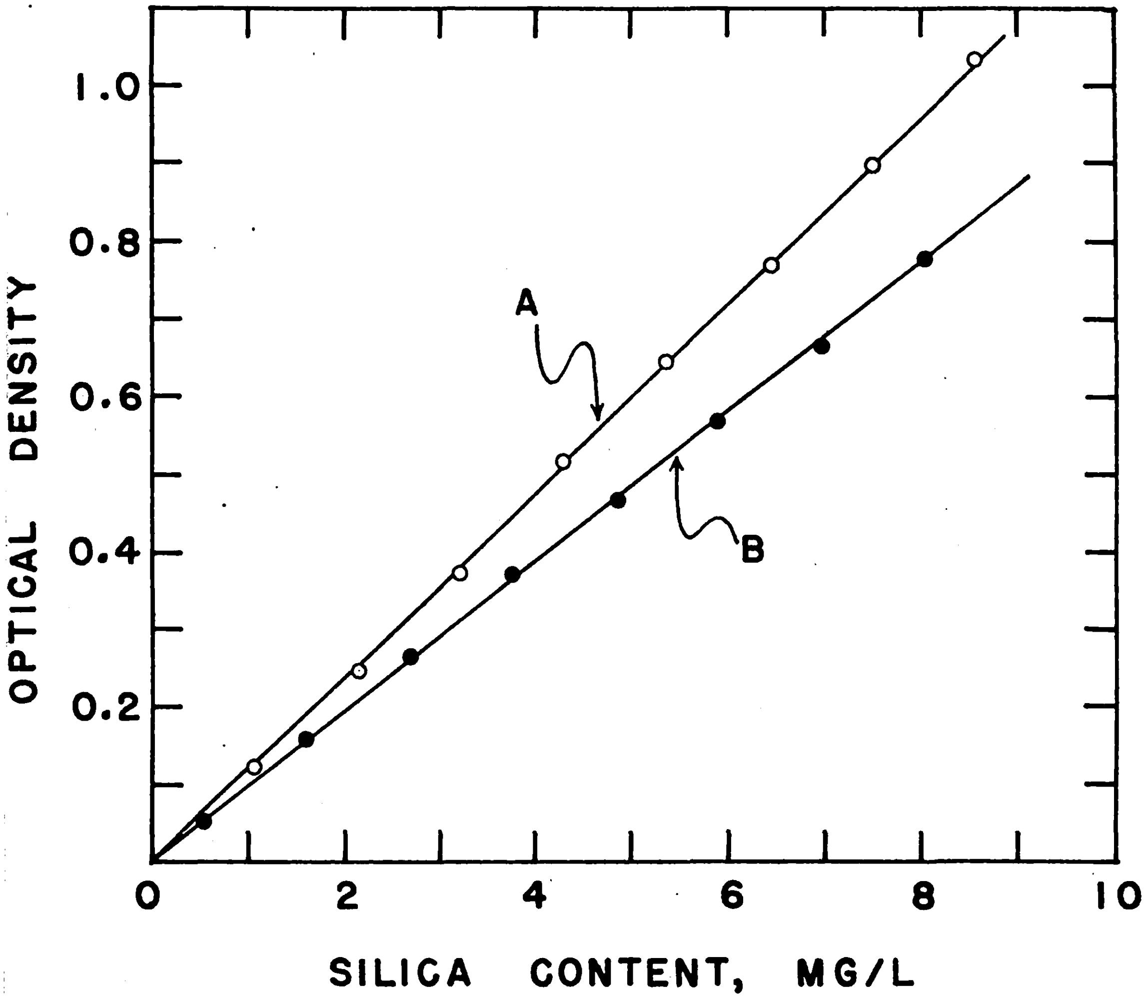

Figure 2. Absorption of Silicomolybdate in Distilled Water and Synthetic Sea Water Media

Curve A: Distilled water

Curve B: Synthetic sea water

Optical density measured at 430 mµ with 10 cm. Corex cells.

Colloidal silicic acid was prepared by pouring sodium silicate solution, with ratios ranging from 1.00/1.97 to 1.00/3.78, into 6 N hydrochloric acid. Electrolytes were removed by dialysis using a parchment paper sack immersed in constantly running tap water. Dialysis was continued until a negative test for chloride ion was obtained with silver nitrate. It was assumed then that only colloidal silicic acid remained. Of course, there was present the small amount of electrolytes present as dissolved solids in the water. The soluble silicate in tap water amounted to approximately 6 mg. per liter. After dialysis, about 50 to 60 ml. of the colloidal silicic acid was diluted to one liter and stored in a plastic bottle. The total silica concentration was determined by the usual gravimetric method. The silica available colorimetrically was noted over a considerable period of time. The results of the analyses of several samples are shown in Table V.

From these results it is seen that colloidal silica was not determined colorimetrically but was gradually transformed to the ionic form upon standing. Not all, but only a portion of the colloidal silica was converted to the ionic state.

Samples of colloidal silicic acid in synthetic and natural sea water media were also prepared by dilution of the colloidal silicic acid in distilled water. The results of periodic colorimetric analyses are given in Table VI.

Colloidal silicic acid apparently lost its colloidal form in sea water and became entirely available colorimetrically. Satisfactory agreement was obtained between the gravimetric and colorimetric results

TABLE V

Effect of Time on Per Cent Availability of Colloidal Silicic Acid in Distilled Water Medium

Hours after Solution was made	SiO_2, mg/l. Grav.	SiO_2, mg/l. Color.	%
0	212	11.5	5.4
27		46.3	21.8
48		64.0	30.2
91		87.5	41.2
169		97.5	46.0
338		106.3	50.1
506		112.0	52.2
1153		131.0	61.8
2400		131.0	61.8
0	83.1	7.0	8.4
49		8.5	10.2
142		10.4	12.5
361		13.9	16.7
696		17.8	21.4
935		19.7	23.7
1295		20.8	25.0
0	37.0	3.9	10.5
19		6.7	18.1
45		10.0	27.0
172		14.0	37.9
478		19.6	53.0
719		21.6	58.4
954		22.2	60.0
1202		22.7	61.4

TABLE VI

Effect of Time on Per Cent Availability of Colloidal Silicic Acid in Sea Water Medium

Hours after Solution was made	SiO_2, mg/l.			%
	Grav.	Color.	Color.*	
	Synthetic Sea Water Medium			
0	21.2	0.9	1.1	5.2
44		15.6	19.2	90.5
122		16.3	20.1	94.8
217		17.3	21.3	100.4
1490		17.3	21.3	100.4
0	52.6	2.2	2.7	5.1
6		35.0	43.1	81.6
27		37.8	46.5	88.4
123		40.0	49.2	93.5
245		42.8	52.6	100.0
592		42.8	52.6	100.0
	Natural Sea Water Medium			
0	83.1	1.8	2.2	2.6
48		61.0	75.0	90.2
90		63.0	77.5	93.2
168		68.0	83.6	100.6
480		68.0	83.6	100.6

* Corrected for the salt effect, using the factor 1.23.

only when the latter were corrected for the salt effect. This was true for both the synthetic and natural sea water media, indicating that the previously determined salt factor, although obtained with synthetic sea water, is applicable equally well to natural waters.

Since in naturally occurring sea water, the silica content is much smaller than used in this investigation, it may be concluded, rather safely, that irrespective of its original form, all the silica should be in the ionic state and determinable by the colorimetric method.

APPLICATION

Although all the conclusions discussed in this paper are based on the results obtained with the yellow silicomolybdate method of Dienert and Wandenbulcke (1923) for the determination of silica, they should also be applicable to the molybdenum blue method (Carlson and Banks, 1952; Kahler, 1941) as well, since in the latter case the yellow silicomolybdate is formed before reduction to the blue colored complex which is then measured. The work on the availability of silica in sea water should also apply to many natural brines and similar media.

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