So-called Silica Content of Natural Waters

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After the work of Dienert and Wandenbulcke(1), many workers have given various analytical methods for the determination of silica in natural waters and have discussed the state of silica. It is probable that various kinds of silicon compounds, such as soluble silica and silicate, colloidal silica, silicates, organic substances (biological materials) containing silicon or silica, etc., exist in natural waters, especially in river waters. Practically, it is very difficult to distinguish these silicon compounds respectively. So we use, for convenience sake, the word silica instead of silicon compounds in this paper.

Silica in natural waters is mainly determined by colorimetric methods, but it is doubtful that the value obtained by the colorimetric method shows the total silica content. It seems that silica obtained by colorimetry is in ionic form and not in colloidal state(1). After the treatment with alkali bicarbonate or carbonate solution, so-called colloidal silica is also considered to produce a yellow color similar to that developed by the compounds in ionic form treated by the same method. On contrary, very small particles of colloidal silicates and quartz, etc., in the waters can not be determined by the colorimetric method, unless these compounds are converted into soluble silicate by fusion with alkali carbonate or hydroxide. (Compare with the suggestive investigations of W. Noll(2), F. W. Correns,(3) etc.).

On the other hand, A. R. Tourkey(4) thought that silica obtained by colorimetric method is mainly colloidal. C. J. Roy(5) stated that in natural waters silica is actually present in the form of acid ions and not in the colloidal state.

We had a doubt concerning these conclusions described above, and have carried out the following experiments to ascertain the real facts.

Experiments

Colloidal Silica in the Mineral Water of Shiroike Hot Spring at Beppu, Oita Prefecture.—The spouting water of Shiroike Hot Spring is colorless and transparent, its temperature is 99°, and the pool water of Shiroike Hot Spring is milky white. Both spouting water and pool water are nearly neutral and the silica contents of these mineral waters show the same value by gravimetric method. The chemical composition of the mineral water of Shiroike Hot Spring is shown in Table 1.

Table 1

	Spouting water		Pool water	
	Sept., 1949	March, 1950	Sept., 1949	March, 1950
Evaporated residue	5.052g./l.	5.045g./l.	5.227g./l.	5.348g./l.
SiO_2	0.559	0.572	0.537	0.529
CaO	0.146	0.244	0.154	0.196
MgO	trace	trace	trace	trace
Cl	—	2.383	—	2.539
SO_4	—	0.235	—	0.263
Alkali halide	3.941	3.642	3.575	3.963
*p*H	7.6	7.4	7.8	7.4

The value of silica content of pool water obtained by colorimetric method is very small compared with that by gravimetric method. From the results of electrodialysis and gravimetric analysis, we found that the pool water contains a considerable quantity of colloidal silica. In the spouting water immediately after sampling, the silica content obtained by colorimetric method is the same as that obtained by gravimetric method, but after sampling, as time goes on, the value of the silica content obtained by colorimetric method decreases until the constant value is reached (Table 2). We found the same phenomena in sodium silicate solution, and Aoki(6) found the same fact independently. More detailed reports will be published elsewhere.

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(1) F. Dienert and F. Wandenbulcke, *Compt. rend.*, **176**, 1478 (1923).

(2) W. Noll, *Chem. der Erde*, **6**, 1 (1931).

(3) C. W. Correns, *Chem. der Erde*, **13**, 92 (1940); *etc.*

(4) A. R. Tourkey and D. H. Bangam, *Nature*, **138**, 584 (1936).

(5) C. J. Roy, *Am. Jour. Sci.*, **243**, 393 (1945).

(6) F. Aoki, *J. Chem. Soc. Japan*, **72**, 15 (1951).

Table 2

March, 1950 A		March, 1950 A		Sept., 1949 B		Sept., 1949 C 3)		July, 1947 D	
Time 1)	SiO_2 mg./l. 2)	Time	SiO_2 mg./l. 2)	Time	SiO_2 mg./l. 2)	Time	SiO_2 mg./l. 2)	Time	SiO_2 mg./l. 2)
15 min.	640	15 min.	640	5 days	250	0	366	436 days	128
30	455	1 days	145	7	225	15 min.	343	586	114
45	310	2	140	8	193	30	338		
1 hr.	310	3	138	15	130	40	329		
2	242	4	139	19	126	4 hr.	236		
5.5	153	5	133	160	125	26	149		
22	145	6	100						
48	140	10	101						

1) The time measured from sampling.

2) Value obtained colorimetric method.

3) The sample is the aged sample of 5 days from sampling. (Sample B, $SiO_2=250$ mg./l.). Measurements are started after boiling for 3 minutes.

We transferred a 100 cc. spouting water into a platinum dish (the silica content of this spouting water reached the constant value by colorimetry.), and added 0.4 g. of sodium bicarbonate in it, and heated it on a boiling water-bath for an hour. We found that the silica content of the aged spouting water treated with sodium bicarbonate found by colorimetry is the same value as that by gravimetric method. Next we tried the electrodialysis of aged spouting water which showed the constant silica content by colorimetry to ascertain the existence of colloidal silica and could obtain colloidal silica. We used in this case cellophane membrane having the pore size of 2-3 mμ measured with dyes.

Colloidal silica in residual water produced no color with ammonium molybdate by the usual colorimetric method, but after treatment with sodium bicarbonate, the silica content obtained by colorimetry is the same as that by gravimetric method (Table 3).

Table 3

	I	II	III	IV
Spouting water	0.559g./l.	0.130g./l.	0.223g./l.	0.222g./l.
Pool water	0.537	0.116	0.338	0.336

I. Total SiO_2 (With gravimetry).

II. SiO_2 reached constant value (Colorimatry).

III. Residual SiO_2 after dialysis (Gravimetry).

IV. SiO_2 treated with sodium bicarbonate of residual sample after dialysis (Colorimetry).

From these results of experiments, we could show that colloidal silica is actually present in the mineral water of Shiroike Hot Spring and colloidal silica having a larger particle size than about 2-3 mμ can not produce the yellow color by ammonium molybdate in acidic solution. The loss of silica content obtained by colorimetry as time goes on after sampling is considered to be due to the fact that ionic silica is coagulated and produces colloidal silica.

Various Kinds of Silicon Compounds in River Water and Japanese Standard Sea Water.—In order to ascertain the presence of various kinds of silicon compounds in natural waters, we have carried out experiments according to the following four different methods for the colorimetric determination of silica.

Method 1. (Usual colorimetric method). To 20 cc. of sample solution are added 2 drops of sulfuric acid (1:1) and 0.5 cc. of 10% ammonium molybdate solution, and the yellow color developed is compared after about ten minutes with that of the standard solution (picric acid and potassium chromate solution). By this method soluble silica and silicate are determined.

Method 2. (Colorimetric method after treatment with sodium bicarbonate). To 50 cc. of sample solution is added 0.2 g. of sodium bicarbonate in a platinum dish, the mixture is heated on a boiling water bath for an hour. Then it is cooled and neutralized with sulfuric acid (1:1) and diluted with water to 50 cc. Colorimetric determination of silica in the solution thus obtained is carried out as the method 1.

Method 3. (Colorimetric determination of silica after treatment with sodium carbonate). In this method, 0.5 g. of sodium carbonate is used instead of sodium bicarbonate. All other procedures are the same as the methods 1 and 2 described above.

By the methods 2 and 3, soluble silica, soluble silicate, so-called colloidal silica, etc. are determined.

Method 4. (Colorimetric determination of silica after carbonate fusion). 20 cc. of sample solution is gently evaporated up to dryness in a platinum crucible, and the residue is covered with about 1 g. of anhydrous sodium carbonate, and then the crucible is heated over a small flame, and the mixture is fused for a further 10 minutes. The crucible is allowed to cool down. After the crucible has cooled down completely it is filled with water to 2/3 of its height and its bottom is gently heated. The melted substance is treated with water, and then the pH-value of the solution thus obtained is adjusted to about 1.4 by means of diluted sulfuric acid (1:1) and 1 cc. of 10% solution of ammonium molybdate is added. The colorimetric method after this treatment is the same as the usual method. By this method, all silicon compounds are determined.

By these analytical methods we can distinguish various silicon compounds in natural waters from each other. For example, the silica content of the water of Tamagawa river, flowing into the Bay of Tokyo, is shown in Tables 4 and 5. Siica content in Table 4 was determined by gravimetric method and in Table 5 by colorimetric method described above.

Table 4

	mg./l.
Evaporated residue (110°C.)	155
Si	41.4
Al	5.8
Fe	0.18
Ca	15.6
Mg	1.8
Na	6.6
K	0.8
Mn	0.032
Cl	12
pH	6.4

Table 5

Silicon Content of the River Water of Tamagawa

Date	Method 1	Method 2	Method 3	Method 4
	mg./l.	mg./l.	mg./l.	mg./l.
9, August	20.0	—	—	—
10, 〃	20.0	21.4	—	44.5
11, 〃	19.5	20.5	20.3	—
13, 〃	18.5	20.7	20.9	35.4
14, 〃	15.8	—	20.2	24.3

As seen in Tables 4 and 5, as time goes on after sampling, the silica content of river water in the sample bottles decreases owing to deposition of dispersed particles in the waters.

As seen in Table 5, the silica content obtained by method 1 is the smallest and that by method 4 is the greatest among them. The silica content obtained by method 2 is almost the same as that by method 3.

From these results we concluded that there are various kinds of silicon compounds in the water of Tamagawa river in addition to the soluble silica and silicates.

In Table 6, similar results obtained on Japanese standard sea water are shown.

Table 6

Silicon Content of the Japanese Standard Sea Water

	Method 1	Method 2	Method 3	Method 4
	mg./l.	mg./l.		mg./l.
Sample No. 1	4.1	4.5	—	—
Sample No. 2	4.0	—	—	6.8

As seen in Table 6, these values are too high compared with that of J. Robinson's and Wattenberg's values. In the other experiments of sea water, however, the silica content of sea water at, for example, Fukuoka, or Enoshima is lower than that described above.

We also observed that the yellow color of the sea water at Hakozaki, Fukuoka City, produced by ammonium molybdate after treatment with sodium bicarbonate is remarkably deeper than that developed by method 1.

The silica content of the sea water containing cultivated diatom is measured by the methods described above, and the results obtained are shown in Table 7.

The silica content of the sea water containing cultivated diatom is 20.7 mg. SiO_2/l. by gravimetric method, and the same value was obtained by method 4. As seen in Table 7, most of the silica in this sample does not produce yellow color by method 1. The silica content of sample 1, obtained by method 2 is greater than that given by method 1, but less than that by method 4. However, in the cases of samples 2 and 3 which are diluted to double volume with distilled water before treatment, there is no difference between the value obtained by method 2 and that by method 4.

Table 7

	Method 1	Method 2	Method 3	Method 4
	mg./l.	mg./l.		mg./l.
Sample No. 1	<1.0	8.6	—	20.7
Sample No. 2	<1.0	10.6	—	10.6
Sample No. 3	<1.0	10.6	—	11.0

Conclusions

From the results obtained above, we reached the following conclusions.

1. Colloidal silica is actually present in natural waters such as Shiroike Hot Springs, the Tamagawa river, etc.
2. Colloidal silica, which has a diameter larger than 2–3 mμ, does not produce yellow

colour with ammonium molybdate in the acidic solution.

3. As ionic silica is coagulated and produces colloidal silica in natural waters, colorimetry for the determination of silica must be performed immediately after sampling. The silica content of an aged sample by method 1 is frequently remarkably less than that obtained from a fresh sample.

4. As colloidal silica can not be determined by method 1, even if it is present, methods 2, 3, and 4 must be used for the determination of silica content.

5. Various kinds of silicon compounds are actually present in natural waters, such as the Tamagawa river, etc.

6. In many cases, the total silica contents of natural waters are obtained by methods 2, and 3, but for the determination of the total silicon in natural waters method 4 must be used.

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