Silica in Water. V. Salt Effect on the Colorimetric Determination of Silica in Concentrated Salt Solution*

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In a concentrated salt solution, the amount of silica obtained by colorimetric methods (silicomolybdate and molybdenum blue method) is lower than that obtained in the absence of salt**. This phenomenon is called the salt effect or the salt error, and the ratio of the true silica content to the value obtained in the presence of salt is called the salt factor, since it gives a measure of the salt effect. Some salt factors were reported for the colorimetric determination of silica in sea water[1-5], and the salt effect was also investigated for the colorimetric determination of small amounts of silica in alkali[6]. The properties of silicomolybdic acid in a concentrated salt solution have not been studied systematically. The following experiments were carried out to make clear the properties of salt effect and to find the method for correcting the salt effect.

Silicomolybdate Method

Reagents and apparatus. — *Silica solution.*— Portions 0.500 g. of anhydrous silica were fused with 4 g. of sodium carbonate, the melt was dissolved in distilled water, and diluted to 1000 cc. Solutions of a suitable concentration of silica were prepared by diluting this stock solution.

Ammonium molybdate solution.—10%.

Sulfuric acid.—Various normalities.

Salts.—All chemicals were of analytical reagent grade or C. P. purity.

Apparatus.—Hitachi EPU-2 spectrophotometer, 10 mm. cell.

Variations of absorption spectrum of molybdate with acidity and salts.—In the measurement of absorbance of silicomolybdic acid by using a spectrophotometer or a photoelectric colorimeter, distilled water or a solution prepared by adding acid and ammonium molybdate solution to distilled water (or salt solution) is used as the reference. When the latter is used, it must be considered that the absorption spectrum of molybdate in the solution varies with acidity. The absorption spectra of molybdate in the solutions prepared by adding 2 cc. of sulfuric acid of various normalities and 2 cc. of 10% ammonium molybdate solution to 50 cc. of distilled water were measured against distilled water. The results are shown in Fig. 1. The absorption spectra of

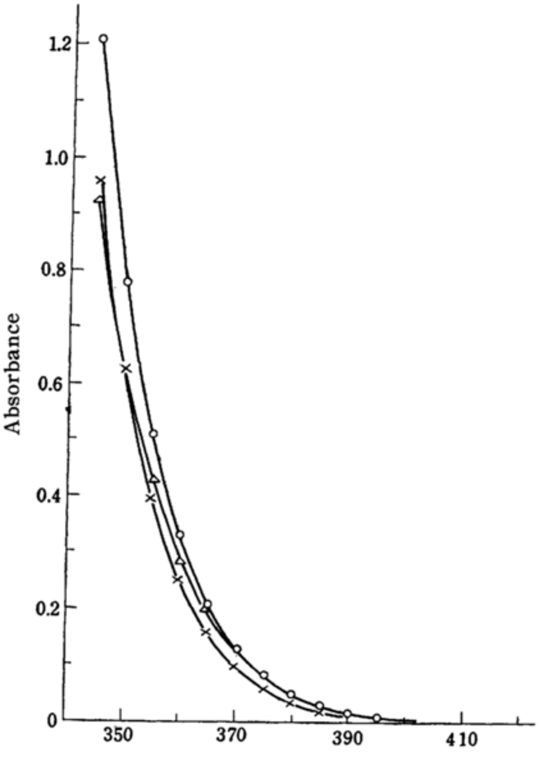

Fig. 1. Variation of absorption spectrum of molybdate with acid concentration.
× 0.037 N
○ 0.11 N (0.074 N, 0.15 N)
△ 0.22 N

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* For previous paper in this series see T. Tarutani, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 1815 (1956).

** The latter gives the true content of silica.

1) D. T. W. Chow and R. J. Robinson, *Anal. Chem.*, **25**, 646 (1953).

2) R. J. Robinson and H. J. Poor, *Ind. Eng. Chem., Anal. Ed.*, **8**, 455 (1936).

3) A. Saeki, *J. Oceanog. Soc. Japan*, **6**, 39 (1950).

4) I. Iwasaki, T. Tarutani, T. Katsura and H. Shimojima, *Japan Analyst* (*Bunseki Kagaku*), **2**, 210 (1953).

5) J. B. Mullin and J. Riley, *Anal. Chim. Acta*, **12**, 162 (1955).

6) O. A. Kenyon and H. A. Bewick, *Anal. Chem.*, **25**, 145 (1953).

molybdate in 0.074 N or 0.15 N sulfuric acid is almost the same as that in 0.11 N. However, in 0.037, 0.11, and 0.22 N sulfuric acid, the spectra are different from one another.

In the concentrated salt solution, the absorption spectrum of molybdate varies with the kind of salt and the concentration of salts, even when quantities of reagents added to the solution are constant. The absorption spectra of molybdate in distilled water, 1 M sodium chloride solution, and 0.5 M sodium sulfate solution, were measured against distilled water (Fig. 2). These solutions contained the same quantity of ammonium molybdate, and the concentration of sulfuric acid was 0.11 N. It can be seen that the absorption spectrum of molybdate varies with the concentration of salts and the kind of salt.

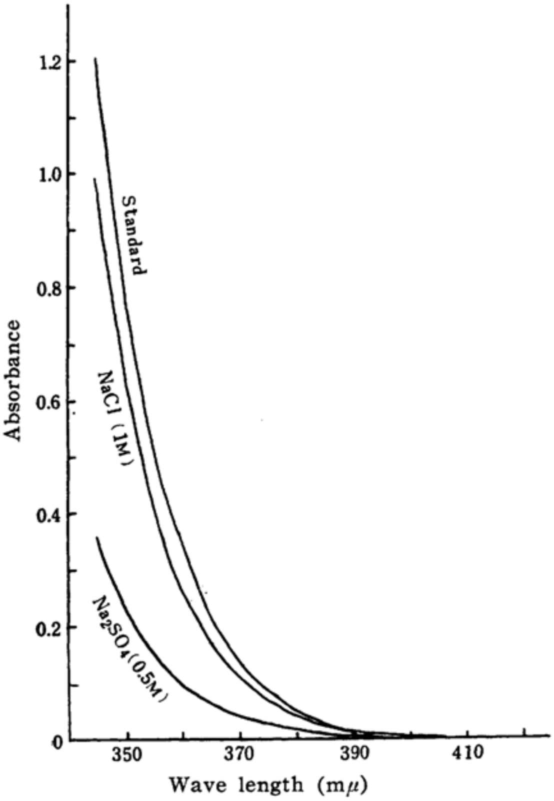

Fig. 2. Variation of absorption spectrum of molybdate with salts.

From the results shown in Figs. 1 and 2, the following conclusions may be drawn. When the solution prepared by adding definite quantities of reagents to distilled water is used for zero standard and the absorbance of silicomolybdic acid in the sample solution containing very small amounts of salt is determined, ultraviolet light can be used.

In the colorimetric determination of silica in the concentrated salt solution, when a wave length above 400 mμ is used, the solution prepared by adding definite quantities of reagents to distilled water can be used as zero standard, but when ultraviolet light is used, the solution of the same concentration of salt as the sample solution has to be used after addition of definite quantities of reagents, because the absorption spectrum of molybdate varies with the concentration of salts.

Time required for the maximum color development of silicomolybdic acid and the stability of color.—The time required for the maximum color development of silicomolybdic acid and the stability of color varies with acidity, temperature, kind of salt, concentration of salts, and quantity of molybdate. The effect of acidity, temperature, and quantity of molybdate on the time required for the maximum color development of silicomolybdic acid were already reported⁷⁾. In a concentrated salt solution, the stability of color is smaller than that in the solution of a negligibly small salt concentration. An example is shown in Fig. 3. These experiments were carried out at 15°C. In Fig. 3, the time necessary for maximum

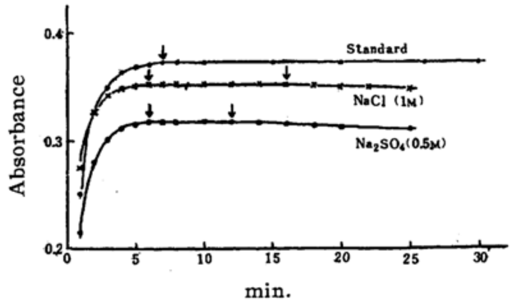

Fig. 3. Stability of color.

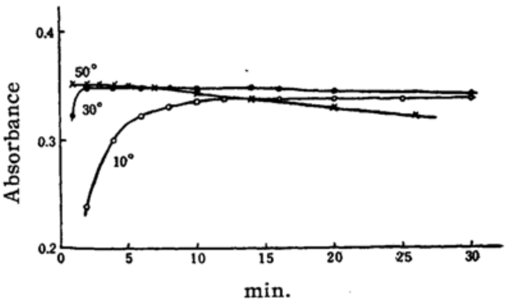

Fig. 4. Color change of silicomolybdic acid with temperature.

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7) T. Tarutani, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 743 (1956).

color development are shown by the left arrow, and the time when the color intensity begins to decrease is shown by the right arrow. The color change of silicomolybdic acid with temperature are shown in Fig. 4. These experiments were carried out by the following procedure. Fifty cc. of the sample solution containing 10 p.p.m. of silica was taken, and 2 cc. of 3 N sulfuric acid and 2 cc. of 10% ammonium molybdate solution were added, and the absorbance of silicomolybdic acid was measured against distilled water at 400 mμ. From the results shown in Figs. 3 and 4, in the determination of absorbance of silicomolybdic acid, the time required for the maximum color development must be measured to obtain an accurate result.

Salt effect.—In this section, the experiments were carried out by the following procedure. The absorbance of silicomolybdic acid in the solution prepared by adding 2 cc. of 3 N sulfuric acid and 2 cc. of 10% ammonium molybdate solution to 50 cc. of the salt solution was measured against a blank containing the same amounts of salt, molybdate and acid.

Table I summarizes the previous data on the salt factor of sea water. The value reported by Iwasaki and Tarutani is differs from others. These data are supposed to suggest that the salt effect may vary with the wave length used. Therefore, the salt effects were measured at various wave lengths (Fig. 5). The concentration of silica in the salt solution was 10 p. p. m. The ordinate in Fig. 5 is the ratio of the absorbance of salt solution to the absorbance of standard silica solution. As will be seen in Fig. 5, the salt effect varies with wave length used and the salt effect at a longer wave length is greater than that at shorter wave length. And also the salt effect varies with the kind of salt, for example, the effect of sulfate is greater than that of chloride. In the salt solution having large salt effect e. g. ammonium sulfate solution, the variation of salt effect with wave length is large, but in the salt solution having smaller salt effect, e. g., sodium chloride solution, this variation is small.

TABLE I

SALT FACTOR OF SEA WATER

Author	Apparatus used	Wave length used	Salt factor
Robinson, Chow[1]	Spectrophotometer	430 mμ	1.23
Robinson, Poor[2]	Pulfrich photometer	430 mμ (filter)	1.16
Saeki[3]	Ukena tube	—	1.25
Iwasaki, Tarutani[4]	Duboscq colorimeter	—	1.09
Mullin, Riley[5]	Spectrophotometer	812 mμ (Mo-blue)	1.1

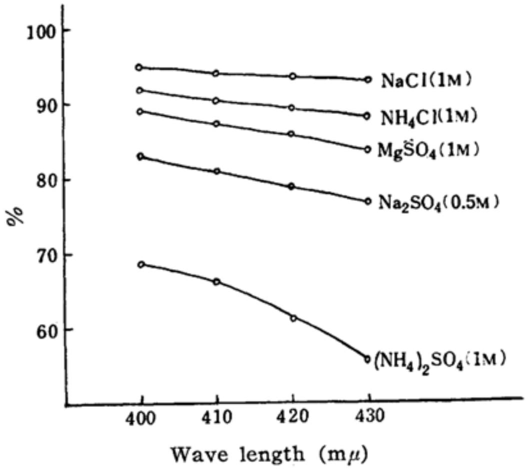

Fig. 5. Salt effect.

The absorbance was measured for a number of concentrations of sodium sulfate solution containing 10 p. p. m. of silica (Fig. 6). The straight line was obtained and it is shown that the salt effect is proportional to the salt concentration.

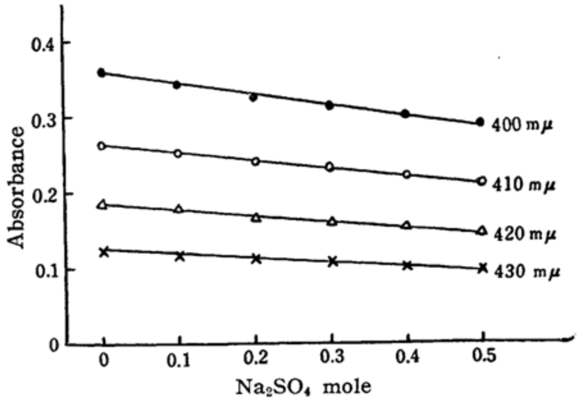

Fig. 6. Relation between absorbance and Na_2SO_4 concentration.

The absorbance was measured for different concentrations of silica in distilled water and in 0.5 M sodium sulfate solution (Fig. 7). Wave length of 400 mμ was used. A straight line was obtained. The absorbance of silicomolybdic acid in the salt solution obeys Beer's law. The ratio of the slopes of the two straight lines obtained for distilled water and salt solution gives the value of salt factor.

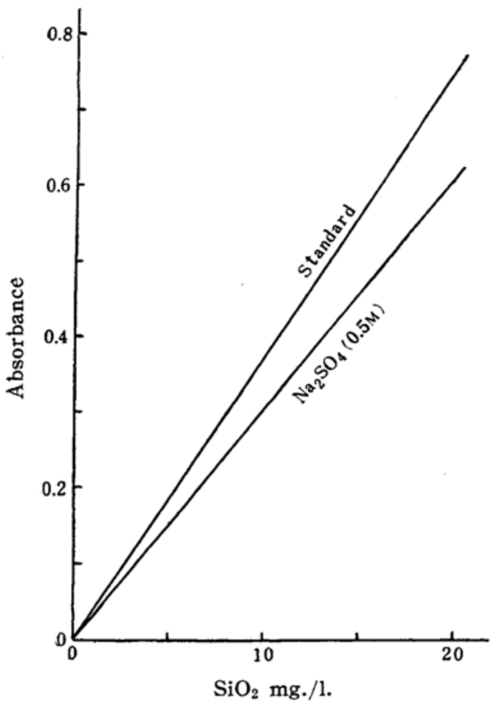

Fig. 7. Calibration curve.

Molybdenum Blue Method

Reagents.—*Sulfuric acid.*—3 N.

Ammonium molybdate solution.—10%.

Reducing agent. — Twenty grams of sodium bisulfite, 2 g. of anhydrous sodium sulfite, and 0.5 g. of 1-amino-2-naphthol-4-sulfonic acid were dissolved in 200 cc. of distilled water, and stored in an amber-colored glass bottle.

Experiments.—Fifty cc. of a sample solution was taken, and 2 cc. of 3 N sulfuric acid and 2 cc. of 10% ammonium molybdate solution were added. After the color of yellow silicomolybdic acid reaches maximum, 5 cc. of reducing agent was added. After the color of molybdenum blue reaches maximum, the absorbance was measured against a blank containing the same amount of reagents at 820 mμ. Fine crystals sometimes separated out from the solution, when the concentration of salts were very high and temperature was low.

The absorbance was measured for different concentrations of silica in distilled water and in 0.5 M sodium sulfate solution, and the results obtained are shown in Fig. 8. Straight lines were obtained—i. e. the absorbance of molybdenum blue complex in the salt solution obeys Beer's law as in silicomolybdate method, and the ratio of the slopes of two straight lines gives the salt factor.

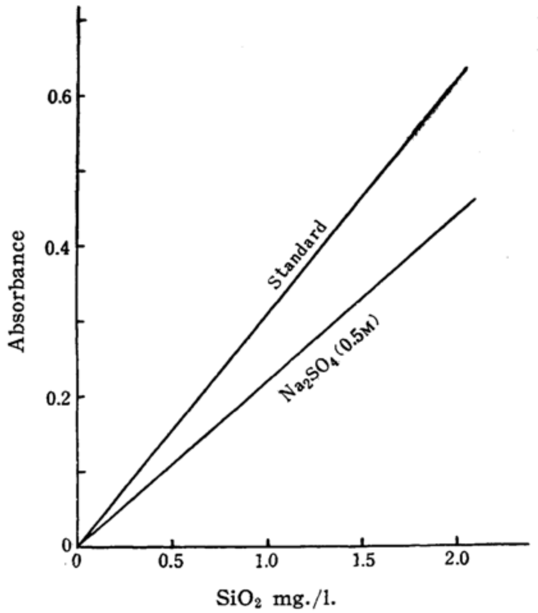

Fig. 8. Calibration curve.

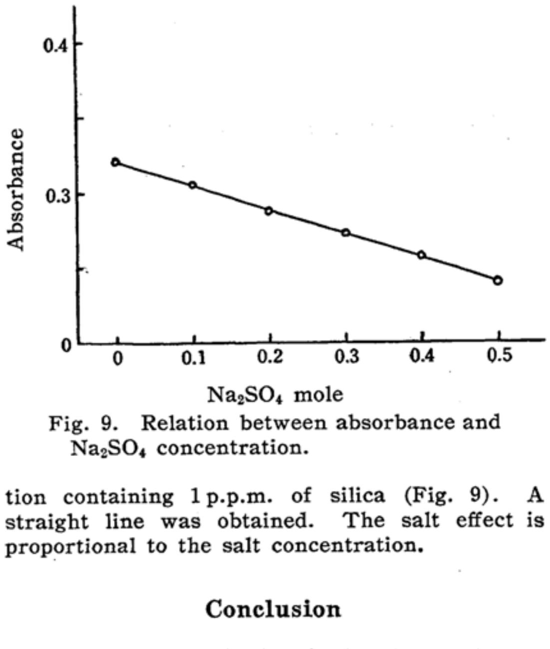

Fig. 9. Relation between absorbance and Na_2SO_4 concentration.

The variation of salt effect with wave length was not measured, but in this method, the salt effect will vary with wave length as in the silicomolybdate method. The absorbance was measured for a number of concentrations of solution containing 1 p.p.m. of silica (Fig. 9). A straight line was obtained. The salt effect is proportional to the salt concentration.

Conclusion

1) Wave length, kind of salt, and concentration of salts are important factors which affect the salt effect in both silicomolybdate method and molybdenum blue method.

2) In the silicomolybdate method, the salt effect is great at a longer wave length. Also, it varies with the kind of salt. The effect of sulfate is greater than that of chloride.

3) The absorbance of both silicomolybdic acid and molybdenum blue complex

in a salt solution obeys Beer's law, when the concentration of salt and reagents are maintained constant, and a definite wave length is used.

4) In the salt solutions containing definite quantities of silica, the absorbance decreases linearly with salt concentration under the conditions described above.

5) From the properties of salt effect mentioned above, it is possible to explain the reasons that several different salt factors were reported for sea water by different authors.

6) In order to obtain the true silica content in the concentrated salt solutions by the colorimetric method, one of the following procedures may be used.

(a) A sample solution is diluted with distilled water to the extent that the salt effect can be neglected, and then absorbance is measured.

(b) The calibration curve is made by using the same concentration of salt as that of the sample solution.

(c) The calibration curve is made by using the standard silica solution, and it is used for the determination of silica in a concentrated salt solution. The concentration (A) of silica in the sample solution is determined and the concentration (B) of silica in the sample solution diluted twice with distilled water is measured. The true silica content (S) can be obtained by the following formula.

$$S = A + 2(2B - A)$$

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