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Spectrophotometric Determination of Silicic Acid by Flow Injection Analysis

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Flow injection analysis (FIA) was developed for the spectrophotometric determination of silicic acid based on the formation of a yellow molybdosilicic acid (yellow method) and a heteropoly blue complex (blue method). In the yellow method, silicic acid in the concentration range of 2 to 100 ppm (SiO_2) could be determined at a sampling rate of 60 samples/h. The FIA system was modified to determine silicic acid in the presence of orthophosphate. Oxalic acid was used for the decomposition of molybdophosphoric acid. The modified system was employed for the rapid and selective determination of silicic acid in well and river waters. In the blue method, ascorbic acid was used to reduce the yellow molybdosilicic acid to a heteropoly blue complex. Silicic acid in the concentration range of 0.02 to 1.0 ppm (SiO_2) could be determined at a sampling rate of 40 samples/h. The FIA system was also modified to determine silicic acid in the presence of orthophosphate. The reducing agent was introduced after molybdophosphoric acid had been completely decomposed by adding oxalic acid. The modified system was employed for the determination of silicic acid in sea water.

The silicic acid content of natural waters is of particular interest in geochemistry inasmuch as it is related to the weathering of rocks and the formation of clay minerals. Recently, interest in the study of the behavior of silicic acid in natural waters has increased, because silicic acid as well as orthophosphate is one of the major inorganic nutrients for planktons and microorganisms. Since it is necessary to analyze a large number of samples, rapid and automatic method of analysis for silicic acid is increasingly becoming important.

Silicic acid is usually determined by spectrophotometric method based on the formation of a yellow molybdosilicic acid (yellow method). Often, to enhance the sensitivity of the analysis, the molybdosilicic acid is reduced to yield a heteropoly blue complex (blue method).

An air-segmented method has been applied to the determination of silicic acid.¹⁾ The method is satisfactory with respect to reproducibility and sensitivity, but the disadvantages are that the instrument is expensive and that the procedure is somewhat time-consuming. Recently a flow-coulometric method has been developed for the rapid determination of silicic acid.²⁾ The method is convenient but less sensitive than the conventional spectrophotometric method.

Flow injection analysis (FIA) is a simple and convenient approach to rapid chemical analysis.³⁾ The present authors have already reported successful applications of FIA to the determination of phosphorus compounds.⁴,⁵⁾ One of the most advantages of FIA is that reaction conditions, *e.g.*, reaction time, reaction temperature, reagent concentration, *etc*, can easily be kept constant with a simple apparatus. The formation of molybdosilicic acid is susceptible to such conditions as described above. Therefore the application of FIA is effective to achieve a rapid and precise analysis for silicic acid.

In a previous paper,⁶⁾ we have briefly reported a successful application of FIA to the determination of silicic acid based on the formation of a molybdosilicic acid. The present work was carried out to attain two purposes. One is to determine silicic acid rapidly and precisely in the wide range of concentration. The other is to modify the FIA system for the determination of silicic acid in the presence of orthophosphate. The FIA system was found to be useful for the determination of silicic acid in natural waters such as well, river and sea waters.

Experimental

Samples and Reagents. All reagents used were of analytical reagent grade. Unless otherwise stated deionized distilled water was used. A monosilicic acid stock solution (100 ppm SiO_2) was prepared by dissolving silica gel (Mallinckrodt Chemical Works) in a boiling water. The concentration of this stock solution was standardized spectrophotometrically. Working standard solutions were prepared by diluting the stock solution with water. A molybdenum(VI) reagent was prepared by dissolving 8.83 g of hexaammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) in *ca.* 0.9 dm^3 of water. After 7.5 cm^3 of concentrated sulfuric acid had been added, the solution was diluted to 1 dm^3 with water. The reagent was composed of 0.05 mol dm^{-3} Mo^{VI} and 0.135 mol dm^{-3} H_2SO_4. A 0.5 mol dm^{-3} oxalic acid solution was prepared by dissolving oxalic acid ($H_2C_2O_4\cdot 2H_2O$). Orthophosphate solution was prepared by dissolving potassium dihydrogenorthophosphate (KH_2PO_4), which had been dried for 1 h at 110 °C. L-Ascorbic acid solutions (0.02 mol dm^{-3}) containing various amounts of sulfuric acid were prepared under cooling with ice. Artificial sea water as a carrier solution for the analysis of sea water was prepared by dissolving 24.7 g of sodium chloride, 13 g of magnesium chloride ($MgCl_2\cdot 6H_2O$) and 4 g of anhydrous sodium sulfate in water, and then the volume was made up to 1 dm^3. Natural water was filtered just after sampling by membrane filter (0.45 μm pore size) and stored in a 50-cm^3 polyethylene bottle. The determination of silicic acid in natural water samples was carried out within 24 h after sampling.

Apparatus, Manifold, and Procedure. Four kinds of manifolds (systems I—IV) were designed (Fig. 1). Two reciprocating pumps (Kyowa KHU-W-104 (P_1) and Kyowa KHU-W-52 (P_2)) with double plungers were used to introduce carrier solutions into analytical lines. A sample (S) was injected into a carrier stream *via* a loop-valve in-

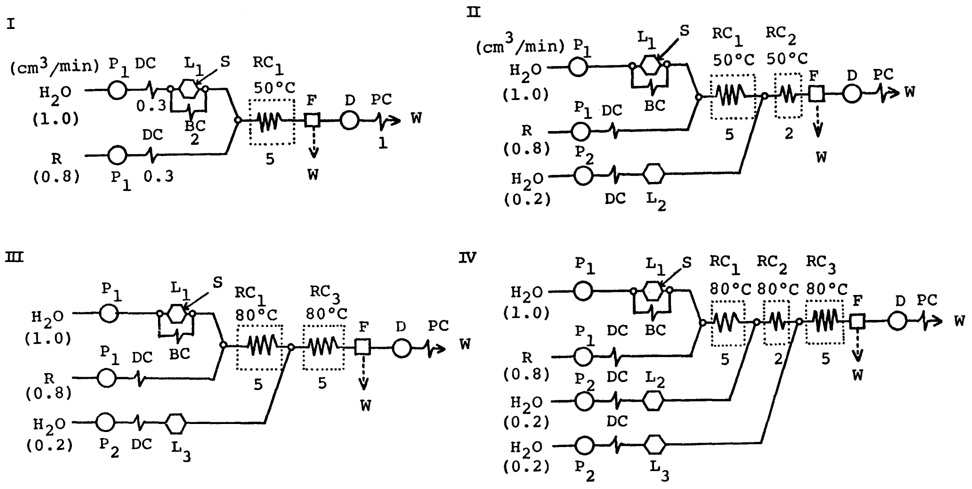

Fig. 1. FIA systems I—IV for the determination of silicic acid based on the yellow method (I and II) and the blue method (III and IV). FIA systems II and IV were designed to determine silicic acid in the presence of orthophosphate. R: molybdenum(VI) reagent, P_1 and P_2: reciprocating pump, DC: damper coil, BC: bypass coil, RC_1, RC_2, and RC_3: reaction coil, PC: back pressure coil, L_1, L_2, and L_3: loop valve injector, F: three way valve, D: detector and W: waste. The numerals under the coils refer to their lengths in meter. The numerals under the pump indicate the flow rate of solutions. The dotted lines show the manifolds immersed in the thermostated silicone oil-bath.

jector (L_1, Seishin VMU-6). The injected sample was then transported through reaction coils (RC_1, RC_2, and RC_3, PTFE 0.5 mm ID). To accelerate chemical reaction the reaction coils were heated in a silicone-oil bath (Thomas-T-201). Color complexes formed in the reaction coils were monitored using a spectrophotometer (D, Hitachi 200—10) with a flow-through cell (8 mm light path, 8 μl volume).

An elastic precoil (DC, Technicon Part No. 065-116-0536-13, 30 cm) was applied to dampen the pressure pulse caused by the reciprocating pumps. A bypass coil (BC, PTFE 0.3 mm i.d., 2 m) was also applied to minimize the injection shock. A three way valve (F, Kyowa KMM-4V) was located just before the detector to observe the variation in absorbance of a sample zone in the flow-through cell (Stopped-flow method). A back pressure coil (PC, PTFE 0.3 mm i.d., 1 m) was attached at the exit of the flow-through detector to eliminate a noise due to gas-bubbling. Both an oxalic acid and an ascorbic acid solutions were introduced *via* loop-valve injectors L_2 and L_3, (Kyowa KMM-4V-2) respectively. The function of these valves was precisely described in a previous paper.[5] This method makes it possible to put in, cut off or exchange a reagent without any reconditioning of a pump.

In FIA system I, a sample was mixed with a molybdenum (VI) reagent (R). A molybdosilicic acid formed in the reaction coil (RC_1) was directly monitored at 400 nm. FIA system II was designed to determine silicic acid in the presence of orthophosphate. The oxalic acid solution was added from another line using the loop-valve injector (L_2) to decompose molybdophosphoric acid formed in the first reaction coil (RC_1). The remaining molybdosilicic acid was monitored at 400 nm. In FIA system III, the ascorbic acid solution was introduced using the loop-valve injector (L_3) to reduce the molybdosilicic acid in the reaction coil (RC_3). The resultant blue complex was monitored at 820 nm. FIA system IV was designed to determine silicic acid in the presence of orthophosphate. After decomposition of molybdophosphoric acid, the remaining molybdosilicic acid was reduced with ascorbic acid to a heteropoly blue complex.

Results and Discussion

Flow Injection Analysis for Silicic Acid Based on the Formation of a Molybdosilicic Acid. Flow rates of carrier solutions through the pump (P_1) and a length of the reaction coil (RC_1) of the FIA system I were designed to determine silicic acid at 60 samples/h. Taking the composition of a molybdosilicic acid (Si:Mo=1:12) and the flow rate of each carrier solution into account, 0.05 mol dm^{-3} molybdenum(VI) reagent solution was used to determine silicic acid up to 100 ppm (SiO_2). The acid concentration of the molybdenum(VI) reagent was adjusted to 0.135 mol dm^{-3} in H_2SO_4.[7] The temperature of the heating bath was kept at 50 °C to accelerate the chemical reaction. The residence time of a sample in the reaction coil was about 1 min.

Figure 2 shows a normal FIA signal and a stopped-flow signal. The same sample was injected twice. At the top of the second signal, the valve F was switched to hold the sample zone in the flow-through cell.

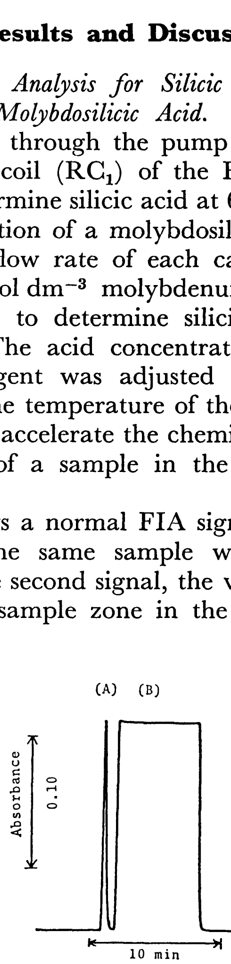

Fig. 2. FIA profile (A) and stopped flow signal (B) for silicic acid obtained by FIA system I. Sample: 50 ppm (SiO_2), 0.10 cm^3.

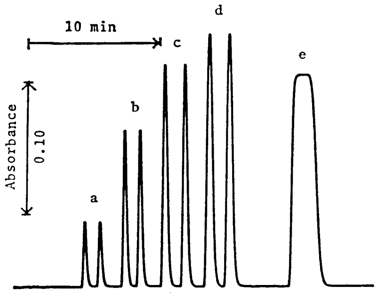

Fig. 3. Effect of the length of sample loop on the FIA signal.
Sample: 10 ppm (SiO_2), a; 0.08, b; 0.50, c; 1.0, d; 1.5, and e; 5.0 m. FIA system I was used.

There was no remarkable change in absorbance. This suggests the completion of the color forming reaction.

Figure 3 shows the effect of the sample volume on the FIA signal. The injection volume of a sample was varied by using the sampling loops (PTFE, 0.5 mm i.d.) with different length. The peak height of the FIA signal increased with lengthening the sampling loop up to 1.5 m and decreased at 5.0 m.[8] Therefore, sampling loops of 0.08 and 1.5 m, corresponding to *ca.* 0.10 and 0.50 cm^3, were used.

To demonstrate the reproducibility, the samples (2, 20, and 100 ppm (SiO_2)) were injected ten times. The precisions (C.V.) were 1.7, 0.2, and 0.07% for silicic acid of 2, 20, and 100 ppm (SiO_2), respectively. The standard sample of silicic acid could be measured in the concentration range of 2 to 100 ppm. The sampling rate was 60 samples/h. The detection limit (S/N=2) was 0.3 ppm.

Orthophosphate reacts with molybdenum(VI) reagent to form a yellow molybdophosphoric acid and the complex interferes with the determination of silicic acid. In order to eliminate the interference, decomposing agents have been employed for the decomposition of molybdophosphoric acid. In Japanese Industrial Standard (JIS) method,[9] oxalic acid is used as the decomposing agent. As it is necessary to add an excessive amount of the decomposing agent compared with that of molybdenum(VI),[10] 0.5 mol dm^{-3} oxalic acid solution was used.

The FIA system II was designed to determine silicic acid in the presence of orthophosphate. Oxalic acid solution was introduced from another line using a loop-valve injector (L_2). As the decomposition of molybdophosphoric acid proceeds rapidly even at room temperature,[10] a short reaction coil (RC_2, 2 m) was applied. The heating bath was kept at 50 °C. The remaining molybdosilicic acid was monitored at 400 nm.

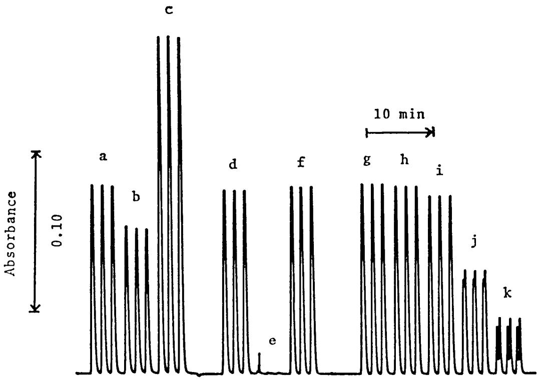

Fig. 4. Detection peaks for silicic acid samples containing various amounts of orthophosphate in the absence (a—c) and presence (d—k) of oxalic acid.
Sample: a; 10 ppm (SiO_2)+0 ppm (PO_4^{3-}), b; 0 ppm (SiO_2)+20 ppm (PO_4^{3-}), c; 10 ppm (SiO_2)+20 ppm (PO_4^{3-}), d; 10 ppm (SiO_2)+0 ppm (PO_4^{3-}), e; 0 ppm (SiO_2)+20 ppm (PO_4^{3-}), f; 10 ppm (SiO_2)+20 ppm (PO_4^{3-}), g; 10 ppm (SiO_2)+50 ppm (PO_4^{3-}), h; 10 ppm (SiO_2)+100 ppm (PO_4^{3-}), i; 10 ppm (SiO_2)+200 ppm (PO_4^{3-}), j; 10 ppm (SiO_2)+300 ppm (PO_4^{3-}), and k; 10 ppm (SiO_2)+400 ppm (PO_4^{3-}), 0.50 cm^3. Each sample was injected in triplicate.

TABLE 1. SILICIC ACID CONCENTRATION IN WELL AND RIVER WATER SAMPLES OBTAINED BY THE FIA AND JIS METHOD

Sample	FIA(SiO_2 ppm)	JIS(SiO_2 ppm)
Well water		
(A)	17.8	17.4
(B)	20.0	19.3
(C)	20.9	20.3
River water		
(D)	9.9	9.5
(E)	12.6	12.1
(F)	12.5	12.1
(G)	12.4	12.1
(H)	12.6	12.3
(I)	11.8	11.5
(J)	13.4	13.1
(K)	13.7	13.3
(L)	14.2	14.0

The efficiency of the decomposition effect of oxalic acid was examined. The results are shown in Fig. 4. From the FIA signals (a—c), it is clear that both molybdosilicic acid and molybdophosphoric acid form independently in the absence of oxalic acid. From the FIA signals (d—k), the interference due to orthophosphate up to 100 ppm (PO_4^{3-}) could be eliminated by the addition of oxalic acid. Further increase in the concentration of phosphate caused a decrease in peak height. At 300 and 400 ppm (PO_4^{3-}), the FIA signals became double peak. The decrease in peak height and the appearance of double peak may be caused by the deficiency of molybdenum(VI) to be required for the formation of molybdosilicic acid, because molybdenum(VI) is consumed by the formation of molybdophosphoric acid.

Determination of Silicic Acid in Well and River Waters. The FIA system II was employed for the determination of silicic acid in well and river waters. Routine runs for the determination are illustrated in Fig. 5, together with that for a series of standard silicic acid. The sampling rate was 40 samples/h. The analytical values obtained by FIA are shown in Table 1, together with those obtained by JIS method. Both results coincide satisfactorily with a correlation coefficient of 0.998.

Flow Injection Analysis for Silicic Acid Based on the Formation of a Heteropoly Blue Complex. To get higher sensitivity and avoid the interference due to absorption by foreign compounds at 400 nm, a method was examined for the determination of silicic acid based on the formation of a heteropoly blue complex. Among many reducing agents,[11] ascorbic acid was used to reduce a yellow molybdosilicic acid to a blue compound because of its simple preparation. The reducing agent was composed of 0.02 mol dm^{-3} ascorbic acid and 2 mol dm^{-3} sulfuric acid. The reducing agent was added after the formation of molybdosilicic acid.[11]

In the FIA system III, the ascorbic acid solution was introduced from the another line using a loop-valve injector (L_3). A five meter reaction coil (RC_3) was applied to reduce a molybdosilicic acid to a heteropoly blue complex. Figure 6 shows that FIA signal and stopped-flow signal greatly depended on the temperature of the heating bath. The stopped-flow signal at 60 °C showed a steep increase in absorbance followed by a steady state. The signal was quite different from the signal observed in Fig. 2. There was no remarkable increase in the base line level when the carrier reagent was stopped in the flow-through cell (Fig. 6(IV)). This indicates that the formation of blue isopolymolybdic acid during the stopping period is negligible. Therefore the difference in height between the FIA signal and the top of the stopped flow signal is regarded as an unreduced portion of the molybdosilicic acid. At 80 °C, more than 90% of molybdosilicic acid was reduced. The determination of silicic acid hereafter was carried out at 80 °C.

The standard sample of silicic acid could be measured in the concentration ranges of 0.02 to 0.1 and 0.2 to 1.0 ppm (SiO_2). The samples were injected successively at the sampling rate of 40 samples/h. The detection limit (S/N=2) was 0.01 ppm (SiO_2). The precision (C.V.) was 0.5% for 0.6 ppm silicic acid.

The formation of a heteropoly blue complex of silicon and molybdenum and blue isopolymolybdic acid is susceptible to acid concentration, temperature and addition of decomposing agent of molybdophosphoric acid.[7] The effect of acid concentration on the FIA signal and the base line level was examined by using FIA system IV. The effect was examined under two conditions. Figure 7 shows the effect of the acid con-

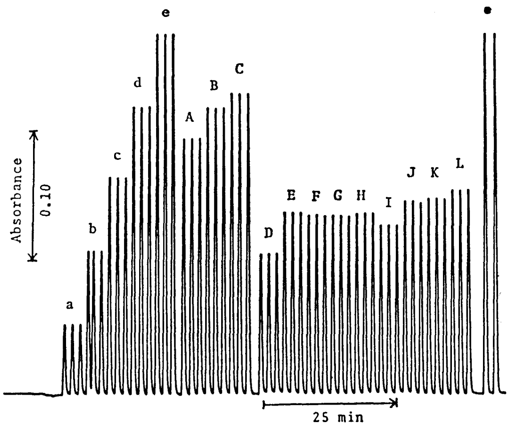

Fig. 5. Determination of silicic acid in well and river waters using FIA system II.
The first fifteen peaks on the left and the last two peaks on the right were obtained by injecting standard samples of silicic acid. Sample: a; 5, b; 10, c; 15, d; 20, and e; 25 ppm (SiO_2), A—C; well waters, D—L; river waters. Sample volume: 0.50 cm^3.

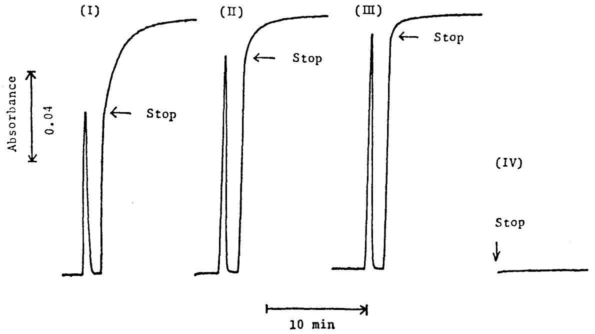

Fig. 6. FIA profiles and stopped flow signals for silicic acid of 1 ppm (SiO_2), 0.50 cm^3.
Temperature of the heating bath: (I); 60 °C, (II); 70 °C, and (III); 80 °C. The signal (IV) shows a stopped flow signal of a base line level at 80 °C. FIA system III was used.

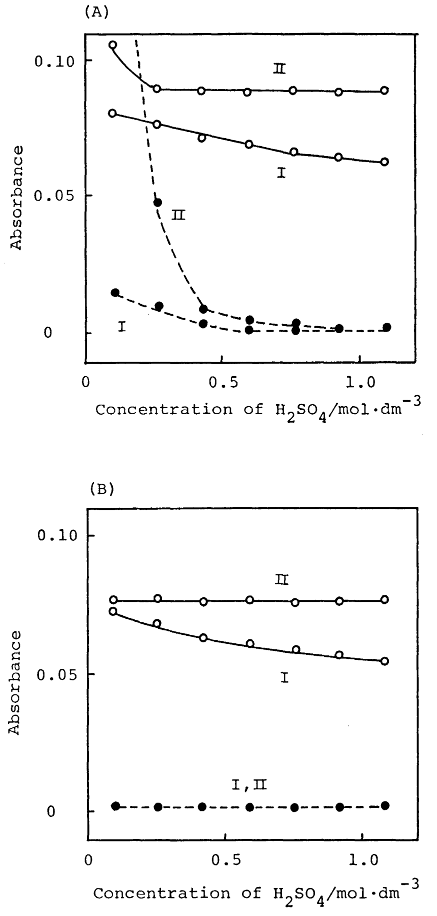

Fig. 7. Effect of acid concentration in the reaction coil (RC_3) and temperature of the heating bath on the FIA peak height and base-line level in the absence (A) and presence (B) of oxalic acid.
FIA system IV was used. ○: Peak height, ●: base line level. I: 50 °C and II: 80 °C. Sample: 1 ppm (SiO_2), 0.50 cm^3.

centration on the FIA signal and the base line in the absence and the presence of oxalic acid, respectively. Oxalic acid and ascorbic acid solutions were introduced with the loop-valve injectors (L_2) and (L_3), respectively. Figure 7(A) shows the results obtained by introducing water in place of oxalic acid solution. The abscissa of Fig. 7 indicates the acid concentration in the reaction coil (RC_3). The acid concentration was controlled by adding various amounts of sulfuric acid to the ascorbic acid solution.

It is clear from Fig. 7(A) that the rate of the formation of both a heteropoly blue complex and blue isopolymolybdic acid increases at higher temperature and at lower acid concentration. Therefore a suitable amount of sulfuric acid must be added to avoid the formation of the blue isopolymolybdic acid in the absence of oxalic acid. It is also necessary to increase the temperature of the heating bath to accelerate the formation of the heteropoly blue complex.

From Fig. 7(B), it is seen that blue isopolymolybdic acid does not form in the presence of oxalic acid. This fact also indicates that oxalic acid reacts with molybdenum(VI). The absorbance of the plateau region of the heteropoly blue complex at 80 °C obtained in the presence of oxalic acid is somewhat lower than that obtained in the absence of oxalic acid, because oxalic acid decomposes a part of molybdosilicic acid at such a high temperature as 80 °C.

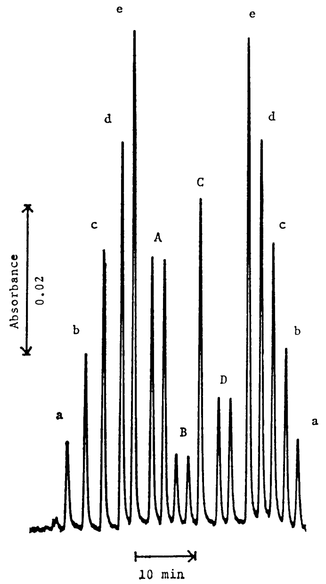

Fig. 8. Determination of silicic acid in sea waters using FIA system IV.
The first five peaks on the left and last five peaks on the right were obtained by injecting standard samples of silicic acid. Sample: a; 0.2, b; 0.4, c; 0.6, d; 0.8, and e; 1.0 ppm (SiO_2), A—D; sea waters, 0.50 cm^3. Each sample was injected in duplicate except C.

It must be noted that there is no need to add sulfuric acid to the ascorbic acid solution, when oxalic acid is used. This fact is favorable for the preparation of ascorbic acid solution, because ascorbic acid is easily oxidized in the presence of sulfuric acid.

Determination of Silicic Acid in Sea Water. The FIA system IV was employed for the determination of silicic acid in sea water. Artificial sea water was introduced as a carrier solution of a sample. Figure 8 shows routine runs for the analysis of sea water. A reducing agent, ascorbic acid solution, was composed of 0.02 mol dm^{-3} L-ascorbic acid and 2 mol dm^{-3} sulfuric acid. The silicic acid concentration of the four samples were (A) 0.57, (B) 0.15, (C) 0.69, and (D) 0.30 ppm (SiO_2), respectively.

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