The Separation of Sulfate, Sulfite, Thiosulfate and Sulfide Ions with Anion-Exchange Resins[*]

By Akira IGUCHI

(Received March 14, 1958)

Several methods of analysis of the mixture of sulfite, thiosulfate and sulfide ions have been reported by some researchers[1], most of which are based on the method of titration without separation of these components. In this study the author has applied the anion-exchange chromatography to the mutual separation of the above-mentioned oxy-acids of sulfur and sulfide, obtaining satisfactory results.

Experimental

Materials. — *Anion-exchange resins.* — Diaion SA ♯ 100, a strongly basic type resin (polystyrene-

---

[*] This paper was presented before the 6th Annual Meeting of Japan Society for Analytical Chemistry held on Oct. 19, 1957 in Kyoto.

[1] For example, A. Kurtenäcker et al., *Z. anorg. allgem. Chem.*, **161**, 201 (1927).

divinyl benzene quaternary amine) prepared by Mitsubishi Kasei Co. was used. It is of mesh size 100∼200 in beads (nitrate form).

Sodium thiosulfate.—The guaranteed reagent of Junsei Chemicals Co. was used. The iodometric titration showed that this sample did not contain impurities which would interfere with the experiment.

Sodium sulfate.— The guaranteed reagent of Junsei Chemicals Co. was used. The result of gravimetric analysis showed that this sample was sufficiently pure for the purpose of this study.

Sodium sulfite and sodium sulfide.—Aqueous solutions of both salts are oxidized easily, but the decrease of the concentration was found to be less than about 1% for sulfite, and less than 2% for sulfide during the process of separation (about 6∼10 hours). The quantity of sulfate in the original sulfite solution was determined from the difference between the quantity of sulfite titrated iodometrically and that of sulfate plus sulfite which was weighed gravimetrically in the form of barium sulfate after oxidizing the sulfite into sulfate. The amount of impurity contained in the sulfide solution newly prepared was found to be negligible.

Procedure.—*Measurement of distribution coefficient.*—For the separation of these readily oxidizable anions, it is not desirable to use resins in the nitrate form, as the nitrate acts as an oxidant. On the other hand, the chloride solution is not suitable for the elution of these anions, as the tail part of the elution curve becomes long. Solution of sodium or ammonium nitrate plus ammonia was found to be an excellent eluant, the oxidizing effect not appearing in these conditions. In a neutral solution, a slight decomposition of sulfite and sulfide was recognized, especially in contact with resins in nitrate form. This decomposition may be due to the catalytic action of resins.

The measurement of distribution coefficient, K_d, was made by the column method. The K_d values of the ion were calculated from the volume of eluant by using the following equation:

$$K_d=(V-i)/M^{2)}$$

where K_d(cc./g.) is the distribution coefficient, V (cc.) the volume of eluant passed through the column until the concentration of solution in the effluent becomes maximum, i(cc.) the interstitial volume of the column and M(g.) the weight of the resin.

Each resin column contains 1 to 3 g. of Diaion SA ♯100. The size of the column is 7.0 mm. in diameter. The flow rate is less than 0.1 cc./min.. The eluant was aqueous solution of sodium nitrate, but the solution of ammonium nitrate containing ammonia was also used for sulfite ion.

Results and Discussion

Relations Between the Distribution Coefficient and the Concentration of Nitrate Ion in the Eluant.—The mean values of the distribution coefficient of triplicate experiments are shown in Fig. 1. From these data a linear relationship between log K_d and the concentration of nitrate (log C) is recognized, especially in the region of low concentration. The curves for sulfite, thiosulfate and sulfate ions are nearly parallel, and the slope is about 2 at 0.1∼0.2 mol./l., hence, as Honda discovered and reported[3], they must be doubly charged ions. In the case of sulfide, the slope of the line is nearly unity, suggesting the probable presence of HS^- ion even in a neutral solution. From the data in Fig. 1, thiosulfate, sulfate and sulfite may be separable using 0.1 mol./l. nitrate solution as an eluant.

The Relation between pH and Distribution Coefficients. — The distribution coefficient K_d of ions of polybasic acids may change with the variation of pH. Accordingly the relationship between pH and K_d was checked in the range of pH 7∼11. The buffer solution, prepared by

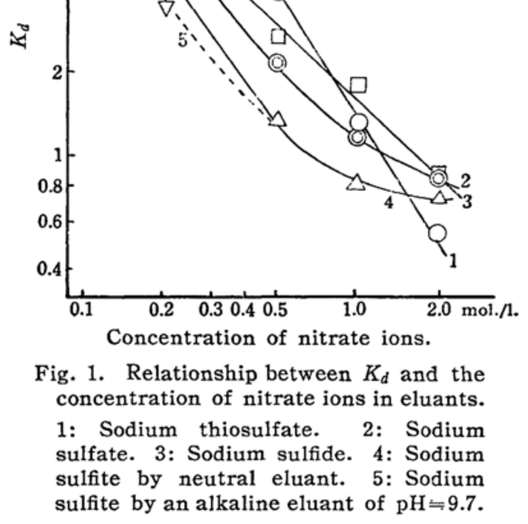

Fig. 1. Relationship between K_d and the concentration of nitrate ions in eluants.

1: Sodium thiosulfate. 2: Sodium sulfate. 3: Sodium sulfide. 4: Sodium sulfite by neutral eluant. 5: Sodium sulfite by an alkaline eluant of pH≒9.7.

---

[2] M. Honda, *Japan Analyst* (*Bunseki Kagaku*), **2**, 155 (1953).

[3] M. Honda, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **72**. 361 (1951).

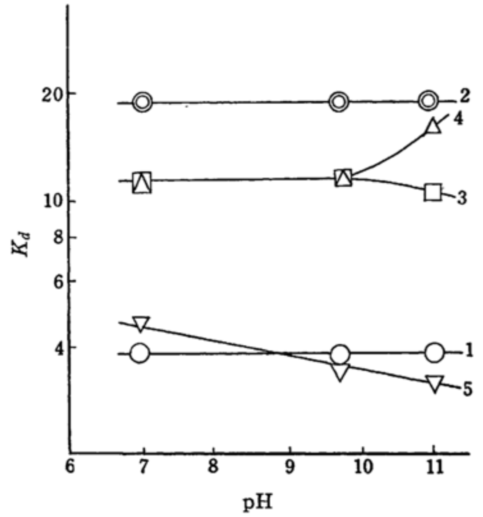

Fig. 2. Relationship between K_d and the pH of eluant.

1: Sodium thiosulfate eluted by 0.5 mol./l. nitrate solution. 2: sodium sulfate eluted by 0.1 mol./l. nitrate solution. 3: sodium sulfide eluted by 0.1 mol./l. nitrate solution. 4: Sodium sulfite eluted by 0.1 mol./l. nitrate solution. 5: Sodium sulfite eluted by 0.2 mol./l. nitrate solution.

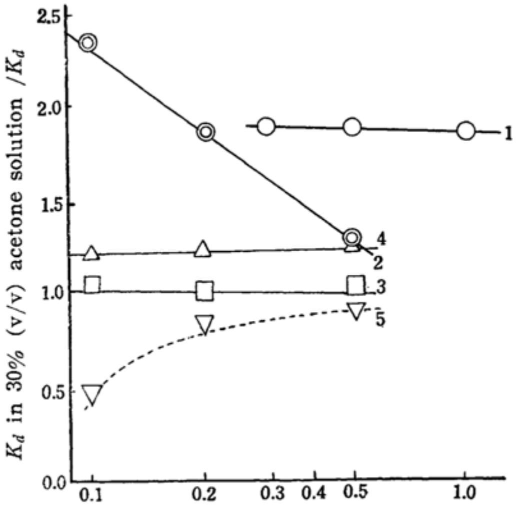

Fig. 3. Relationship between K_d in 30% (v/v) acetone solution /K_d in aqueous solution and the concentration of nitrate ion in eluant.
1: Sodium thiosulfate. 2: Sodium sulfate. 3: Sodium sulfide. 4: Sodium sulfite eluted by neutral eluant 5: Sodium sulfite eluted by alkaline eluant of pH≒9.7.

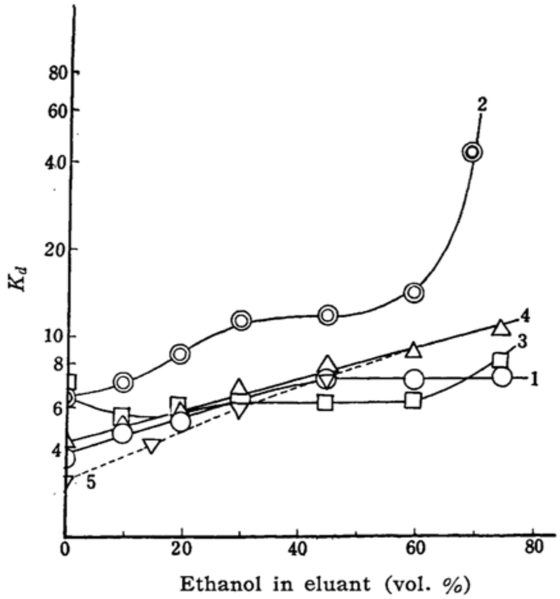

Fig. 4A. Relationship between K_d and the volume percentage of organic solvent in eluant.
1: Sodium thiosulfate. 2: Sodium sulfate. 3: Sodium sulfide. 4: Sodium sulfite eluted by neutral eluant. 5: Sodium sulfite eluted by alkaline eluant of pH≒9.7. The concentration of nitrate ion used as the eluant was 0.5 mol./l. for thiosulfate, and 0.2 mol./l. for the other salts.

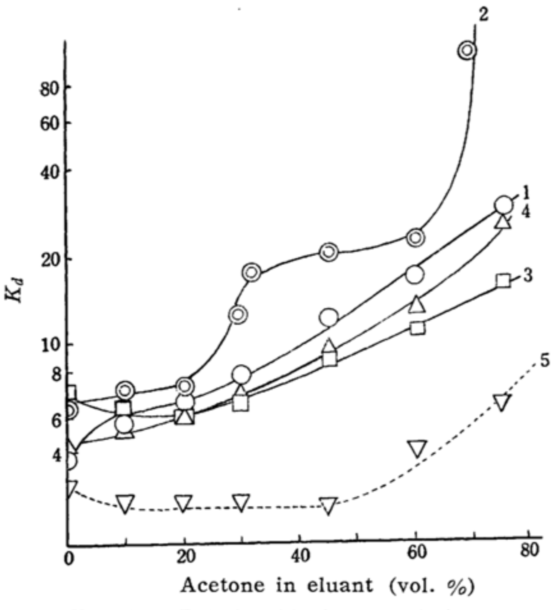

Fig. 4B. Relationship between K*d* and the volume percentage of organic solvent in eluant. The same legend as Fig. 4A. stands for Fig. 4B.

mixing ammonium nitrate, sodium nitrate and ammonia, was used. The pH was checked by a glass electrode pH meter (Type 43, made by Iio Denki Co.). The results are shown in Fig. 2. There is no remarkable change of K_d in this pH region, though the K_d of sulfite and sulfide eluted with 0.1 mol./l. nitrate solution showed a slight deviation with increase in pH at about pH 9~11.

The Effect of Organic Solvent on the Distribution Coefficient.—When the eluant which contained 30% (by volume) of acetone was employed together with various quantities of nitrate in place of aqueous solution, the value of the distribution coefficient showed deviation. The relation between the ratio of the K_d values thus determined in 30% (by volume) acetone solution to the K_d values of the original aqueous solution of the nitrate ion and the concentration of eluant was shown in Fig. 3. In the case of sulfide, the K_d in 30% (by volume) acetone solution is not affected by the addition of acetone, while the K_d values of thiosulfate and sulfite in 30% (by volume) acetone solution become 1.9 and 1.1 times greater than the values of K_d determined in the original aqueous solution, respectively. The concentration of nitrate does not affect the ratio K_d in 30% (by volume) acetone solution and that in aqueous solution. In the case of sulfate, this ratio increased with the decrease of the concentration of nitrate. Generally the increase of K_d in 30% acetone solution by the addition of organic solvent may be caused by the stripping off of the hydrated water molecules surrounding the anion of oxy-acid of sulfur. In the case of sulfite in alkaline solution, however, a decrease of K_d was recognized in 30% acetone solution.

In the next place, in order to clarify the effect of organic solvent on the adsorbability of these anions, the relationship between K_d and concentration of ethanol or acetone was examined, the concentration of nitrate being kept constant (0.5 mol./l. for thiosulfate and 0.2 mol./l. for other anions). The results were shown in Figs. 4A and 4B.

Experimental results showed a remarkakle increase of K_d values with the percentage of organic solvent. In general, the increase of K_d values by the addition of acetone is greater than that by the addition of the same percentage of ethanol. But exceptions were recognized in cases of sulfite by acetone, and of sulfide by ethanol. In these cases the K_d values decrease until they reach constant in spite of the increase in amount of organic solvent (even up to 40~60% by volume). From this result, the method of separation of sulfite, sulfide and sulfate is suggested, that is, the use of eluant which contains 30% (by volume) of actone and 0.1 mol./l. of nitrate, with pH adjusted to 9.7 by ammonia.

In addition to these measurements of K_d values using Diaion SA #100, the measurements by the use of Amberlite IRA-410 were also carried out. But the K_d values for the latter resin almost exactly coincided with those for the former resin within the range of experimental error.

Discussion on the Variation of Distribution Coefficients.—Judging from the slopes of the curves shown in Figs. 1 and 2, sulfate and thiosulfate may exist in the form of doubly charged anion, and their adsorbability does not change in the range of pH 7~11. The effect of organic solvent upon thiosulfate and sulfate is shown in Figs. 4A and 4B. In these data, an inflexion point is recognized at about 10% (by volume) in acetone for thiosulfate and at about 30% for sulfate. These facts may be attributed to some discontinuous dehydration grade of these anions. In the case of sulfide, as is shown in Fig. 1, the HS^- ion may be a predominant species as is expected from the slope of the curve. The effect of adding ethanol, as is shown in Fig. 4A, keeps the K_d constant even up to 60%, while the increase of K_d by acetone appeared even at 30%. These phenomena may be caused by a special interaction between ethanol and sulfide, ions. In the case of sulfite, the formation of a compound between sulfite ions and acetone is expected,[4] whereas, as is shown in Figs. 4A and 4B, the K_d in a neutral solution shows no special change compared with the other oxy-acid ions; in other words, only a monotonous increase of K_d with the increase of the content of organic solvent was observed. But, in the case of alkaline solution, the K_d decreases and then remains constant even up to 45% of acetone. This fact can perhaps be ascribed to the formation of special compounds between acetone and sulfite or between acetone, ammonia

---

[4] G. Gabrielson and O. Samuelon, *Svensk. Kem. Tid.*, **62**, 214 (1950).

TABLE I

THE ANALYSIS OF MIXED SAMPLES OF SULFITE, SULFATE, AND THIOSULFATE

		Sulfite	Sulfate	Thiosulfate
Added.	mg.	6.39	19.4	20.0
Observed.	mg.	6.32±0.064	19.0±0.41	20.0±0.20
	%	99.0±1.0	98.0±2.0	100.0±1.0

TABLE II

THE ANALYSIS OF MIXED SAMPLE OF SULFITE, SULFATE, SULFIDE AND THIOSULFATE

		Sulfite	Sulfide	Sulfate	Thiosulfate
Added	mg.	7.00	2.96	19.3	21.98
Observed.	mg.	6.93±0.69	2.78±0.16	18.58±0.30	22.20±0.22
	%	99.0±1.0	94.1 ±5.5	96.3 ±1.5	101.1 ±1.0

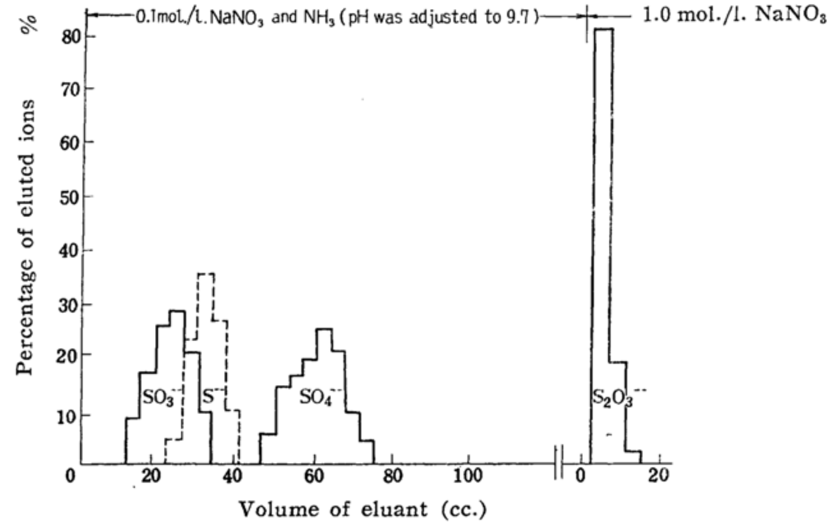

Fig. 5A. Elution curve of a mixed sample. The flow rate was 0.3 cc./min.

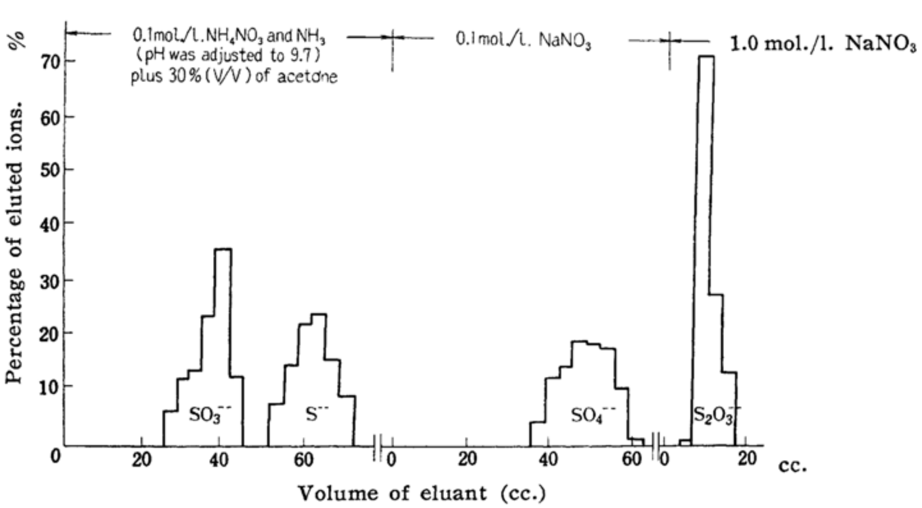

Fig. 5B. Elution curve of a mixed sample. The flow rate was 0.1 cc./min.

and sulfite[5]. In alkaline solution without acetone the K_d of the sulfite ion shows only slight deviation from the K_d of sulfite ion in a neutral solution as shown in Fig. 1, from which it is inferred that this phenomenon is due neither to the change in the form of the sulfite ion only, nor to the reaction between the ammonia and the sulfite ion before the addition of acetone.

The Chromatographic Separation of Sulfate, Sulfite and Thiosulfate.—When sulfide does not coexist with the other three, the result shown in Fig. 1 may be applicable to their separation. By using 0.1 mol./l. of nitrate solution, first sulfite, and next sulfate were eluted; then thiosulfate was eluted by 1.0 mol./l. of nitrate solution. But, when the neutral nitrate solution was used as an eluant, recovery of sulfite did not reach 100%, and accordingly it was necessary to use an alkaline eluant. The 0.1 mol./l. ammonium nitrate solution with the pH adjusted to 9.7 by ammonia was most suitable. The ion-exchange resin Diaion SA ♯100 of analytical grade mounted in a column of 0.7 cm. in diameter and 17 cm. in length was employed. The amount of the resin used was 4.9 g. The results are shown in Fig. 5A. The collected sulfite and thiosulfate were titrated with the standard solution of iodine, while the quantity of sulfate was determined gravimetrically in the form of barium sulfate.

The analysis by this method is simpler than the method which is shown in the next paragraph, because the flow rate is kept relatively great and the quantity of sulfite is determined by titration.

The recovery percentage of oxy-acid ions of the known composition shown in Table I was calculated from the data of the experiments repeated five times.

The Chromatographic Separation of Sulfate, Thiosulfate, Sulfite and Sulfide.—When sulfide is present, sulfide and sulfite are not separable by an elution with simple nitrate solution. The nitrate solution containing acetone can be employed for this purpose, as was expected from the data shown in Fig. 4B. The resin column is the same as that used in the experiment shown in Fig. 5A.

Sulfite and sulfide are first eluted successively by the eluant containing 30% (by volume) of acetone, 0.1 mol./l. of ammonium nitrate, with its pH adjusted to 9.7 by ammonia; second, sulfate is eluted with 0.1 mol./l. sodium nitrate, and finally thiosulfate by 1.0 mol./l. sodium nitrate. A typical run of such experiments is illustrated in Fig. 5B.

The quantity of collected sulfite is determined gravimetrically in the form of barium sulfate after oxidation by sodium peroxide in alkaline solution. Sulfide is titrated by standard iodine solution.

A example of recovery of each salt by this method, with the percentage calculated from the experiments repeated twelve times is shown in Table II.

From the results of these experiments it was found that this method can be used for the analysis of these salts. In the results shown in Table II, however, the recovery of sulfide is slightly less than the theoretical value. This defect may be remedied by improving the acceptor of the effluent so as to protect hydrogen sulfide from escaping.

Summary

1. The distribution coefficients of sulfate, thiosulfate, sulfite and sulfide in the nitrate solution were measured.

2. By the addition of ethanol or acetone to the neutral eluant solution, the adsorbability of sulfate, sulfite, thiosulfate and sulfide was increased, while that of sulfite in alkaline acetone solution showed a marked decrease.

3. By the use of these results a mutual separation of sulfate, thiosulfate, sulfite and sulfide was effected by the anion-exchange chromatography.

The author desires to express his gratitude to Professor T. Shirai, Dr. Y. Yoshino and to his colleagues in the laboratory for their suggestions and for the discussion helpful in publishing this paper.

Institute of Chemistry, College of
General Education, University
of Tokyo, Meguro-ku, Tokyo

---

[5] For example, G. Palmer, "Experimental Inorganic Chemistry" Cambridge Univ. Press, England, p. 330 (1954).