Determination of sulfur anions at the ppb level by ion chromatography utilizing their catalytic effects on the postcolumn reaction of iodine with azide

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Abstract

A sensitive method has been developed for ion chromatographic determination of sulfide, sulfite, thiosulfate and thiocyanate in their mixtures. Sulfide, sulfite, thiosulfate and thiocyanate were eluted at retention times of 5.1, 8.8, 15.0 and 21.5 min, respectively, from an ion-exchange column with a $6 \cdot 10^{-3}$ M carbonate eluent containing 15% (v/v) acetonitrile at a flow-rate of 0.5 ml min^{-1}. The sulfur anions in the effluent from the column were monitored by photometric measurement of the excess of iodine (triiodide) for a postcolumn iodine–azide reaction catalyzed by each of sulfide, thiosulfate and thiocyanate and for a postcolumn reaction of iodine with sulfite. Therefore, chromatograms obtained for the sulfur anions gave negative peaks, based on the decrease in the absorbance from background. The optimal conditions for the catalytic postcolumn reaction in the presence of the sulfur anions, with the exception of sulfite, were established by varying concentrations of iodine, iodide, acetic acid and azide in the postcolumn-reaction mixture, reaction temperature and length of the reaction tube. Calibration graphs, plotted as peak heights vs. concentrations, were linear up to $5.00 \cdot 10^{-7}$ M for sulfide, $4.50 \cdot 10^{-6}$ M for sulfite, $5.00 \cdot 10^{-7}$ M for thiosulfate and $2.00 \cdot 10^{-7}$ M for thiocyanate respectively. Detection limits at $S/N=3$ were 0.14 ng for sulfide, 2.40 ng for sulfite, 0.16 ng for thiosulfate and 0.05 ng for thiocyanate. The proposed method was successfully applied to the determination of sulfide, sulfite and thiosulfate in hot-spring water samples. © 1998 Published by Elsevier Science B.V.

Keywords: Detection, LC; Water analysis; Sulfite; Inorganic anions; Sulfide; Thiosulfate; Thiocyanate

1. Introduction

Sulfur species of sulfide, sulfite and thiosulfate are very reactive and unstable; these anions can react with one another and undergo decomposition or air oxidation. Sulfite and thiosulfate are formed as intermediate products by oxidation of sulfide and finally oxidized to sulfuric acid, which causes the acidification of natural waters of river and lake waters [1,2]. There is a growing interest in rapid and/or sensitive determination of the sulfur species.

However, the difficulty in the analysis of sulfide, sulfite and thiosulfate in mixtures usually arises from their instabilities. Various methods, spectrophotometry [3–5], chromatography [6–10] and flow-injection analysis [11], have been proposed for the determination of these anions. Recently, we have reported ion chromatographic methods for the determination of sulfide, sulfite and thiosulfate at 10^{-5} mol l^{-1} level [12,13]; they were based on the resolution of each anion from their mixtures, followed by the photometric measurement of excess iodine (as triiodide) for its postcolumn reaction with each sulfur anion separated. On the other hand,

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sensitive photometric determinations of sulfide [14,15], thiosulfate [14] and thiocyanate [14,16] have been reported by means of their catalytic effects on the reaction between iodine and azide. If the catalytic reaction were employed as a postcolumn-reaction for detection of the sulfur anions in ion chromatography, a rapid and sensitive method can be expected for the determination of sulfide, thiosulfate and thiocyanate in mixtures. No consideration has been given to chromatographic determination of the sulfur anions using their catalytic effects on the postcolumn-reaction of iodine with azide.

In this work, ion chromatography has been proposed for the highly sensitive determination of sulfide, sulfite, thiosulfate and thiocyanate in their mixtures. This method is based on the resolution of each sulfur anion in their mixtures on the separating column, and then the photometric measurement of the excess iodine (as triiodide) for a postcolumn iodine–azide reaction catalyzed by each of sulfide, thiosulfate and thiocyanate in the effluent and for a postcolumn reaction of iodine with sulfite. The proposed method was successfully applied to the determination of sulfide, sulfite and thiosulfate in hot-spring water samples. This method gives a higher sensitivity when compared with previous methods [3,4,6–13].

2. Experimental

2.1. Chromatographic system

A flow diagram of the ion chromatographic system

used in this study is shown in Fig. 1. This system comprised a Model LC-9A pump with dual pistons (Shimadzu, Kyoto, Japan) to run an eluent to a TSK-gel IC-Anion-PW separating column (50 mm× 4.6 mm I.D., Toso, Tokyo, Japan), a sample injection-valve equipped with a sample loop of 50 μl, a Model DMX-2000 pump (SNK, Tokyo, Japan) to allow two solutions of iodine and azide to flow through a mixing tee, and a Model S-372 photometric detector (Soma, Tokyo, Japan). Desired temperature on a postcolumn iodine–azide reaction catalyzed by sulfur anions was controlled by a Model BT-15 thermostat (Yamato, Tokyo, Japan). The chromatograms were recorded with a Model R-111 recorder (Shimadzu).

2.2. Chemicals

The water used was double distilled and then deionized with a Model Milli-QII instrument (Nippon Millipore, Yonezawa, Yamagata, Japan). All of the chemicals used, with the exception of sodium azide, were of analytical-reagent grade and were used without further purification. In preliminary experiments, the use of sodium azide reagent without purification was found to give poor reproducibility of the chromatographic peak heights for the sulfur anions. Therefore, the azide reagent used in this work were purified as follows. Sodium azide (200 g) was dissolved in about 400 ml water and diluted to 500 ml with water. To the azide solution cooled to about 0°C, 500 ml ethanol (0°C) were added. The sodium azide precipitate obtained was filtered by
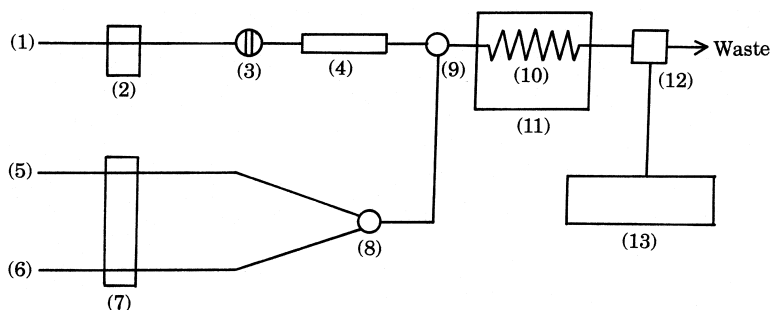

Fig. 1. Flow diagram of the ion chromatographic system with the catalytic postcolumn reaction between iodine and azide. (1) Eluent, (2) pump, (3) injection-valve, (4) separating column, (5) an iodine solution containing iodide and acetic acid, (6) an azide solution, (7) pump, (8) T-union, (9) mixing tee, (10) reaction tube, (11) thermostat, (12) UV–Vis detector, (13) recorder.

suction with a sintered-glass filter (G3), washed with ethanol (0°C), and air dried at room temperature.

A $5.0 \cdot 10^{-6}$ M iodine–0.1 M iodide–0.8 M acetic acid solution was prepared by adding 20 ml of $1.0 \cdot 10^{-4}$ M iodine in methanol to a solution containing 8.3 g of potassium iodide and 40 ml of 10 M acetic acid, and diluting the mixture to 500 ml with water.

A 10% (w/v) azide solution was prepared by dissolving 50 g of the sodium azide in water and diluting to 500 ml.

A $6 \cdot 10^{-3}$ M sodium carbonate solution containing 15% (v/v) acetonitrile was prepared by adding 75 ml of acetonitrile to about 400 ml of water containing 30 ml of 0.1 M sodium carbonate and diluting to 500 ml with water.

A sulfide solution was prepared from large crystals of sodium sulfide nonahydrate using oxygen-free water. To remove trace amounts of impurities from the surface of the crystals, they were rapidly washed with water and then dried by absorption of the water with filter paper. A sulfide solution of about 0.05 M was obtained by dissolving 2.40 g of the crystals in 200 ml of water. This solution was continuously deaerated with nitrogen gas and standardized by iodometry. After the standardization, working sulfide solutions were prepared immediately by suitable dilution with oxygen-free water containing a small amount of sodium carbonate as a stabilizer. A $1 \cdot 10^{-4}$ M standard sulfide in $3 \cdot 10^{-3}$ M carbonate solution was stable for 33 min after preparation [12].

A sulfite solution (about 0.05 M) was prepared by dissolving 0.52 g of sodium hydrogen sulfite in 100 ml of oxygen-free water, and was standardized by iodometry. Working sulfite solutions were obtained by appropriate dilution with an acetate buffer solution containing a small amount of formaldehyde as a stabilizing agent. A $5.0 \cdot 10^{-5}$ M standard sulfite solution containing $1 \cdot 10^{-4}$ M formaldehyde and $2 \cdot 10^{-4}$ M acetate buffer (pH 5.7) was stable for at least 90 min after preparation [12].

A thiosulfate solution of about 0.1 M was prepared by dissolving sodium thiosulfate pentahydrate in water containing a small amount of sodium carbonate (0.01%) as a stabilizer, and was standardized by iodometry one week after preparation. Working solutions of standard thiosulfate were obtained by appropriate dilution with oxygen-free water.

A thiocyanate solution (about 0.1 M) was prepared by dissolving potassium thiocyanate in water. The solution was standardized by Volhard's method [17]. Working solutions of standard thiocyanate were prepared by suitable dilution.

2.3. Recommended procedure

A $6.0 \cdot 10^{-3}$ M sodium carbonate solution containing 15% (v/v) acetonitrile was pumped as an eluent at a flow-rate of 0.5 ml min^{-1}, and then a 50-μl aliquot of a sample solution containing sulfide, sulfite, thiosulfate and thiocyanate was injected into the separating column. The effluent from the column containing separated sulfur anions was allowed to flow through a mixing tee. In addition, a $5 \cdot 10^{-6}$ M iodine solution containing 0.1 M iodide and 0.8 M acetic acid, and a 10% (w/v) azide solution were each allowed to flow at a rate of 0.25 ml min^{-1} to mix with each other at a T-union, and subsequently to flow through the mixing tee in order to mix with the effluent. The mixture obtained was passed through a reaction tube (3 m × 0.5 mm I.D.) maintained at 40°C in a thermostat, in which the catalytic effects of sulfide, thiosulfate and thiocyanate gave the reaction of iodine with azide and sulfite reacted with iodine occurred. The absorbance of the residual iodine (as triiodide) in the stream was monitored at 350 nm.

3. Results and discussion

3.1. Calibration plots

A standard solution (50 μl) containing sulfide, sulfite, thiosulfate and thiocyanate was treated as described in Section 2.3. Fig. 2 shows the chromatograms obtained for a mixture of the four sulfur anions. Each calibration graph for the sulfur anions, plotted as peak height vs. concentration, gave a straight line up to $5.50 \cdot 10^{-7}$ M (17.6 ppb) for sulfide, $4.50 \cdot 10^{-6}$ M (360 ppb) for sulfite, $5.00 \cdot 10^{-7}$ M (56.9 ppb) for thiosulfate and $2.00 \cdot 10^{-7}$ M (11.6 ppb) for thiocyanate, respectively. The precision of this method and the detection limits of the sulfur anions are shown in Table 1. The proposed method gave a higher sensitivity for the determination of
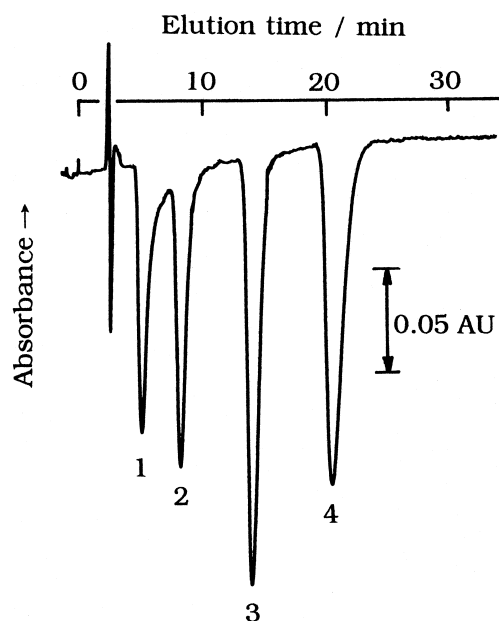
Elution time / min

Fig. 2. Chromatograms of four sulfur anions in a mixture. Peak identification: $1 = S^{2-}$ $(4 \cdot 10^{-7}$ $M)$; $2 = SO_3^{2-}$ $(4 \cdot 10^{-6}$ $M)$; $3 = S_2O_3^{2-}$ $(2 \cdot 10^{-7}$ $M)$; $4 = SCN^{-}$ $(1 \cdot 10^{-7}$ $M)$.

sulfide, thiosulfate and thiocyanate in their mixtures, when compared with previous methods [3–13].

3.2. Resolution of sulfide, sulfite, thiosulfate and thiocyanate in their mixtures

At first, in measuring the effect of concentration of the sodium carbonate eluent on elutions of sulfide, sulfite, thiosulfate and thiocyanate, carbonate solutions of various concentrations $(3 \cdot 10^{-3}$ to $1 \cdot 10^{-2}$

$M)$ were used. Increasing the concentration of carbonate in the eluent accelerated the elutions of the four sulfur anions. A $6 \cdot 10^{-3}$ M carbonate solution eluted the three sulfur anions of sulfide, sulfite and thiosulfate at short retention times (5.5, 9.2 and 15.7 min, respectively), but eluted thiocyanate at a very long time of 70.0 min due to its strong adsorption on to the ion-exchange resin. Also, the chromatographic peak obtained for thiocyanate was not sufficiently sharp. However, use of carbonate eluent of higher concentration could not resolve sulfide and sulfite ions, owing to their close retention times. Therefore, in order to separate completely the four sulfur anions at short elution times and also to obtain a sharp peak for the thiocyanate anion, an attempt was made to add small amounts of acetonitrile to the $6 \cdot 10^{-3}$ M carbonate eluent. An increase in the acetonitrile concentration of the carbonate eluent shortened the elution time of each sulfur anion. When acetonitrile was added to the $6 \cdot 10^{-3}$ M carbonate eluent to a content of 15% (v/v), sulfide, sulfite, thiosulfate and thiocyanate could be eluted at retention times of 5.1, 8.8, 15.0 and 21.5 min, respectively, and the peak for thiocyanate became much sharper. Consequently, a $6 \cdot 10^{-3}$ M carbonate–15% (v/v) acetonitrile solution was employed as an eluent in this work.

3.3. Optimal concentrations of iodine, iodide and acetic acid in an iodine solution

In this method, a mixture of iodine, iodide and acetic acid was used as an iodine solution. Therefore, various concentrations of iodine, iodide and acetic acid in their mixtures were investigated in order to

Table 1
Precision of the proposed method and detection limits of sulfur anions

Sulfur anion	Precision[a]			Detection limit at $S/N=3$ (ng)
	Mean value (ppb)	S.D.[b] (ppb)	R.S.D.[c] (%)	
S^{2-}	15.7	0.4	2.5	0.14
SO_3^{2-}	325	5.5	1.7	2.40
$S_2O_3^{2-}$	33.8	0.5	1.5	0.16
SCN^{-}	10.2	0.2	2.0	0.05

[a] The precision was determined from five replicate results obtained for a mixture containing 16.0 ppb sulfide, 320 ppb sulfite, 33.6 ppb thiosulfate and 10.2 ppb thiocyanate.
[b] S.D. means a standard deviation.
[c] R.S.D. means a relative standard deviation.

obtain an increased peak height for each sulfur anion. In this experiment, thiosulfate was used as an analyte, because the thiosulfate ion was eluted at a shorter retention time than the thiocyanate ion and also was much more stable than the sulfide ion (the sulfite ion did not have a catalytic action on the reaction between iodine and azide). The results obtained are shown in Fig. 3. Fig. 3A shows the peak height for $5 \cdot 10^{-7}$ M thiosulfate obtained by using various iodine solutions ($1.0 \cdot 10^{-6}$ to $2.5 \cdot 10^{-5}$ M) containing 0.1 M iodide and 0.8 M acetic acid. The height of the peak was increased by increasing the concentration of iodine up to $3.0 \cdot 10^{-6}$ M. The highest peak height was obtained by using iodine in the concentration range $3.0 \cdot 10^{-6}$–$6.0 \cdot 10^{-6}$ M. At a concentration of iodine above $6.0 \cdot 10^{-6}$ M, the peak height was decreased; this decrease might be attributed to a decrease in the amount of thiosulfate because its reaction with iodine took place, instead of the catalytic postcolumn reaction of iodine with azide.

As described in Section 2.3, the excess of iodine for the postcolumn reaction catalyzed by sulfur anions was measured photometrically as a triiodide. Therefore, the concentration of iodide in the iodine–acetic acid solution was thought to affect the peak height for each sulfur anion. Various iodide solutions (0.01 to 0.5 M) containing $5.0 \cdot 10^{-6}$ M iodine and 0.8 M acetic acid were used. As can be seen in Fig.

3B, the maximum peak height for $5 \cdot 10^{-7}$ M thiosulfate was obtained when a 0.1–0.12 M iodide solution was used. At higher concentrations of iodide, the peak height decreased because the concentration of iodine was decreased as a result of a further shift of the equilibrium ($I_2 + I^- \rightleftarrows I_3^-$) to the right.

Sulfur species such as sulfide and thiocyanate were known to catalyze the reaction of iodine with azide in an acidic medium [15,16]. Therefore, we tried to add various amounts of acetic acid to a $5 \cdot 10^{-6}$ M iodine–0.1 M iodide solution in order to acidify the catalytic postcolumn-reaction solution. The results are given in Fig. 3C. Increasing the concentration of acetic acid increased the peak height for $5 \cdot 10^{-7}$ M thiosulfate.

Consequently, a mixture of $5 \cdot 10^{-6}$ M iodine–0.1 M iodide–0.8 M acetic acid was employed as an iodine solution in the procedure.

3.4. Effect of concentration of an azide solution

To measure the effect of the concentration of sodium azide solution on the chromatographic peak height for the sulfur anions, azide solutions of various concentrations (3–15% w/v) were used. The results are shown in Fig. 4. The peak height for $5 \cdot 10^{-7}$ M thiosulfate was increased by an increase in the concentration of azide to 10% (w/v), because the
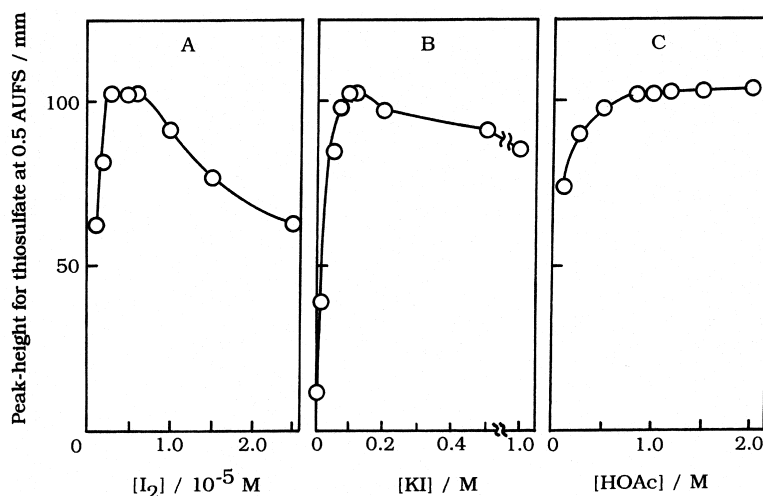

Fig. 3. Effects of concentrations of iodine, iodide and acetic acid in an iodine solution. Thiosulfate solution ($5 \cdot 10^{-7}$ M) was used as a sample. (A) Effect of the concentration of iodine in a 0.1 M iodide–0.8 M acetic acid solution; (B) effect of the concentration of iodide in a $5 \cdot 10^{-6}$ M iodine–0.8 M acetic acid solution; (C) effect of the concentration of acetic acid in a $5 \cdot 10^{-6}$ M iodine–0.1 M iodide solution.
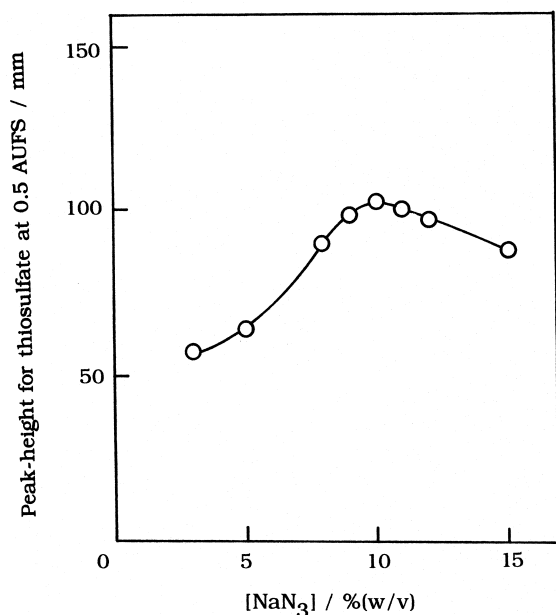
Fig. 4. Effect of the concentration of an azide solution. Thiosulfate solution ($5 \cdot 10^{-7}$ M) was used as an analyte.

Table 3
Effect of temperature on catalytic postcolumn-reaction of iodine with azide

Temperature	Peak height[a] (mm)	
	$2 \cdot 10^{-7}$ M $S_2O_3^{2-}$	$5 \cdot 10^{-7}$ M $S_2O_3^{2-}$
20	35.9	89.6
25	38.1	95.3
30	41.0	104.2
35	41.5	102.9
40	42.0	104.5

[a] Obtained at 0.5 AUFS.

iodine–azide reaction catalyzed by the sulfur anions. Therefore, reaction tubes (0.5 mm I.D.) of various length were studied. The results are shown in Table 2. An increase in the tube length increased the peak height for $5 \cdot 10^{-7}$ M thiosulfate. However, tubes of 5 and 10 m gave low peak height due to an increase in the peak width. A 10-m tube also gave lower peak heights for chromatograms of each sulfide, sulfite and thiocyanate ion compared with a 3-m tube. Therefore, a 3-m reaction tube was employed.

rate of the catalytic reaction of iodine with azide was increased. But, when azide solutions of 12–15% (w/v) were used, the peak height was decreased. This decrease may be caused by a decrease in the acidity of the catalytic postcolumn-reaction solution due to an increase in azide concentration. Hence, a 10% (w/v) azide mixture was used in the procedure, in which pH of the postcolumn-reaction mixture was 4.8.

3.5. Effect of length of postcolumn-reaction tube

The length of the reaction tube used affected the

3.6. Effect of temperature on the catalytic postcolumn reaction of iodine with azide

In order to measure the effect of temperature on the catalytic postcolumn iodine–azide reaction, the reaction tube was allowed to stand in a thermostat adjusted to a temperature in the range of 20 to 40°C. As can be seen in Table 3, an increase in the temperature up to 40°C increased the peak height of the chromatogram for $5 \cdot 10^{-7}$ M thiosulfate because the postcolumn reaction was accelerated. The chromatographic peak heights for sulfide and thiocyanate

Table 2
Effect of the length of the postcolumn-reaction tube

Length of postcolumn-reaction tube	Peak height[a] (mm)	
	$2 \cdot 10^{-7}$ M $S_2O_3^{2-}$	$5 \cdot 10^{-7}$ M $S_2O_3^{2-}$
0.5	39.1	98.9
1.5	41.0	102.5
3.0	42.0	104.5
5.0	40.0	99.0
10.0	33.2	82.8

[a] Obtained at 0.5 AUFS.

were similarly increased by an increase in the temperature. Therefore, the temperature was adjusted to 40°C.

3.7. Determination of sulfide, sulfite and thiosulfate in real samples

At first, the effect of foreign ions on the determination of sulfide, sulfite, thiosulfate and thiocyanate was investigated. Ions such as F^-, Cl^-, NO_2^-, NO_3^-, Br^-, SO_4^{2-}, $S_2O_6^{2-}$, $H_2PO_4^{2-}$, ClO_4^-, $HCOO^-$, CH_3COO^-, $C_2O_4^{2-}$, tartrate, K^+, Na^+, NH_4^+, Ca^{2+}, Mg^{2+} and Ba^{2+} did not give any interferences at concentrations as high as 0.005 M. The proposed method was used for the determination of sulfide, sulfite, thiosulfate and thiocyanate, mixed in various ratios. The results obtained are given in Table 4. Good recoveries were obtained for each anion. Next, an attempt was made to apply this method to the determination of sulfide, sulfite or thiosulfate in hot-spring waters and river water. Fig. 5 shows that the chromatograms for the hot-spring water, in which A was obtained for the hot-spring water (a) diluted 50-fold, B for the hot-spring water (a) diluted 50-fold to which thiosulfate was added, and C for the hot-spring water (a) diluted 2000-fold to which sulfide and sulfite were added. The determinations of the sulfur anions in the hot-spring waters and river water are listed in Table 5. Potential matrix interferences from unknown species in real samples were also investigated by adding known amounts of sulfide, sulfite and thiosulfate to the sample solutions. The recoveries of the sulfur anions added to the real samples ranged from 94.6 to 104%. The precision of this method was estimated from six
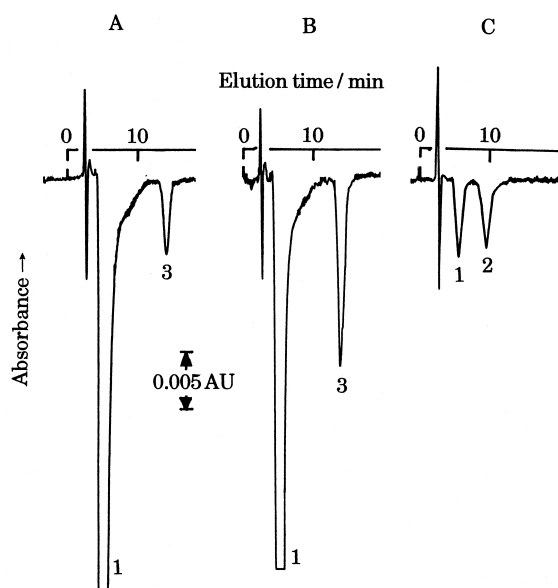

Fig. 5. Chromatograms of sulfide, sulfite and thiosulfate in hot-spring water. (A) The hot-spring water (a) diluted 50-fold; (B) the hot-spring water (a) diluted 50-fold to which $S_2O_3^{2-}$ was added to obtain a concentration of 28.0 ppb; (C) the hot-spring water (a) diluted 2000-fold to which S^{2-} and SO_3^{2-} were added to obtain concentrations of 2.40 and 320 ppb, respectively. Peak identification: $1 = S^{2-}$; $2 = SO_3^{2-}$; $3 = S_2O_3^{2-}$.

results obtained for the hot-spring water (b). The proposed method gave a mean value of 0.49 ppm with a standard deviation (S.D.) of 0.017 ppm and a relative standard deviation (R.S.D.) of 3.5% for sulfide, 1.52 ppm (S.D.=0.056 ppm, R.S.D.=3.7%) for sulfite and 0.11 ppm (S.D.=0.004 ppm, R.S.D.= 3.6%) for thiosulfate. This method was successfully applied to the determination of the sulfide, sulfite and thiosulfate in hot-spring water and river water samples without any pretreatment.

Table 4
Determination of sulfide, sulfite, thiosulfate and thiocyanate in mixtures

Taken (10^{-7} M)				Found (10^{-7} M)				Error (%)			
S^{2-}	SO_3^{2-}	$S_2O_3^{2-}$	SCN^-	S^{2-}	SO_3^{2-}	$S_2O_3^{2-}$	SCN^-	S^{2-}	SO_3^{2-}	$S_2O_3^{2-}$	SCN^-
1.50	35.0	3.50	1.50	1.52	34.3	3.44	1.51	1.3	−2.0	−1.7	0.7
1.50	10.0	1.00	1.50	1.51	10.1	1.01	1.49	0.7	1.0	1.0	−0.7
3.00	30.0	1.00	1.00	2.94	29.7	0.99	0.99	−1.0	−1.0	−1.0	−1.0
1.50	15.0	2.00	2.00	1.51	15.0	2.02	1.99	0.7	0	1.0	−0.5
3.50	25.0	1.50	1.00	3.49	24.9	1.50	1.01	−0.3	−0.4	0	1.0
1.00	15.0	1.75	2.00	0.99	14.8	1.78	2.00	−1.0	−1.3	−1.7	0

Table 5
Determination of sulfide, sulfite and thiosulfate in hot-spring waters and river water

Sample	Dilution (fold)	Added (ppb)			Found (ppb)			Found in original sample (ppm)			Recovery (%)		
		S^{2-}	SO_3^{2-}	$S_2O_3^{2-}$	S^{2-}	SO_3^{2-}	$S_2O_3^{2-}$	S^{2-}	SO_3^{2-}	$S_2O_3^{2-}$	S^{2-}	SO_3^{2-}	$S_2O_3^{2-}$
Hot-spring water A (pH 2.1)	50	0	0	0	[a]	[a]	18.8	[a]	[a]	0.94	–	–	–
		0	0	5.60	[a]	[a]	24.4	[a]	[a]	0.94	–	–	100
		0	0	2.80	[a]	[a]	21.5	[a]	[a]	0.94	–	–	96.4
	2000	0	0	0	13.1	[b]	[b]	26.2	0	0	–	–	–
		0	160	0	13.1	159	[b]	26.2	0	0	–	99.4	–
		2.40	320	0	15.6	318	[b]	26.4	0	0	104	99.4	–
Hot-spring water B (pH 8.6)	5	0	0	0	[a]	305	21.5	[a]	1.53	0.11	–	–	–
		0	56.0	22.4	[a]	358	43.9	[a]	1.51	0.11	–	94.6	100
	50	0	0	0	9.79	[b]	[b]	0.49	0	0	–	–	–
		5.60	0	0	15.4	[b]	[b]	0.49	0	0	100	–	–
River water (pH 6.3)	1	0	0	0	[b]	[b]	[b]	0	0	0	–	–	–
	2	11.2	160	11.2	11.2	158	11.2	0	0	0	100	98.8	100
		16.0	320	33.6	15.8	317	33.2	0	0	0	98.8	99.1	98.8

[a] The content was too much to be determined.
[b] The content was too low to be determined.

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