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Stabilization of sulfide and sulfite and ion-pair chromatography of mixtures of sulfide, sulfite, sulfate and thiosulfate

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Abstract

Ion chromatography of sulfide, sulfite, sulfate and thiosulfate in a mixture is often difficult because of instability of sulfide and sulfite, poor separation of sulfide from common anions such as bromide or nitrate and similar elution-times for sulfite and sulfate. An ion-pair chromatographic method for the determination of these sulfur anions has been established by stoichiometric conversion of sulfide and sulfite into stable thiocyanate and sulfate, respectively, prior to the chromatographic run. Sulfate, thiosulfate and thiocyanate were resolved on an octadecylsilica column with an acetonitrile–water mobile phase containing tetrapropylammonium salt (TPA) as an ion-paring reagent, and thiosulfate and thiocyanate in the effluent could be measured with a photometric detector (220 nm) and sulfate with a suppressed conductivity detector. When an acetonitrile–water (6:94, v/v) mobile phase (pH 5.0) containing 15 mM TPA and small amounts of acetic acid was used at a flow-rate of 0.6 ml min^{-1}, the three anions could be eluted within 32 min. Calibration plots of peak height versus concentration for sulfide (detected as thiocyanate) and thiosulfate gave straight lines up to 35 and 60 μM, respectively. The calibration plot for sulfide coincided with that obtained by using thiocyanate. A calibration plot for sulfite, measured as sulfate, was also linear up to 135 μM and was in accord with that of sulfate. Each calibration plot gave a correlation coefficient greater than 0.999. For six replicates obtained for a mixture of 30.0 μM sulfide, 50.0 μM sulfite, 50.0 μM sulfate and 20.0 μM thiosulfate, the proposed method gave a mean value of 30.1 μM with a standard deviation (SD) of 0.77 μM and a relative standard deviation (RSD) of 2.6% for sulfide, 101 μM (SD = 3.5 μM, RSD = 3.5%) for the total of sulfite and sulfate and 20.1 μM (SD = 0.44 μM, RSD = 2.2%) for thiosulfate. Recoveries for sulfide, sulfite plus sulfate, and thiosulfate in hot-spring water samples using the proposed method were found to be quantitative.

Keywords: Stabilization, LC; Detection, LC; Water analysis; Sulfur anions; Sulfide; Sulfite; Sulfate; Thiosulfate; Thiocyanate; Ion-paring reagent

1. Introduction

In aqueous solution, sulfur exists in different chemical forms such as sulfide, sulfite, sulfate and thiosulfate, and frequently these are present in natural waters (river, lake and hot-spring waters) and industrial effluents (food, pharmaceutical, leather and photographic wastewaters). Sulfide and sulfite in an aqueous solution are very reactive and therefore are unstable, readily yielding sulfate and thiosulfate via air oxidation [1–3]. Various investigations have been made regarding the spectrophotometric [2,9] and ion chromatographic [4–8,10–12] determination of sulfur anions in mixtures containing sulfide and/or sulfite. Ion chromatographic (IC) analysis is difficult due to poor separation of sulfide from both the void volume [4,5] and common inorganic anions such as chloride, nitrite and nitrate [5,6]. Similar retention times for sulfite and sulfate [4,5,7,8] are also observed commonly. Recently, IC determination of sulfide, sulfite, sulfate and thiosulfate in the presence of large amounts of chloride has been accomplished, but detection by inductively coupled plasma mass spectrometry was necessary [13]. IC determination of sulfide, sulfite, sulfate, thiosulfate and thiocyanate in tannery wastewater has also been reported [14] and in this case, sulfide was estimated indirectly by oxidation of the five sulfur anions to sulfate and subtracting the calculated amount of sulfate equivalent to the total sulfur anions excluding sulfide.

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The instability of sulfite has been addressed by reaction of sulfite with formaldehyde to form a stable sulfite–formaldehyde adduct [2,3,12,15,16], but this reaction is strongly dependent on pH and has an optimal pH range of 5.6–8.6 [2]. Sulfite in photographic fixer has been determined by this method [16], and the sample solution was diluted appropriately to decrease interferences prior to stabilization of sulfite. A potential problem is that even a simple dilution step can cause the air-oxidation of sulfite. Therefore, there is a growing interest in the establishment of a method for the accurate determination of sulfide and sulfite in mixtures with the other sulfur species and also in the presence of common inorganic anions in large amounts. A possible approach is to utilize the fact that sulfide and sulfite are converted quantitatively into stable thiocyanate and sulfate, respectively, which can then be determined by ion chromatography. These conversions not only stabilize these anions but also permit the complete separation of their reaction products from common anions. No investigation has yet appeared describing this approach.

In this study, an ion-pairing IC method has been developed for determination of sulfide, sulfite, sulfate and thiosulfate, after conversion of sulfide and sulfite into stable thiocyanate and sulfate, respectively. Sulfide was evolved from acidified solution as hydrogen sulfide, which was then collected in an alkaline mixture containing cyanide and hydrogen peroxide. This produces thiocyanate according to Eq. (1).

$$H_2S + CN^- + H_2O_2 \rightarrow SCN^- + 2H_2O \quad (1)$$

Sulfite in the sample was oxidized to sulfate with hydrogen peroxide in an alkaline solution, according to reaction (2).

$$SO_3^{2-} + H_2O_2 \rightarrow SO_4^{2-} + H_2O \quad (2)$$

Thiocyanate (for sulfide), sulfate (for the total of sulfite and sulfate) and thiosulfate were then determined chromatographically, with thiocyanate and thiosulfate being measured with a UV detector and sulfate with a suppressed conductivity detector. Common anions up to 10 mM did not give any interference for the determination of these sulfur species. This method was applied to the determination of sulfide, sulfate (as the sum of sulfite and sulfate) and thiosulfate in hot-spring water samples.

2. Experimental

2.1. Reagents

The water used was distilled twice and then deionized with a MilliQ-Labo system (Nippon Millipore, Tokyo, Japan). All of the chemicals used were of analytical reagent grade and were used without further purification. A mobile phase comprising acetonitrile–water (6:94, v/v) at pH 5.0 containing 15 mM tetrapropylammonium hydroxide (TPA) was prepared by adding 30 ml of acetonitrile to a mixture of 15.3 ml of 0.49 M TPA and small amounts of acetic acid, then diluting it to 500 ml with water. The acetic acid was employed to adjust the mobile phase to pH 5.0. The mobile phase so obtained was filtered through a membrane filter (pore size, 0.2 μm) before use.

A sulfide solution was prepared from large crystals of sodium sulfide ($Na_2S{\cdot}9H_2O$) using oxygen-free water. The crystals were washed rapidly with water in order to remove any trace amounts of impurities from their surfaces and then dried by adsorption of the water with filter paper. An approximately 0.05 M sulfide solution was prepared by dissolving approx. 2.5 g of the crystals in 200 ml of oxygen-free water and then standardized by iodimetric back-titration [2,17]. Sulfite solution (approx. 0.05 M) was prepared by dissolving 0.52 g of sodium hydrogen sulfite in 100 ml of the water, followed by standardization using an iodimetric back-titration [2,18]. Standard sulfate solution (0.1 M, $f = 1.000$) was prepared by dissolving 7.172 g of sodium sulfate (99.0%) in the water and diluting to 500 ml. A thiosulfate solution of approx. 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 the solution was then standardized by iodimetric back-titration one week after preparation [2,3]. A thiocyanate solution (approx. 0.1 M) was prepared by dissolving potassium thiocyanate in water, followed by standardization using Volhard's method [19]. This standard solution was used to confirm the stoichiometry and completion of formation of thiocyanate from sulfide according to Eq. (1). Working solutions of sulfide, sulfite, sulfate, thiosulfate and thiocyanate were obtained by appropriate dilution of their standards with water. Standard solutions (at the 10^{-5} M level) of each sulfide and sulfite were used within 30 min after preparation in order to prevent time-dependent changes in their concentration via air-oxidation [2,3,17]. A commercial hydrogen peroxide solution (1 + 200) was standardized by iodometry, and was diluted with water.

2.2. Apparatus

The IC system used comprised a pump (Model LC-10AD, Shimadzu, Kyoto, Japan), a sample injection valve (Model 7725, Rheodyne, Berkeley, CA, USA) equipped with a 100 μl loop, a silica ODS column (Lichro CART ODS, 4.6 mm I.D. × 150 mm, Kanto Chemical Co. Inc., Tokyo, Japan), a photometric detector (Model SPD-10AV, Shimadzu) and a conductivity detector (Model CDM-1, Dionex, Sunnyvale, CA, USA) used with a suppressor (Model AMMS, Dionex). The conductivity and photometric detectors were connected in series, chromatograms obtained with each detector being recorded separately by recorder (Model U-135, Shimadzu). A thermostat (Model BT-15, Yamato, Tokyo, Japan) was employed to maintain the separation column at 23 ± 2 °C.

The apparatus used for evolution and absorption of hydrogen sulfide is shown in Fig. 1. The tips of the gas dispersers

[(C) and (D)] were fixed just above the bottom of a 30 ml vessel (A) and a 25 ml volumetric flask (B), respectively. The flow-rate of nitrogen was regulated by a flow meter (Model RK 1200, Kojima, Tokyo, Japan).

2.3. Recommended procedure

2.3.1. Step I (for determination of sulfide, sulfate, thiosulfate and thiocyanate)

The acetonitrile–water (6:94, v/v) mobile phase (pH 5.0) containing 15 mM TPA was pumped through the ODS separation column ($23 \pm 2\,^{\circ}C$) at a flow-rate of 0.6 ml min^{-1}, and a 100 μl aliquot of sample containing sulfide, sulfite, sulfate, thiosulfate and thiocyanate was injected. Photometric detection at 220 nm was used to quantify sulfide, thiosulfate and thiocyanate and conductivity detection was used to quantify sulfate.

2.3.2. Step II (for determination of sulfide as thiocyanate)

A 0.5 ml of 5 mM sodium hydroxide, 2.5 ml of 10 mM sodium cyanide, 1 ml of 0.5 M hydrogen peroxide and 10 ml of water were placed into a 25 ml volumetric flask [(B) in Fig. 1]. A 10 ml aliquot of sample solution containing sulfide, sulfite, sulfate, thiosulfate and thiocyanate was added to a 30 ml glass-stoppered vessel [(A) in Fig. 1]. The flask was then connected as shown in Fig. 1. Two milliliters of 2 mM hydrochloric acid was added to the sample solution in the vessel, and immediately after this, nitrogen was bubbled through the solution for 5 min at a flow-rate of 150 ml min^{-1}. The hydrogen sulfide evolved from the acidified sample solution was completely transferred to the reaction mixture in the flask. The collection flask was then diluted to the mark with water and allowed to stand for 10 min to permit the hydrogen sulfide to be converted into thiocyanate according to Eq. (1). A 100 μl of the solution was injected under the same chromatographic conditions as Step I to obtain a chromatographic peak for thiocyanate which was equivalent to sulfide in the sample.

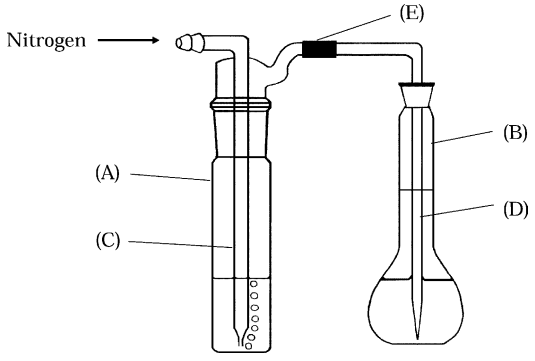

Fig. 1. Apparatus for evolution and absorption of hydrogen sulfide. (A) 30 ml glass stoppered vessel, (B) 25 ml volumetric flask, (C and D) gas dispersers, (E) silicone tubing.

2.3.3. Step III (for determination of total amount of sulfite and sulfate)

A 10 ml aliquot of the sample solution containing the sulfur species, 0.5 ml of 5 mM sodium hydroxide and 1 ml of 15 mM hydrogen peroxide were added to a 25 ml volumetric flask, which was allowed to stand for 1 min in order to oxidize completely sulfite to sulfate as shown in a Eq. (2). Sulfide, thiosulfate and thiocyanate did not undergo any oxidation under these conditions. After diluting the mixture to the mark with water, a 100 μl aliquot was injected under the same chromatographic conditions as Step I to obtain chromatographic peaks after suppressed conductivity detection for sulfate (equivalent to the sum of sulfite and sulfate), thiosulfate and thiocyanate.

3. Results and discussion

3.1. Separation of the sulfur anions

In order to accomplish separation of sulfide, sulfate, thiosulfate and thiocyanate at reasonable elution-times using the silica ODS column, mobile phases containing various amounts of TPA ion-pairing reagent and acetonitrile were evaluated. The effect of changing the TPA concentration in an acetonitrile–water (6:94, v/v) mobile phase (pH 5.0) is shown in Fig. 2, which indicates that a concentration of TPA in the range 10–18 mM is required for all four anions to be resolved and to give acceptable chromatographic peaks. The effect of concentration of acetonitrile in the mobile phase (pH 5.0) containing 15 mM TPA is shown in Table 1. Increased acetonitrile concentration greatly accelerated elution of the sulfur anions and concentrations in the range 5–8% (v/v) provided good resolution and peak shape. A mobile phase (pH 5.0) of acetonitrile–water (6:94, v/v) containing 15 mM TPA was selected as optimal. A chromatogram obtained for the four sulfur anions is shown in Fig. 3. Anions of sulfide, sulfate, thiosulfate and thiocyanate were detected at elution times of 6.4, 16.6, 20.0 and 31.2 min, respectively. Sulfate,

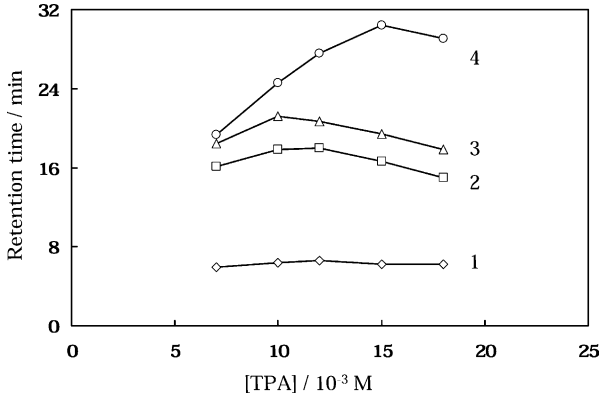

Fig. 2. Effect of concentration of TPA in mobile phase of 6% (v/v) acetonitrile on elution of the sulfur anions. (1) Sulfide, (2) sulfate, (3) thiosulfate, (4) thiocyanate.

Table 1
Effect of concentration of acetonitrile in mobile phase[a] (pH 5.0) containing 15 mM TPA on elution of the sulfur anions

Concentration of acetonitrile (%, v/v)	Elution time (min)			
	S^{2-}	SO_4^{2-}	$S_2O_3^{2-}$	SCN^-
5	6.5	18.8	22.8	34.5
6	6.4	16.6	20.0	31.2
7	6.3	14.6	16.8	25.7
8	6.2	13.3	15.2	21.6
10	6.2	11.0	12.4	15.7
12	6.2	9.5	10.1	13.7

[a] Mobile phase was pumped at a flow-rate of 0.6 ml min^{-1}.

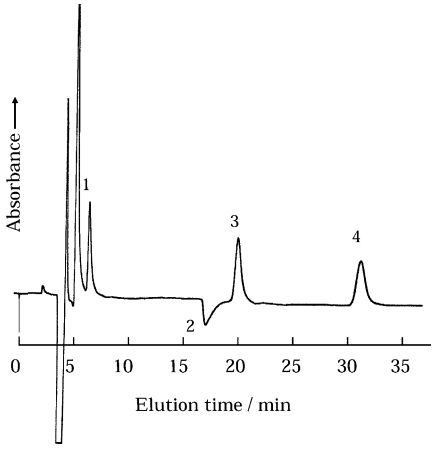

Fig. 3. Separation of the four sulfur anions obtained according to Step I. Photometric detection was used. Peaks: (1) sulfide (0.1 mM), (2) sulfate (1.0 mM), (3) thiosulfate (0.01 mM), (4) thiocyanate (0.01 mM).

which shows low absorptivity at 220 nm, appeared as a small negative peak because of its decreased absorbance relative to that of the background. Measurement of sulfate was therefore performed using a suppressed conductivity detection.

3.2. Measurement of sulfide as thiocyanate

In order to stabilize sulfide and to measure it without interference from common inorganic anions, sulfide was evolved as hydrogen sulfide and converted into thiocyanate. Conditions for the quantitative evolution of sulfide from mixture of the sulfur anions were investigated. This could be achieved using 2 ml of each 1, 1.5, 2 and 2.5 mM hydrochloric acid to acidify the sample solution, with nitrogen then being bubbled through the solution for each 3, 5 and 10 min at a flow-rate of 150 ml min^{-1}. Therefore, 2 ml of 2 mM hydrochloric acid was used and the nitrogen was bubbled for 5 min at 150 ml min^{-1}, as described in Step II.

The effects of amounts of sodium hydroxide, cyanide and hydrogen peroxide on the conversion of the sulfide separated from the sample matrix as hydrogen sulfide into thiocyanate were measured. The results are shown in Table 2. When 0.5 ml of 5.0–10 mM sodium hydroxide, 2.5 ml of 8–2 mM cyanide and 1 ml of 0.25–1.0 M hydrogen peroxide were used in the reaction mixture and the mixture was allowed to stand for 10 min to convert the sulfide into thiocyanate (as described in Step II), height of the chromatographic peak obtained for the sulfide was the same as that obtained for an equivalent amount of thiocyanate. The fact indicates that under the above conditions, the evolved sulfide can be completely converted to thiocyanate. A reaction mixture comprising 0.5 ml of 5 mM sodium hydroxide, 2.5 ml of 10 mM sodium cyanide and 1 ml of 0.5 M hydrogen peroxide was therefore selected for conversion of sulfide into thiocyanate. The reaction time on formation of thiocyanate from the evolved sulfide was changed. At a reaction time in the range 5–10 min, the sulfide was found to produce quantitatively thiocyanate according to Eq. (1). A reaction time of 10 min was used.

3.3. Measurement of sulfite as sulfate

Sulfite in an aqueous solution undergoes air oxidation, which is accelerated when species such as copper(II) and iron(III) are present [5,11,12]. In this work, sulfite was therefore determined, after oxidation to sulfate, with the original concentration of sulfate in the sample. Table 3 shows the effect of amount of hydrogen peroxide used on the oxidation of sulfite. One milliliter of hydrogen peroxide in the range 5–20 mM was found to oxidize completely sulfite to sulfate according to Eq. (2). When 1 ml of 15 mM hydrogen peroxide

Table 2
Effects of concentrations of NaOH, NaCN and H_2O_2 on conversion of sulfide (1.25×10^{-4} M) into thiocyanate

[NaOH][a] (M)	Peak-height[b] (mm)	[NaCN][c] (M)	Peak-height[b] (mm)	[H_2O_2][d] (M)	Peak-height[b] (mm)
0.001	122[e]	0	122[e]	0	123[e]
0.001	110	0.001	65	0.050	59
0.005	122	0.002	91	0.125	108
0.01	123	0.005	109	0.25	119
0.01	122[e]	0.008	122	0.35	122
		0.01	123	0.5	121
		0.02	122	1.0	123
		0.02	121[e]	1.0	122[e]

[a] 0.5 ml of NaOH was used with 2.5 ml of 10 mM NaCN and 1 ml of 0.5 M H_2O_2.
[b] Peak height was obtained from three replicated at 0.2 AUFS and 220 nm.
[c] 2.5 ml of NaCN was used with 0.5 ml of NaOH and 1 ml of 0.5 M H_2O_2.
[d] 1 ml of H_2O_2 was used with 0.5 ml of NaOH and 2.5 ml of 10 mM NaCN.
[e] 10 ml of 1.25×10^{-4} M thiocyanate solution was used in place of sulfide.

Table 3
Effect of concentration of H_2O_2 on oxidation of sulfite to sulfate

Concentration of H_2O_2[a] (M)	Height of peak for SO_4^{2-} formed (mm)			
	4×10^{-4} M SO_3^{2-}	4×10^{-4} M S^{2-}	4×10^{-4} M $S_2O_3^{2-}$	4×10^{-4} M SCN^-
0.001	129[b]	–[c]	–[c]	–[c]
0.001	75	–[c]	–[c]	–[c]
0.002	124	–[c]	–[c]	–[c]
0.005	130	ND	ND	ND
0.010	131	ND	ND	ND
0.015	129	ND	ND	ND
0.02	130	ND	ND	ND
0.1	129	19.0	5.5	ND
0.1	131[b]	–[c]	–[c]	–[c]

ND, chromatographic peak of sulfate could not detected.
[a] 1 ml of H_2O_2 solution was used.
[b] 10 ml of 4×10^{-4} M sulfate solution was used.
[c] Measurement was not carried out.

was employed, sulfite was quantitatively converted to sulfate at an oxidation time in the range 0.5–10 min. In Step III, 1 ml of 15 mM hydrogen peroxide and the oxidation of sulfite for 1 min therefore were selected. Under the same conditions, sulfide, thiosulfate and thiocyanate were not converted to sulfate, as shown in Table 3. However, use of hydrogen peroxide at concentrations greater than 100 mM did cause production of sulfate from sulfide and thiosulfate and should therefore be avoided.

The sum of sulfite and sulfate in a range of samples was determined to validate the proposed procedure, the results being given in Table 4. This table shows that conversion of sulfite to sulfate was quantitative and the method gave a true value for the total sulfite and sulfate in the samples.

3.4. Analytical performance characteristics

Standard mixture containing sulfide, sulfite, sulfate, thiosulfate and thiocyanate has been treated under the conditions described in Section 2.3 and the chromatograms obtained are shown in Fig. 4. Fig. 4A shows the chromatogram from Step I on the UV detector (quantification of thiosulfate and thiocyanate), Fig. 4B shows the chromatogram from Step II on the UV detector (quantification of sulfide as thiocyanate), and Fig. 4C shows the chromatogram from Step III on the conductivity detector (quantification of total sulfite and sulfate).

Table 4
Measurement of the total amount of sulfite and sulfate

Amount taken (mM)		SO_4^{2-} peak height in chromatogram[a] (mm)
SO_3^{2-}	SO_4^{2-}	
0	0.10	117.8
0.025	0.075	117.5
0.050	0.050	117.2
0.075	0.025	117.2
0.10	0	117.2
0	0.020	23.1
0.010	0.010	22.9
0.020	0	23.0

[a] Conductivity detection was used at 3 μS cm^{-1} FS.

Height of the chromatographic peak being plotted versus concentration, calibration plots were linear in the range from the origin up to 60 μM for each sulfide and thiocyanate, 135 μM for each sulfite and sulfate and 35 μM for thiosulfate, respectively. The calibration plot for sulfide (as thiocyanate) coincided exactly with that obtained by using standard thiocyanate, and also the plot for sulfite was in agreement with that for sulfate. Each calibration plot gave a correlation coefficient greater than 0.999. For six replicates obtained for a mixture of 30.0 μM sulfide, 50.0 μM sulfite, 50.0 μM sulfate, 20.0 μM thiosulfate and 30.0 μM thiocyanate, the proposed method gave a mean value of 30.1 μM with a relative standard deviation (RSD) of 2.6% for sulfide, 101 μM (RSD = 3.5%) for sulfate, 20.1 μM (RSD = 2.2%) for thio-

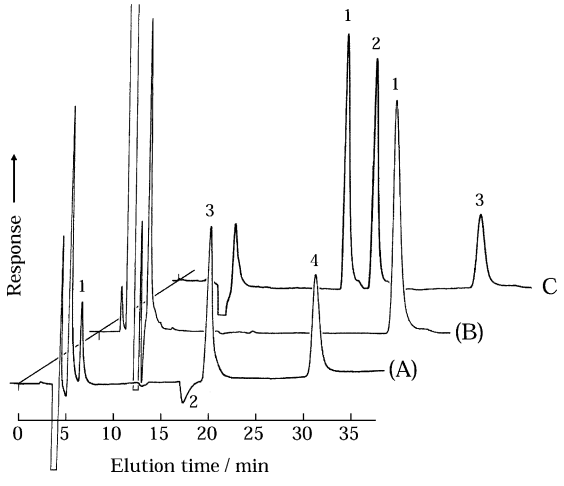

Fig. 4. Chromatograms for the mixture of sulfide, sulfite, sulfate, thiosulfate and thiocyanate (A and B) were measured at 0.2 AUFS and 0.05 AUFS, respectively, by a photometric detector (220 nm) and (C) was measured at 10 μS cm^{-1} FS by a suppressed conductivity detector. (A) Chromatogram obtained according to Step I. Peaks: 1, sulfide (0.1 mM); 2, sulfite (0.5 mM) and sulfate (0.5 mM), (3) thiosulfate (50 μM), (4) thiocyanate (50 μM). (B) Chromatogram for sulfide as thiocyanate treated according to Step II. Peak 1, sulfide (30 μM). (C) Chromatogram for the mixture treated according to Step III. Peaks: 1, sulfite (0.2 mM) and sulfate (0.2 mM); 2, thiosulfate (0.4 mM); 3, thiocyanate (0.4 mM).

sulfate and 30.1 μM (RSD = 2.7%) for thiocyanate. The detection limits (as S/N = 3) were 0.5 μM (16 ppb) for sulfide, 0.7 μM (67 ppb) for sulfate, 0.3 μM (34 ppb) for thiosulfate and 0.3 μM (17 ppb) for thiocyanate.

The effects of various foreign ions on the determination of the sulfur anions were investigated using a sample containing sulfide (30.0 μM), sulfite (50 μM), sulfate (50 μM) and thiosulfate (20.0 μM), treated according to Section 2.3. Cl^-, NO_2^-, NO_3^-, Br^-, I^-, CN^-, HCO_3^-, $H_2PO_4^-$, Na^+, K^+, NH_4^+, Mn(II), Mg(II) and Ca(II) did not give any interference for the determination of the sulfur anions even when present at concentrations as high as 10 mM. For the determination of sulfide, ions of sulfite, copper(II) and iron(III) also did not interfere up to 5, 0.1 and 0.1 mM, respectively. Sulfide and thiosulfate at low concentrations (≤0.5 mM) did not give any interference in the measurement of the total amount of sulfite and sulfate, but these ions interfered at concentrations above 0.5 mM due to the formation of small amounts of sulfate during the oxidation of sulfite in Step III. Copper(II) and iron(III) up to 0.1 and 1 mM, respectively, did not interfere with the thiosulfate determination, but copper(II) of higher concentration gave interference due to formation of its complex with thiosulfate.

3.5. Recoveries for the sulfur anions in the hot-spring waters

The proposed method was applied to determination of sulfide, the sum of sulfite and sulfate, and thiosulfate in hot-spring water samples. The results are given in Table 5, and Fig. 5 shows chromatograms obtained for hot-spring water sample II in Table 5. Recoveries for sulfide, sulfite plus sulfate, and thiosulfate in the hot-spring waters tested were quantitative (99.5–101.3%), showing that there was no discernible matrix interferences for these samples.

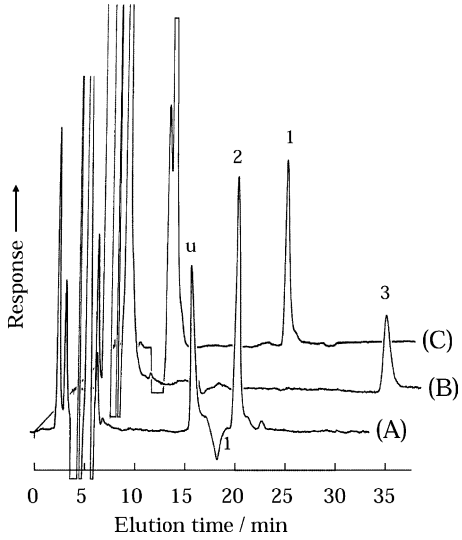

Fig. 5. Chromatograms of sulfur anions in a hot-spring water sample. (A) Chromatogram obtained for the sample diluted 10-fold and analyzed according to Step I, (B) chromatogram obtained for the sample diluted 100-fold and analyzed according to Step II, (C) chromatogram obtained for the sample diluted 100-fold and analyzed according to Step III. Peaks: 1, sulfite and sulfate; 2, thiosulfate; 3, thiocyanate; u: unknown species.

Table 5
Determination of sulfur anions in hot-spring waters

Sample	Dilution factor	Analyte added (μM)				Analyte found (μM)			Recovery (%)		
		$S_2O_3^{2-}$	S^{2-}	SO_3^{2}	SO_4^{2}	$S_2O_3^{2-}$ [a]	S^{2-} [b]	SO_4^{2-} [c]	$S_2O_3^{2-}$	S^{2-}	SO_4^{2-}
I	1	0	0	0	0	[d]	0	0		0	
	1.5	20.0	15.0	40.0	60.0	–	15.0	–	100.0		
	1.5	10.0	20.0	30.0	20.0	–	20.0	–	100.0		
	10	0	0	0	0	0	–	19.8			
	10	20.0	10.0	50.0	50.0	19.9	–	119.8	99.5	–	99.8
II	10	0	0	0	0	20.3	[d]	[d]		0	
	10	0	0	0	0	20.0	9.1	66.6			
	100	20.0	10.0	20.0	50.0	–	19.0	–		99.0	
	100	10.0	20.0	50.0	50.0	–	29.1	–	–	100.0	–
	100	25.0	10.0	15.0	10.0	27.2	–	92.5	100.8	–	101.2
	100	13.0	30.0	10.0	20.0	15.0	–	97.2	100.0	–	100.0
III	1	0	0	0	0	–	0	–	–		
	1.5	20.0	10.0	50.0	50.0	–	10.1	–		101.0	
	1.5	15.0	30.0	40.0	10.0	–	29.9	–		99.7	
	10	0	0	0	0	[d]	–	[d]			
	100	0	0	0	0	7.4	–	64.1			
	100	15.0	10.0	20.0	10.0	22.4	–	94.5	100.0	–	101.3
	100	30.0	20.0	30.0	10.0	12.4	–	104.3	100.0	–	100.0

(–) Measurement was not carried out.
[a] Obtained by Step I.
[b] Obtained by Step II.
[c] Obtained by Step III.
[d] The content was too high to be determined.

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