ELSEVIER

Journal of Chromatography A, 770 (1997) 157–164

JOURNAL OF CHROMATOGRAPHY A

Determination of sulfur oxyanions by ion chromatography on a silica ODS column with tetrapropylammonium salt as an ion-pairing reagent

Yasuyuki Miura*, Ayako Saitoh, Tomozo Koh

Department of Chemistry, Faculty of Science, Tokai University, Hiratsuka, Kanagawa 259-12, Japan

Abstract

The difficulty in using conventional ion chromatography for the determination of sulfate, thiosulfate, dithionate and polythionates (tri-, tetra-, penta- and hexathionate) in their mixtures, comes mainly from very late elutions of polythionates due to their strong retentions onto a separating column. Rapid and sensitive determination of these sulfur oxyanions has been achieved by ion-pair chromatography using a silica octadecylsilane (ODS) column with mobile phases of 10% or 20% (v/v) acetonitrile in water (pH, 5.0) containing 0.2 m*M* phthalate and 7 m*M* tetrapropylammonium salt (TPAOH). The sulfur species separated on the column were monitored with a conductivity detector after passing through a micro membrane suppressor in the H^+ form. When an acetonitrile–water (10:90, v/v) mobile phase (pH, 5.0) of 0.2 m*M* phthalate and 7 m*M* TPAOH was used at a flow-rate of 0.8 ml min^{-1}, sulfate, thiosulfate, dithionate and trithionate were eluted at short retention times of 9.1, 9.7, 11.4 and 15.8 min, respectively; however, the higher polythionates required more than 30 min to elute. When the concentration of acetonitrile in the mobile phase was raised to 20% (v/v), all polythionates of tri- to hexathionate were completely separated from their mixtures within 21 min; in this instance, both sulfate and thiosulfate failed to be resolved due to their close retention times. Good recoveries were obtained for these sulfur oxyanions when added to various hot-spring water samples.

Keywords: Ion-pairing reagents; Mobile phase composition; Sulfur oxyanions; Inorganic anions; Polythionates; Thiosulfate

1. Introduction

Sulfur oxyanions, polythionates ($S_xO_6^{2-}$: $x=3$ to 6) and thiosulfate, are produced by the reaction of hydrogen sulfide with sulfite in an acid medium (Wackenroder's solution) [1] and also formed as intermediate oxidation products of sulfide minerals [2,3]. It is desirable to develop the determination of the oxyanions in mixtures to clarify their chemical behaviour. It is difficult to determine individual polythionates in their mixtures as their chemical and physical properties are very similar. Recently, a number of ion-chromatographic (IC) [4,5] and reversed-phase ion-pair liquid chromatographic (RP-IPC) [6–9] methods for the separation and detection of polythionates and thiosulfate in mixtures have been published; in many cases thiosulfate and three polythionates ($x=3$ to 5) have been separated on a resin-based column [4–9]. But the separations of thiosulfate and four polythionates ($x=3$ to 6) have been difficult because hexathionate requires a long elution time. When compared with a resin-based column, anions are less strongly retained on a silica-based column. Therefore, if a silica column were to be used, the sulfur oxyanions in their mixtures might be expected to be separated at shorter retention

*Corresponding author. Tel.: 0463-58-1211; Fax: 0463-58-1812.

PII S0021-9673(97)00022-8

times. However, no consideration has been given in the literature to the chromatographic determinations of sulfate, thiosulfate, dithionate and polythionates ($x=3$ to 6) in their mixtures using a silica-based column.

In this study, separations of sulfate, thiosulfate, dithionate and polythionates ($x=3$ to 6) from their mixtures, were investigated using a silica octadecylsilane (ODS) column as a stationary phase. The optimal conditions for their rapid separation were established using an acetonitrile–water mobile phase containing phthalate and tetrapropylammonium hydroxide ion-pair reagent. Even when acidic mobile phases (pH 5.0) were used, conductometric detection sensitivities of the separated species could be greatly increased by a suppressor which uses a regenerant of dilute sulfuric acid. The proposed method was successfully applied to the determination of the oxyanions of sulfur added to hot-spring waters.

2. Experimental

2.1. Chromatographic system

The Model 4000i ion chromatographic system (Dionex, Sunnyvale, CA, USA) used in this study comprised a pump with dual pistons, an injection-valve equipped with a sample loop of 50-μl, a silica ODS separating column (Kaseisorb LC ODS super of 150 mm×4.6 mm I.D., Tokyo Kasei, Tokyo, Japan), a HPIC-AMMS suppressor (Dionex) and a conductivity detector (Dionex). The suppressor was provided with a strongly acidic cation-exchange membrane in the hydronium form. The chromatograms were recorded with a Model R-111 recorder (Shimadzu, Kyoto, Japan).

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 exception of the potassium polythionates, were of analytical-reagent grade and were used without further purification as obtained from Kanto Chemicals (Tokyo, Japan).

Acetonitrile–water (10:90 or 20:80, v/v) mobile phases containing 0.2 m*M* phthalate and 7 m*M* tetrapropylammonium hydroxide (TPAOH) were prepared by adding 50 or 100 ml of acetonitrile, respectively, to a mixture of 5.0 ml of 0.02 *M* phthalic acid, 7.0 ml of 0.5 *M* TPAOH and small amounts of acetic acid, and then diluting the mixtures to 500 ml with water. The acetic acid was used to adjust pH of the mobile phase to 5.0. The mobile phases obtained were filtered through a membrane filter (pore size, 0.2 μm) before use.

Polythionates were prepared as follows. Potassium trithionate ($K_2S_3O_6$) was prepared by the reaction of sulfurous acid with sulfur dichloride [10]. The trithionate so obtained was recrystallized with water at temperatures below 35°C and then dried at room temperature before storage at −10±2°C. Potassium tetrathionate ($K_2S_4O_6$) was prepared by the reaction of sulfurous acid with sulfur monochloride (disulfur dichloride) [10]. The tetrathionate obtained was recrystallized with water at temperatures below 60°C and then dried at room temperature before storage at −10±2°C. Potassium pentathionate ($K_2S_5O_6 \cdot 1.5H_2O$) was obtained by the reaction of thiosulfate with sulfur dichloride [11]. This pentathionate was purified by recrystallizing twice in 0.5 *M* hydrochloric acid at temperatures below 50°C and then dried at room temperature before storage at −10±2°C. Potassium hexathionate ($K_2S_6O_6$) was prepared by the reaction of thiosulfate with sulfur monochloride (disulfur dichloride) [11]. This hexathionate was recrystallized twice in 2 *M* hydrochloric acid at temperatures below 60°C and then dried at room temperature before storage at −10±2°C. Stock solution of standard polythionates (1.0 m*M*) were prepared by dissolving 68.3 mg of the trithionate, 75.6 mg of tetrathionate, 90.4 mg of the pentathionate or 92.0 mg of the potassium hexathionate, respectively, in water and diluting to 250 ml. The concentration of each standard stock solution of tri-, tetra-, penta- and hexathionate was checked by their cyanolysis [12,13] and/or sulfitolysis [14], and these solutions could be used in the present work for six weeks, six months, four months and two months, respectively, when stored at 5±2°C in a refrigerator after preparation. The working solutions of polythionates were prepared by carefully diluting each of 1.0 m*M* standard solutions with water.

A standard sulfate solution (0.1 *M*) was prepared

by dissolving 7.174 g of sodium sulfate in water and diluting to 500 ml. 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. A solution of standard dithionate (0.01 *M*) was prepared by dissolving 1.235 g of sodium dithionate dihydrate in water and diluting to 500 ml. Working solutions of standard sulfate, thiosulfate and dithionate were obtained by appropriate dilution with water.

2.3. Procedure

Mobile phases (pH 5.0) of 10 or 20% (v/v) acetonitrile–water containing 0.2 m*M* phthalate and 7 m*M* TPAOH were pumped at a rate of 0.8 ml min^{-1}, and then a 50-μl sample solution containing sulfate, thiosulfate, dithionate and polythionates ($x=3$ to 6) was injected into the separating column, which was kept at 23±2°C. The effluent was allowed to flow through a suppressor (HPIC-AMMS) and then a conductivity detector cell. A regeneration solution of 0.025 *M* sulfuric acid was passed through the suppressor at a flow-rate of 1.5 ml min^{-1}.

3. Results and discussion

3.1. Selections of separating column and ion-pair reagent

In general, retentions of analyte species are thought to be affected by the affinity of column materials (silica and resin) as well as ion-pair reagents. At first, two different types of column, a silica ODS column and resin-based column (MPIC-NS1 column with a MPIC-NG1 guard column), were investigated to elute sulfur oxyanions at short retention times. An acetonitrile–water (20:80, v/v) mobile phase (pH 5.0) containing 0.2 m*M* phthalate and 7 m*M* TPAOH was used for the silica ODS column and an acetonitrile–water (30:70, v/v) mobile phase (pH 5.0) containing 3 m*M* phthalate and 2.5 m*M* tetra-*n*-butylammonium hydroxide (TBAOH) was used for the resin-based columns. Each concentration of TPAOH, TBAOH, phthalate and CH_3CN in these mobile phases and their pH values were prepared to give the optimal resolution for the sulfur oxyanion mixtures. The results are shown in Table 1. The resin-based columns required longer retention times for the elution of polythionates, and the chromatographic peaks obtained showed considerable tailing due to the high affinity that the polythionate species have for such columns. Use of the silica column made it possible for the sulfur species to elute earlier with sharp chromatographic peaks. We therefore chose the silica-based column in this work.

Retention times of sulfur oxyanions are affected by the carbon-chain length of alkyl groups on the tetraalkylammonium salt, R_4N^+, used as an ion-pair reagent. Tetraethylammonium hydroxide (TEAOH), TPAOH and TBAOH were tested as tetraalkylammonium reagent of elutions of the sulfur oxyanions from the silica column. The TEAOH ion-pair reagent barely retained the four oxyanions of sulfate, thiosulfate, dithionate and trithionate on the silica column. As a result, chromatographic peaks for these four sulfur oxyanions could not be separated from the negative peak for water elution. On the other hand, the TBAOH reagent strongly retained the sulfur oxyanions onto the silica ODS column due to its strongly hydrophobic properties and consequently hexathionate required a long elution time. When compared with these two reagents, TPAOH ion-pair reagent eluted the sulfur oxyanions at reasonable retention times when an acetonitrile–water (20:80, v/v) mobile phase (pH 5.0) containing 0.2 m*M*

Table 1
Relative adjusted retention times for various sulfur oxyanions using different columns (t' for $S_2O_3^{2-}=1.00$)

Column	$t'_{A^-}/t'_{S_2O_3^{2-}}$					
	$S_2O_3^{2-}$	$S_2O_6^{2-}$	$S_3O_6^{2-}$	$S_4O_6^{2-}$	$S_5O_6^{2-}$	$S_6O_6^{2-}$
Silica[a]	1.00[b]	1.08	1.19	1.89	2.25	3.58
Resin[c]	1.00[d]	1.32	1.70	2.39	3.17	5.91

[a] Kaseisorb LC ODS super column with a CH_3CN–water (20:80, v/v) mobile phase (pH 5.0) containing 0.2 m*M* phthalate and 7 m*M* TPAOH.
[b] t' for $S_2O_3^{2-}$ was 2.36 min.
[c] Dionex MPIC-NS1 and MPIC-NG1 columns in series with an CH_3CN–water (30:70, v/v) mobile phase (pH 5.0) containing 3 m*M* phthalate and 2.5 m*M* TBAOH.
[d] t' for $S_2O_3^{2-}$ was 7.78 min.

phthalate and 7 m*M* TPAOH was used. Therefore, TPAOH proved to be the most effective of three ion-pair reagents for the elution of the sulfur oxyanions from the silica column.

3.2. Optimization of mobile phase

3.2.1. Effect of pH of mobile phase on elution of sulfur oxyanions

In preliminary experiments, elution of sulfur oxyanions were found to be accelerated by an increase in the pH value of the mobile phase. Therefore, acetonitrile–water (20:80, v/v) mobile phase, adjusted to various pH values by adding small amounts of acetic acid, was used to measure the pH effect on the elution of the sulfur oxyanions; the acetonitrile–water mobile phase contained 0.2 m*M* phthalate and 7 m*M* TPAOH. At pH 4.5 of the mobile phase, higher polythionates (x=4 to 6) required retention times of more than 30 min for their elution, while at pH 6.5 and 7.5, the polythionates were eluted earlier, however, the tetrathionate peak overlapped with a system peak (phthalate ion elution). The mobile phase at pH 5.0 gave complete separation of dithionate and all polythionates (x=3 to 6) within 21 min.

3.2.2. Effect of concentration of TPAOH on elution of sulfur oxyanions

In order to establish the optimal concentration of TPAOH in mobile phase, an acetonitrile–water (20:80, v/v)–2 m*M* phthalate mobile phase (pH 5.0) containing various concentrations of TPAOH (1.5 to 10 m*M*) was used. An increase in TPAOH concentration resulted in increased retention times for the sulfur species. When the mobile phase of 7 m*M* TPAOH was employed, the seven sulfur species, sulfate, thiosulfate, dithionate and polythionates (x= 3 to 6) were eluted at shorter retention times (within 21 min) and their species were separated completely with the exception of sulfate and thiosulfate. The mobile phases using concentrations of 1.5 and 3.5 m*M* TPAOH failed to separate sulfate, thiosulfate, dithionate, trithionate and tetrathionate due to decreased retention times. On the contrary, the mobile phase of TPAOH in the high concentration of 10 m*M* failed to elute hexathionate early.

3.2.3. Effect of concentration of acetonitrile on elution of sulfur oxyanions

Addition of a water-miscible organic solvent to the mobile phase might be expected to decrease the sulfur oxyanions retention times as it reduces the polar-adsorptions of sample anions and/or their ion-pair species onto the separator. An attempt was made to add small amounts of acetonitrile to a mobile phase (pH 5.0) of 0.2 m*M* phthalate and 7 m*M* TPAOH. The results are shown in Table 2. Increasing the concentration of acetonitrile in the mobile phase (pH 5.0) accelerated the elutions of the seven sulfur oxyanions. When an acetonitrile–water (10:90, v/v) mobile phase (pH 5.0) was used, the four anions of sulfate, thiosulfate, dithionate and trithionate were eluted within 16 min, however the higher polythionates of tetra- to hexathionate required very long elution times. When the acetonitrile concen-

Table 2
Effect of concentration of CH_3CN in a 0.2 m*M* phthalate −7 m*M* TPAOH mobile phase (pH 5.0) on retention times of various sulfur oxyanions

Concentration	Retention time (t) min^{-1}						
of CH_3CN/% (v/v)	SO_4^{2-}	$S_2O_3^{2-}$	$S_2O_6^{2-}$	$S_3O_6^{2-}$	$S_4O_6^{2-}$	$S_5O_6^{2-}$	$S_6O_6^{2-}$
10	9.10	9.70	11.4	15.8	[a]	[a]	[a]
15	6.48	6.76	7.66	9.72	14.0	18.0	51.7
20	5.06	5.30	5.74	6.77	8.64	10.3	20.2
25	4.28	4.32	4.76	5.50	6.40	7.08	11.1
30	3.68	4.00	4.12	4.28	5.28	5.80	7.72

[a] Peak could not be detected owing to very late elution.

tration was increased to 20% (v/v), the five anions of dithionate and polythionates ($x=3$ to 6) were separated completely, with the exception of sulfate and thiosulfate. Addition of phthalate (0.2 m*M*) to a mobile phase (pH 5.0) of 7 m*M* TPAOH and acetonitrile–water (20:80, v/v) promoted the elution of the higher polythionates and improved peak shape. Consequently, acetonitrile–water (10:90, v/v) and (20:80, v/v) mobile phases (pH 5.0) were used to separate the four anions (sulfate, thiosulfate, dithionate and trithionate) and the five anions (dithionate and polythionates) in mixtures, respectively.

3.3. Effect of suppressor on using acidic mobile phase

A micro membrane suppressor, in which sulfuric acid was used as a regenerant, was employed to reduce the background conductivity of the basic mobile phase of carbonate and also to enhance the conductivity of analyte ions [7,10,12]. In the present work, the suppressor was found to greatly enhance the peak heights of chromatograms for the sulfur oxyanions, even when acidic mobile phases of 10 and 20% (v/v) acetonitrile in water (pH 5.0) containing 7 m*M* TPAOH and 0.2 m*M* phthalate were employed; the background conductivity was reduced from 392 to 140 μS cm^{-1}. Therefore, the suppressed system gave lower detection limits in comparison with the non-suppressed system (Table 3). Hence, the suppressor was utilised in our method.

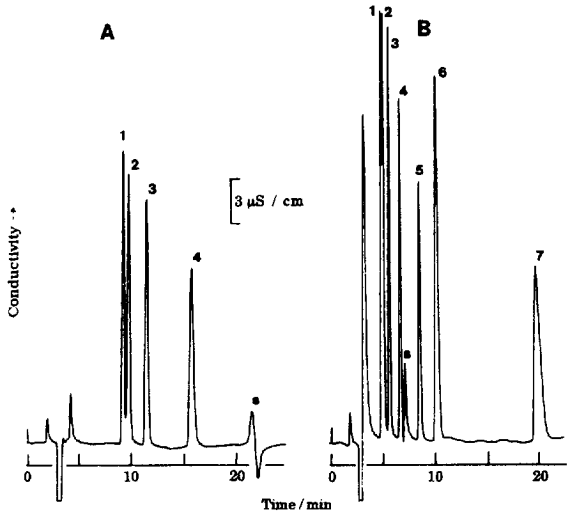

Fig. 1. Chromatograms of seven sulfur oxyanions in a mixture. Column, Kaseisorb LC ODS super (150 mm×4.6 mm I.D.); (A) obtained by a CH_3CN–water (10:90, v/v) mobile phase (pH 5.0) containing 0.2 m*M* phthalate and 7 m*M* TPAOH; (B) obtained by a CH_3CN–water (20:80, v/v) mobile phase (pH 5.0) containing 0.2 m*M* phthalate and 7 m*M* TPAOH; 1, SO_4^{2-} (50 μ*M*); 2, $S_2O_3^{2-}$ (50 μ*M*); 3, $S_2O_6^{2-}$ (50 μ*M*); 4, $S_3O_6^{2-}$ (50 μ*M*); 5, $S_4O_6^{2-}$ (50 μ*M*); 6, $S_5O_6^{2-}$ (100 μ*M*); 7, $S_6O_6^{2-}$ (100 μ*M*); s, system peak.

Table 3
Sensitivity and detection limit for sulfur oxyanions by suppressed and non-suppressed systems

Sulfur	Sensitivity (μS $cm^{-1}/10^{-5}$ *M*)		Detection limit (as *S/N*=3)[a]/ppm	
oxyanion	Suppressed	Non-suppressed	Suppressed	Non-suppressed
SO_4^{2-} [b]	4.18	0.95	0.03	0.19
$S_2O_3^{2-}$ [b]	3.91	0.93	0.05	0.22
$S_2O_5^{2-}$ [b]	3.88	0.78	0.10	0.38
$S_3O_6^{2-}$ [b]	2.23	0.45	0.16	0.79
$S_2O_6^{2-}$ [c]	5.72	1.35	0.04	0.22
$S_3O_6^{2-}$ [c]	4.88	1.17	0.07	0.31
$S_4O_6^{2-}$ [c]	3.49	0.75	0.11	0.56
$S_5O_6^{2-}$ [c]	2.93	0.45	0.14	1.06
$S_6O_6^{2-}$ [c]	1.47	0.20	0.29	2.68

[a] Signal-to-noise level is 0.186 μS cm^{-1}.
[b] CH_3CN–water (10:90, v/v) mobile phase (pH 5.0) containing 0.2 m*M* phthalate and 7 m*M* TPAOH was used.
[c] CH_3CN–water (20:80, v/v) mobile phase (pH 5.0) containing 0.2 m*M* phthalate and 7 m*M* TPAOH was used.

3.4. Calibration plots

A 50-μl aliquot of standard solution containing sulfate, thiosulfate, dithionate and polythionates (x= 3 to 6) was treated according to Section 2.3. Chromatograms obtained are shown in Fig. 1. Calibration graphs were plotted as peak height vs. concentration. When acetonitrile–water (10:90, v/v; pH 5.0) containing 0.2 m*M* phthalate and 7 m*M* TPAOH was used as a mobile phase, each graph of the four oxyanions of sulfate, thiosulfate, dithionate and trithionate was linear up to 50.0 μ*M*. From six results obtained for a 50-μl aliquot of mixture of sulfate, thiosulfate, dithionate and trithionate in each concentration of 30.0 μ*M*, the proposed method gave a mean value of 30.8 μ*M* with a standard deviation (S.D.) of 0.75 μ*M* and a relative standard deviation (R.S.D.) of 2.41% for sulfate, 30.5 μ*M* (S.D.=0.27 μ*M*, R.S.D.=0.88%) for thiosulfate, 30.5 μ*M* (S.D.=0.18 μ*M*, R.S.D.=0.59%) for dithionate and 30.6 μ*M* (S.D.=0.17 μ*M*, R.S.D.=0.56%) for trithionate, respectively. With a mobile phase (pH 5.0) of acetonitrile–water (20:80, v/v), 0.2 m*M* phthalate and 7 m*M* TPAOH, each calibration graph was linear up to 50.0 μ*M* for dithionate, 60.0 μ*M* for trithionate, 60.0 μ*M* for tetrathionate, 60.0 μ*M* for pentathionate, 50.0 μ*M* for hexathionate. When an injection of a 50-μl aliquot mixture of dithionate (20.0 μ*M*), trithionate (20.0 μ*M*), tetrathionate (20.0 μ*M*), pentathionate (40.0 μ*M*) and hexathionate (40.0 μ*M*) was repeated six times, the proposed method afforded a mean value of 20.5 μ*M* (S.D.=0.14 μ*M*, R.S.D.=0.68%) for dithionate, 20.7 μ*M* (S.D.=0.12 μ*M*, R.S.D.=0.58%) for trithionate, 20.6 μ*M* (S.D.= 0.18 μ*M*, R.S.D.=0.87%) for tetrathionate, 39.7 μ*M* (S.D.=0.12 μ*M*, R.S.D.=0.30%) for pentathionate and 39.8 μ*M* (S.D.=0.30 μ*M*, R.S.D.=0.75%) for hexathionate, respectively.

3.5. Determination of the sulfur oxyanions added to hot-spring water samples

The hot-spring water samples used, contained large amounts of both chloride and sulfate ions,

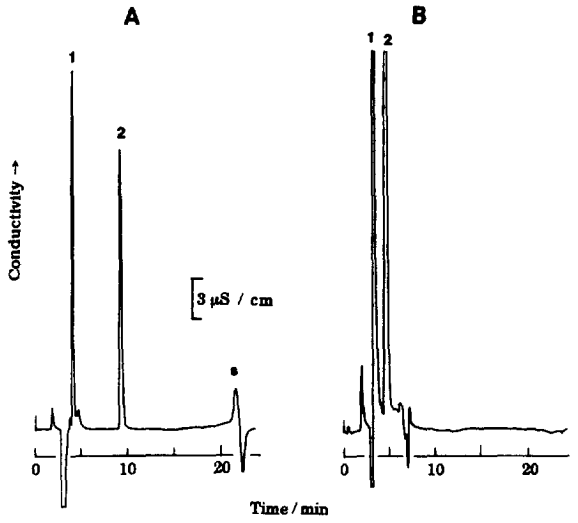

Fig. 2. Chromatograms obtained for diluted hot-spring waters. (A) a 25-fold dilution of the original volume using an acetonitrile–water (10:90, v/v) mobile phase (pH 5.0) containing 0.2 m*M* phthalate and 7 m*M* TPAOH; (B) a 5-fold dilution of the original volume using an acetonitrile–water (20:80, v/v) mobile phase (pH 5.0) containing 0.2 m*M* phthalate and 7 m*M* TPAOH; 1, Cl^-; 2, SO_4^{2-}; s, system peak.

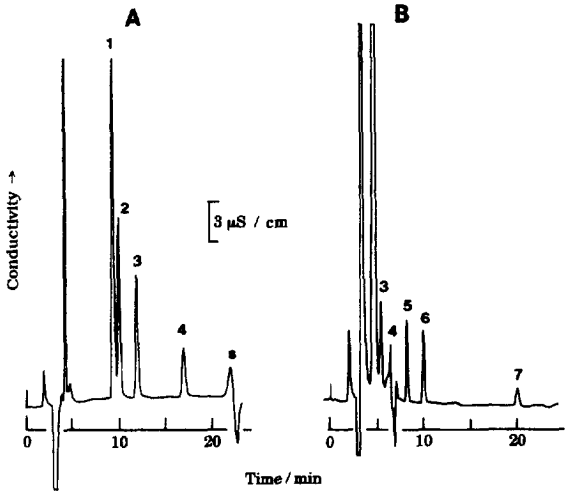

Fig. 3. Chromatograms of sulfur oxyanions added to hot-spring waters. (A) a 25-fold dilution of the original volume to which SO_4^{2-}, $S_2O_3^{2-}$, $S_2O_6^{2-}$ and $S_3O_6^{2-}$ have been added to be 10.0, 36.0, 30.0 and 21.0 μ*M*, respectively, using an acetonitrile–water (10:90, v/v) mobile phase (pH 5.0) containing 0.2 m*M* phthalate and 7 m*M* TPAOH; (B) a 5-fold dilution of the original volume to which each of $S_2O_6^{2-}$ $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$ and $S_6O_6^{2-}$ has been added to be 15 μ*M* using an acetonitrile–water (20:80, v/v) mobile phase (pH 5.0) containing 0.2 m*M* phthalate and 7 m*M* TPAOH; 1, SO_4^{2-}; 2, $S_2O_3^{2-}$; 3, $S_2O_6^{2-}$; 4, $S_3O_6^{2-}$; 5, $S_4O_6^{2-}$; 6, $S_5O_6^{2-}$; 7, $S_6O_6^{2-}$; s, system peak.

Table 4
Determination of sulfate, thiosulfate, dithionate and trithionate added to hot-spring water samples

Sample	Dilution /fold	Added/10^{-5} M				Found/10^{-5} M				Recovery, %			
		SO_4^{2-}	$S_2O_3^{2-}$	$S_2O_6^{2-}$	$S_3O_6^{2-}$	SO_4^{2-}	$S_2O_3^{2-}$	$S_2O_6^{2-}$	$S_3O_6^{2-}$	SO_4^{2-}	$S_2O_3^{2-}$	$S_2O_6^{2-}$	$S_3O_6^{2-}$
A	5					[a]	[b]	0	0				
	5			1.80	2.80	[a]	[b]	1.78	2.79			98.9	99.6
	25		3.60	3.00	2.10	[a]	3.58	3.00	2.08		99.4	100.0	99.0
	50					[a]	0	0	0				
	50	1.20	1.60	0.50	2.10	3.78	1.62	0.48	2.06	101.7	101.3	96.0	98.1
B	5					[a]	[b]	0	0				
	5			0.90	1.60	[a]	[b]	0.93	1.62			103.3	101.3
	100		3.20	3.40	3.60	[a]	3.21	3.39	3.58		100.3	99.7	99.4
	100		1.20	3.00	4.00	[a]	1.20	3.04	3.96		100.0	101.3	99.0
	500					1.78	0	0	0				
	500	2.40	0.80	1.00	0.80	4.08	1.75	1.02	0.81	95.8	97.2	102.0	101.3

A CH_3CN–water (10:90, v/v) mobile phase (pH 5.0) containing 0.2 mM phthalate and 7 mM TPAOH was used.
[a] The content was too much to be measured.
[b] The peak of $S_2O_3^{2-}$ was not separated from that of SO_4^{2-}.

Table 5
Determination of tetra-, penta-, and hexathionate added to hot-spring water samples

Sample	Dilution/fold	Added/10^{-5} M			Found/10^{-5} M			Recovery, %		
		$S_4O_6^{2-}$	$S_5O_6^{2-}$	$S_6O_6^{2-}$	$S_4O_6^{2-}$	$S_5O_6^{2-}$	$S_6O_6^{2-}$	$S_4O_6^{2-}$	$S_5O_6^{2-}$	$S_6O_6^{2-}$
A	3.3				0	0	0			
	3.3	0.30	0.20	0.70	0.29	0.20	0.73	96.7	100.0	104.3
	5	1.00	1.00	1.00	0.99	0.98	1.02	99.0	98.0	102.0
	5	1.50	1.50	1.50	1.52	1.56	1.46	101.3	104.0	97.3
B	2				0	0	0			
	2	0.80	0.50	0.20	0.78	0.49	0.20	97.5	98.0	100.0
	5	2.00	2.00	2.00	2.02	2.05	1.98	101.0	102.5	99.0
	5	3.50	3.50	3.50	3.49	3.48	3.42	99.7	99.4	97.7

A CH_3CN–water (20:80, v/v) mobile phase (pH 5.0) containing 0.2 nM phthalate and 7 mM TPAOH was used.

which gave big peaks as well as a large negative peak caused by the overload for column. These peaks interfered with the separation of sulfur oxyanions in this method. Fig. 2 shows the chromatograms obtained for the hot-spring waters diluted 25-fold and 5-fold and Fig. 3 shows the chromatograms of the sulfur oxyanions added to the hot-spring waters. In these experiments, mobile phases of 10 and 20% (v/v) acetonitrile in water (pH 5.0) containing 0.2 mM phthalate and 7 mM TPAOH were used. The determinations and recoveries of the sulfur oxyanions added to hot-spring waters are shown in Table 4 Table 5. The recoveries for the sulfur oxyanions in both Tables 4 and 5 ranged from 96. 0 to 104. 3%. The proposed method was successfully applied to the determination of the sulfur oxyanions in hot-spring waters.

References

[1] L.V. Haff, in J.H. Karchmer (Editor), The Analytical Chemistry of Sulfur and Its Compounds, Interscience, New York, 1970, pp. 225–240.
[2] R. Mahkhija and A. Haichen, Talanta, 25 (1978) 79.
[3] R. Mahkhija and A. Haichen, Anal. Chim. Acta, 105 (1979) 375.
[4] A.W. Wolkoff and R.H. Larose, Anal. Chem., 47 (1975) 1003.

[5] Y. Miura, Y. Yonemura and T. Koh, Nippon Kagaku Kaishi, 1991 (1991) 101.
[6] S.B. Rabin and D.M. Stanbury, Anal. Chem., 57 (1985) 1130.
[7] M. Weidenauer, P.H. Hoffman and K.H. Lieser, Fresenius' Z. Anal. Chem., 331 (1988) 372.
[8] H. Zou, Z. Jia, Y. Zhang and P Lu, Anal. Chim. Acta, 284 (1993) 59.
[9] S.I. Weir, E.C.V. Butler and P.R. Haddad, J. Chromatogr. A, 671 (1994) 197.
[10] H. Stamm, M. Goehring and U. Feldmann, Z. Anorg. Allgem. Chem., 250 (1942) 226.
[11] M. Goehring and U. Feldmann, Z. Anorg. Chem., 257 (1942) 223.
[12] T. Koh, A. Wagai and Y. Miura, Anal. Chim. Acta, 71 (1974) 367.
[13] T. Koh and K. Taniguchi, Anal. Chem., 45 (1973) 2018.
[14] T. Koh, K. Taniguchi, Y. Miura and I. Iwasaki, Nippon Kagaku Kaishi, 1979 (1979) 348.