Sulfur speciation and tetrathionate sulfitolysis monitoring by capillary electrophoresis

S. Motellier*, M. Descostes

Commissariat à l'Energie Atomique, C.E. Saclay, DCC/DESD/SESD/LIRE, Bat. 450, 91191 Gif-sur-Yvette Cedex, France

Abstract

Capillary electrophoresis (CE) with indirect detection was used to analyse mixtures of sulfur-containing compounds. An optimised electrolyte, composed of 2 mM sulfosalicylic acid–0.5 mM Waters osmotic flow modifier OFM-OH, pH adjusted to 7.00 with Bis–Tris, allowed the analysis of sulfide (H_2S/HS^-), thiosulfate ($S_2O_3^{2-}$), tetrathionate ($S_4O_6^{2-}$), trithionate ($S_3O_6^{2-}$), sulfite (HSO_3^-/SO_3^{2-}), sulfate (SO_4^{2-}), and peroxodisulfate ($S_2O_8^{2-}$). Only sulfate showed a single-peak electropherogram that gives evidence of its stability in aqueous solutions. Thiosulfate, tetrathionate and peroxodisulfate showed an additional minor peak of sulfate that did not seem to be time-dependent and was supposed to be due to salt impurities. Sulfide and sulfite showed rapid conversion into their oxidation products in solutions exposed to air. Linear calibration curves were obtained for all these species, taking the oxidation process into account for sulfide and sulfite. Limits of detection were in the low- to mid-μM range, except for sulfide, for which the limit of detection was 10^{-5} M. The identity of trithionate was not determined via standard solutions (not commercially available) but after the rearrangement of tetrathionate with sulfite that yields thiosulfate and trithionate. The time-dependence of the concentrations of both the reagents and products could be followed simultaneously by the proposed CE method and the reaction kinetics were found to be second order in the pH range 7 to 11. A calibration curve for trithionate could be deduced from this study. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Background electrolyte composition; Sulfur compounds; Inorganic anions

1. Introduction

The analysis of the distribution of aqueous sulfur species is of particular interest to the geochemist who wishes to describe the redox state and equilibria of natural polyphasic systems [1–3]. However, it is a challenging problem to the analyst, mainly because most of these species are unstable and easily reduced or oxidised. Standard methods rely on general oxidimetry [4] that involve important sample handling that may lead to possible contamination and biased results. In this regard, separative techniques appear to be particularly well suited for speciation analysis in the way that they allow the simultaneous analysis of several species of the same element, provided slow kinetics of their conversion to one another compared with the analysis time.

Capillary electrophoresis (CE) should be considered as a technique of interest because of high overall resolution and single-phase separation

*Corresponding author. Tel.: +33-1-6908-3271; fax: +33-1-6908-3411.

E-mail address: sylvie.motellier@cea.fr (S. Motellier).

medium. Sulfate and thiosulfate are routinely ana-lysed with a chromate-based electrolyte [5,6]. Un-stable sulfide and sulfite species need no-oxidising conditions; they have been analysed using either direct [7] or indirect [8,9] spectrophotometric de-tection. Amperometric [10] or conductimetric [11] detections have also been proposed.

Other CE features like shortness of analysis times and automated injection of small sample volumes enable repeated analyses of a sample without inter-fering with the chemical processes it may be under-going. Despite these interesting characteristics, only a few papers deal with CE application to kinetic studies. Some examples are reported that exploit the target peak of the reactant of interest: methanolysis of sulfonylureas [12,13], acid hydrolysis of tetrade-canedisulfate [14], and photocatalytic oxidation of substituted anilines [15] could be studied and their rates could be determined using this technique.

The purpose of this study was to evaluate the performance of CE in the simultaneous analysis of several sulfur species in order to describe leachates from oxidised pyrite. Reactions between tetrathionate and some nucleophilic sulfur species could be ob-served in the course of this analytical work, which was taken advantage of for an investigation of the kinetics of the reaction between tetrathionate and sulfite.

2. Experimental

2.1. Chemicals and preparations

OFM-OH is a patented electroosmotic flow modi-fier from Waters. Sulfosalicylic acid (SULSAL), lactic acid, bis(2-hydroxyethyl)amino–tris(hydrox-ymethyl)methane (Bis–Tris), 1-ephedrin, ethanol-amine, as well as sodium sulfide hydrate (35%) Na_2S, xH_2O ($x=7$–9), sodium thiosulfate (97%) $Na_2S_2O_3$, sodium dithionite (87%) $Na_2S_2O_4$, so-dium sulfate (99%) Na_2SO_4, potassium disulfate (97.5%) $K_2S_2O_7$, and potassium peroxodisulfate (99%) $K_2S_2O_8$ were purchased from Merck. Sodium tetrathionate dihydrate (99%) $Na_2S_4O_6$, $2H_2O$, so-dium sulfite (98%) Na_2SO_3, and potassium disulfite (97%) $K_2S_2O_5$ were from Fluka. The water used

throughout the study was purified with a Milli-Q system (Millipore).

The electrolyte was composed of 2 mM SULSAL–0.5 mM OFM-OH, and its pH was ad-justed to 7.00 with Bis–Tris. It was prepared with degassed water and filtered through a 0.2-μm SFCA filter (Nalgene). Small flakes probably due to the precipitation of OFM-OH–SULSAL salts may de-velop in the electrolyte when keeping it at low temperature. They readily disappear when the tem-perature is increased.

Standard stock solutions of each sulfur species were $2 \cdot 10^{-2}$ M, except for $Na_2S_4O_6$ ($5 \cdot 10^{-3}$ M). They were prepared daily with degassed water except for the established stable species (sulfate, thiosulfate). They were diluted to the desired con-centration with degassed water.

2.2. Apparatus and conditions

All CE experiments were performed with a P/ACE MDQ (Beckman) equipped with a UV detector. The fused-silica capillary was 61 cm (51 cm effective length to the detector window)×75 μm I.D. The sample was introduced into the capillary by a 5-s pressure injection of 0.5 p.s.i. and the temperature was set at 25°C (1 p.s.i.=6894.76 Pa). A negative voltage of −25 kV was applied for the separation and indirect spectrophotometric detection was performed at 214 nm.

The electrophoretic mobility of each analyte was determined by duplicate injections in an electrolyte composed of 2 mM SULSAL–0.5 mM OFM-OH, pH adjusted to 9.1 with ethanolamine. All standard injections for the setting up of the calibration curves were made in duplicates. Kinetic studies were con-ducted by repeated injections from the same sample vial filled with 500 μl of the solution of interest. Time-corrected areas were used for quantitative treatment of the data.

3. Results and discussion

3.1. Choice of the background electrolyte

In a previous study [9], pyromellitate was selected as the chromogenic probe because it shows no

Table 1
Characteristics of the studied sulfur species[a]

Sulfur species	Formal oxidation number	pK_a [25]	Effective mobility (pH 9.1) ($\cdot 10^{-5}$ cm^2 V^{-1} s^{-1})	Identified peaks of the electropherogram
Sulfide (S^{2-})	$-$II	6.99, 12.90	-66.3	S^{2-}, $S_2O_3^{2-}$, SO_3^{2-}, SO_4^{2-}
Thiosulfate ($S_2O_3^{2-}$)	$+$II	0.6, 1.72	-79.6	$S_2O_3^{2-}$, SO_4^{2-} +unknown
Tetrathionate ($S_4O_6^{2-}$)	$+$III1/2		-53.3	$S_4O_6^{2-}$, SO_4^{2-}
Dithionite ($S_2O_4^{2-}$)	$+$III	0.35, 2.45	$-$	$S_2O_3^{2-}$, SO_3^{2-}, SO_4^{2-}
Sulfite (SO_3^{2-})	$+$IV	1.89, 7.21	-66.5	SO_3^{2-}, SO_4^{2-}
Disulfite ($S_2O_5^{2-}$)	$+$IV		$-$	SO_3^{2-}, SO_4^{2-}
Sulfate (SO_4^{2-})	$+$VI	-3, 1.98	-73.8	SO_4^{2-}
Disulfate ($S_2O_7^{2-}$)	$+$VI		$-$	SO_4^{2-}
Peroxodisulfate ($S_2O_8^{2-}$)	$+$VII	<0, 0.9	-63.5	SO_4^{2-}, $S_2O_8^{2-}$

[a] The last column gives the identified peaks of the electropherogram of the corresponding species.

oxidising properties and its mobility lies in the middle-range of the sulfur species. In this study, SULSAL, the characteristics of which (mobility and molar absorptivity) are comparable with those of pyromellitate, was preferred because of its higher solubility when associated with OFM-OH as the electroosmotic flow modifier. The electrolyte pH was adjusted in order to optimise the overall separation.

3.2. Speciation

Several aqueous solutions of sulfur species were injected (Table 1). Some examples of electropherograms are given in Fig. 1. The injection of sulfate yields one single peak characteristic of the species.

The injections of the other species give a major peak and a number of minor peaks which correspond to their hydrolysis and/or oxidation products (see Table 1). For instance, the electropherogram of the injection of a thiosulfate standard solution shows a major peak that stands for this species as well as a minor peak of sulfate (ca. 1% in concentration) and another peak located in between. The electropherogram profile does not evolve in an hour time scale and it was supposed that sulfate and the unknown product occurred as impurities in the thiosulfate salt. Due to their relative small contributions, they were not corrected for in further quantitative analyses. Tetrathionate and peroxodisulfate were found to behave similarly.
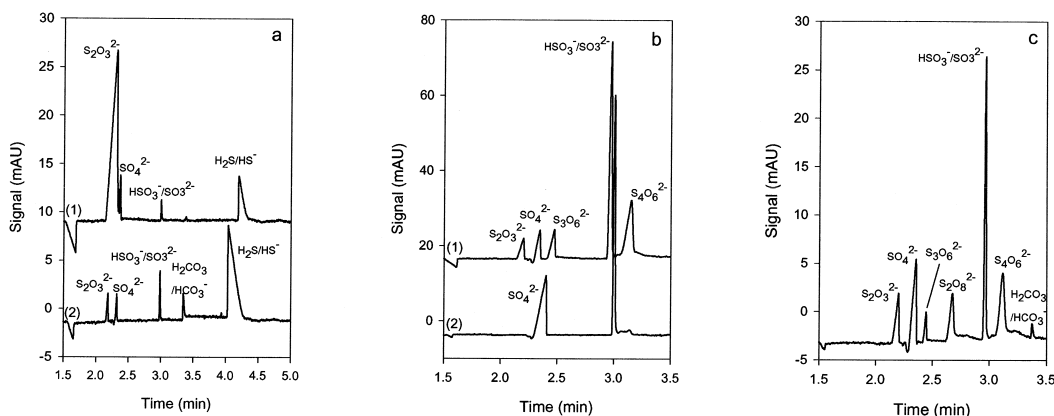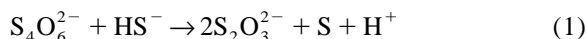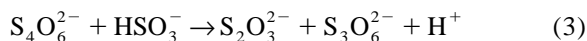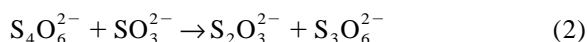

Fig. 1. Examples of electropherograms of sulfur species. Injection of (a) (1): $6 \cdot 10^{-4}$ *M* Na$_2$S$+3 \cdot 10^{-4}$ *M* Na$_2$S$_4$O$_6$, (2): $6 \cdot 10^{-4}$ *M* Na$_2$S; (b) (1): $6 \cdot 10^{-4}$ *M* Na$_2$SO$_3$$+3 \cdot 10^{-4}$ *M* Na$_2$S$_4$O$_6$, (2): $6 \cdot 10^{-4}$ *M* Na$_2$SO$_3$; (c) $5 \cdot 10^{-5}$ *M* Na$_2$S$_2$O$_3$$+10^{-4}$ *M* Na$_2$S$_4$O$_6$$+2 \cdot 10^{-4}$ *M* Na$_2$SO$_3$$+5 \cdot 10^{-5}$ *M* Na$_2$SO$_4$$+5 \cdot 10^{-5}$ *M* K$_2$S$_2$O$_8$. Analytical conditions: capillary: fused-silica 61 cm (51 cm effective length)$\times$75 μm I.D.; electrolyte: 2 m*M* SULSAL–0.5 m*M* OFM-OH, pH adjusted to 7.00 with Bis–Tris; injection: 0.5 p.s.i., 5 s; separation: applied voltage $-$25 kV, temperature 25°C; detection: indirect at 214 nm.

The injection of a sulfide standard solution yields four different peaks that correspond to sulfide, thiosulfate, sulfite and sulfate (Fig. 1a(2)). Their relative contributions are time-dependent: contrary to thiosulfate, sulfide undergoes fast oxidation in solution. A similar remark can be drawn for sulfite (Fig. 1b(2)). Condensed disulfite and disulfate ions are readily rehydrated in solution to give sulfite (and its oxidation product sulfate) and sulfate, respectively.

In aqueous solution, tetrathionate spontaneously reacts with a series of nucleophilic species, like sulfide and sulfite [16]. When added (in excess) to tetrathionate in the same standard solution, sulfide gives a modified distribution between the resulting species (Fig. 1a(1)). The peak of thiosulfate is increased while that of sulfide is decreased and that of tetrathionate totally disappears. A white precipitate can be observed in the solution that accounts for the formation of S(0). According to potential–pH equilibrium diagrams [17], sulfide and tetrathionate cannot coexist and it is supposed that $S_4O_6^{2-}$ splits into $S_2O_3^{2-}$ in its reaction with HS^- [18] according to:

$$S_4O_6^{2-} + HS^- \rightarrow 2S_2O_3^{2-} + S + H^+ \qquad (1)$$

A mixture of tetrathionate and sulfite yields quite a different electropherogram (Fig. 1b(1)). Both peaks of $S_4O_6^{2-}$ and HSO_3^-/SO_3^{2-} decreased simultaneously while the peak of $S_2O_3^{2-}$ increased and another peak appears after that of sulfate. This peak was assigned to trithionate ($S_3O_6^{2-}$) after the following reactions [19]:

$$S_4O_6^{2-} + SO_3^{2-} \rightarrow S_2O_3^{2-} + S_3O_6^{2-} \qquad (2)$$

$$S_4O_6^{2-} + HSO_3^- \rightarrow S_2O_3^{2-} + S_3O_6^{2-} + H^+ \qquad (3)$$

Reaction (3) was found to proceed several hundred times slower than reaction (2) at $0°C$ [20]. Given the experimental conditions of this study, it may be neglected in a first approach.

When SO_3^{2-} is in excess, reaction (2) occurs spontaneously and quantitatively [21] and, contrary to the kinetics of reaction (1), that of reaction (2) is slow enough to be followed by CE.

Fig. 1c shows the electropherogram of a mixture containing six separated sulfur species.

3.3. Quantification

Standard calibration curves were obtained for peroxodisulfate, sulfate, sulfite, tetrathionate, thiosulfate and sulfide. The main difficulty is the quantification of the unstable species sulfite and sulfide. Hydrolysis was fast enough, especially for sulfite, to alter the profile between the two electropherogram replicates of a same standard. In order to limit the alteration of the standards, the calibration curve for sulfite was established by preparing each dilute standard immediately prior to its injection. By doing so, the amount of sulfate produced did never exceed 50% of the total sulfite concentration.

The calibration curve for sulfite is established as follows: for each injection of sulfite standard, the concentration of sulfate produced by hydrolysis $[SO_4^{2-}]_{hyd}$ is calculated from the sulfate calibration curve, and the remaining sulfite concentration in solution $\{[SO_3^{2-}]+[HSO_3^-]\}$ is deduced from the original sulfite concentration $\{[SO_3^{2-}]+[HSO_3^-]\}_0$ according to: $\{[SO_3^{2-}]+[HSO_3^-]\}=\{[SO_3^{2-}]+[HSO_3^-]\}_0-[SO_4^{2-}]_{hyd}$.

Similarly, the calibration curve for sulfide is deduced from those of thiosulfate, sulfite, and sulfate to reach the effective sulfide concentration in solution: $\{[HS^-]+[H_2S]\}=\{[HS^-]+[H_2S]\}_0-2[S_2O_3^{2-}]_{hyd}-\{[SO_3^{2-}]+[HSO_3^-]\}_{hyd}-[SO_4^{2-}]_{hyd}$.

Linear calibration curves are obtained for all sulfur species (Fig. 2 and Table 2). Because of the intrinsic absorptivity of sulfide at the working wavelength,
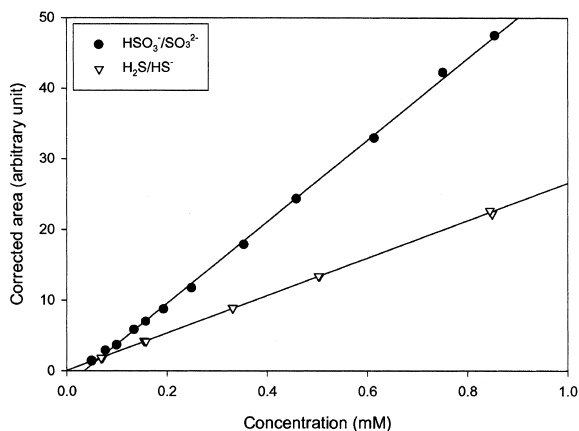

Fig. 2. Calibration curves and corresponding linear regressions for sulfite and sulfide.

Table 2
Parameters of the linear regression of the calibration curves {corrected area}=$b(0)+b(1)${concentration} and limits of detection (a) determined after the tetrathionate sulfitolysis monitoring in water and (b) determined after the tetrathionate sulfitolysis monitoring in the ephedrine matrix

Species	Range (mM)	$b(0)$	S.E. $b(0)$	$b(1)$	S.E. $b(1)$	r^2	LOD (μM)
$S_2O_8^{2-}$	0.05–0.3	-0.5	0.3	81.4	1.5	0.9973	5
SO_4^{2-}	0.05–0.2	0.02	0.05	78.7	0.4	0.9998	2.5
SO_3^{2-}	0.05–1.0	-2.0	0.2	57.7_5	0.5	0.9991	1.5
$S_4O_6^{2-}$	0.05–0.4	0.1	0.2	60.5	0.8	0.9988	5
$S_2O_3^{2-}$	0.05–0.4	0.2	0.1	56.5	0.6	0.9990	3
S^{2-}	0.1–1.0	0.05	0.08	26.5	0.2	0.9996	10
$S_3O_6^{2-}$ (a)	0.02–0.3	-0.5	0.3	78.8	1.3	0.9891	6
$S_3O_6^{2-}$ (b)	0.02–0.3	-1.1	0.3	78.9	1.2	0.9920	6

S.E.=Standard error.

reduced sensitivity is observed for this species, leading to a higher limit of detection (LOD) [9]. The linear regression for sulfite shows a significant negative intercept, that was first supposed to be due to an overestimation of the sulfite concentration in the standard solutions. This possible bias was investigated by first treating diluted sulfite standard solutions with an excess of hydrogen peroxide to convert sulfite to sulfate to completeness. The measured sulfate concentrations compared well with the supposed sulfite concentrations. Identical calibration curves in alkaline (10^{-4} M NaOH) and acidic (10^{-3} M HCl) media indicated that the possible degassing of SO_2 from sulfite solutions was to be excluded. Finally, no evident explanation could be found for this shift.

LODs, estimated as three times the short-term noise, are in the low- to mid-μM range, except for sulfide (LOD=10^{-5} M) that shows a broader and asymmetric peak.

3.4. Kinetics monitoring

The kinetics of reaction (2) was followed by capillary electrophoresis. Three different media were investigated: acidic (10^{-2} M lactic acid, initial pH 3.2), slightly alkaline (water, initial pH 8.3, final pH 7.3), alkaline (10^{-2} M 1-ephedrine, initial pH 10.8, final pH 10.5). Sulfite and tetrathionate initial concentrations were set to ca. $6 \cdot 10^{-4}$ M and $3 \cdot 10^{-4}$ M, respectively. Sulfite, tetrathionate, and thiosulfate concentrations were calculated according to the standard calibration curves. They are reported as a

function of time in Fig. 3. Sulfate concentration is also displayed to evaluate the competitive oxidation processes.

In acidic conditions, HSO_3^- predominates over SO_3^{2-} and only reaction (3) should possibly occur. In fact, reaction (3) is too slow compared with SO_2 degassing and only the latter can be observed through the decrease of sulfite concentration. The concentration of sulfate is steady and indicates that no oxidation takes place under these conditions.

The concentration profiles are quite similar in both other media. Sulfite and tetrathionate concentrations show a simultaneous decrease that is balanced by the increase of the thiosulfate concentration. Reaction (2) was supposed to proceed with second-order kinetics:

$$\frac{d[S_2O_3^{2-}]}{dt} = k[S_4O_6^{2-}][SO_3^{2-}] \qquad (4)$$

that is solved to:

$$kt = \frac{1}{[SO_3^{2-}]_0 - [S_4O_6^{2-}]_0}$$
$$\cdot \ln \frac{[S_4O_6^{2-}]_0([SO_3^{2-}]_0 - [S_2O_3^{2-}])}{[SO_3^{2-}]_0([S_4O_6^{2-}]_0 - [S_2O_3^{2-}])} \qquad (5)$$

where k is the rate constant of the reaction and $[S_4O_6^{2-}]_0$ and $[SO_3^{2-}]_0$ are the initial concentrations of tetrathionate and sulfite, respectively.

Parameter k is determined by plotting $d[S_2O_3^{2-}]/dt$ as a function of $[S_4O_6^{2-}][SO_3^{2-}]$; the initial concentrations $[S_4O_6^{2-}]_0$ and $[SO_3^{2-}]_0$ are obtained by the mean values of $([S_4O_6^{2-}]+[S_2O_3^{2-}])$ and
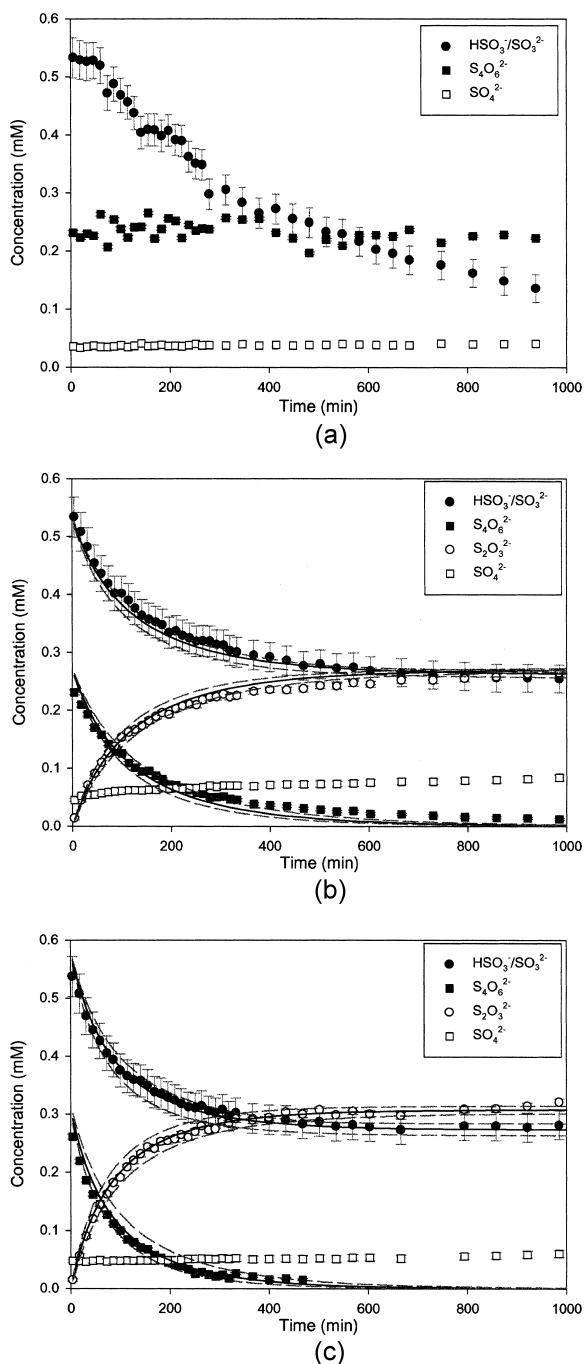
Fig. 3. Time-course monitoring of the concentrations of sulfite, tetrathionate, thiosulfate and sulfate in the frame of reaction (2). Sulfite and tetrathionate initial concentrations were set to ca. $6 \cdot 10^{-4}$ M and $3 \cdot 10^{-4}$ M, respectively. (a) In lactic acid (pH~3.2), (b) in water (pH~8), (c) in ephedrine (pH~10.5).

($[SO_3^{2-}] + [S_2O_3^{2-}]$), respectively. The results are collected in Table 3 and the calculated time-course curves of concentrations are displayed in Fig. 3. The two dashed curves on both sides of each calculated curve correspond to the upper and lower limits at a 95% confidence level for k, $[S_4O_6^{2-}]_0$, and $[SO_3^{2-}]_0$. The deduced k values are close to that obtained by Von Foerster and Centner [21], $k = 1.03 \cdot 10^{-2}$ mM^{-1} min^{-1}, even though the latter was determined at 0°C. It is observed that the calculated curves satisfactorily fit the experimental data, although there seems to be some bias when reaction (2) proceeds in water. As already observed [20,22], the rate of reaction (2) decreases with acidity. This difference in the rate constant as well as the observed bias in water was assigned to the occurrence of HSO_3^- in concentration that can no longer be neglected at the pH of the experiment (especially at the longest reaction times for which the pH had dropped to 7.3). As a consequence, the reaction reverse to reaction (2) may no longer be neglected; the occurrence of a remaining concentration of tetrathionate even after a long time-period seems to confirm the existence of a metastable equilibrium between the four species. Side reaction between tetrathionate and thiosulfate produced via reaction (2) may also possibly play a part in chain-lengthening of the polythionate [23,24]. Foss and Kringlebotn [25] have found a rate constant of ca. 78 mM^{-1} min^{-1} (pH 6.8, $T = 25$°C) for the reaction $S_4O_6^{2-} + S_2O_3^{2-} \rightarrow SO_3^{2-} + S_5O_6^{2-}$ that lies to the right-hand side all the more so as the formation of hydrogensulfite removes sulfite from the medium.

Calibration curves for trithionate can be deduced in both media by plotting the time-corrected area of the corresponding peak as a function of the calculated concentration of thiosulfate, which is equal to that of trithionate, except for competitive reactions (Fig. 4). Regression parameters are given in Table 2. The two calibration curves are statistically parallel but different, with a shift of less than 4%.

4. Conclusions

CE was successfully applied to the separation and the quantification of several sulfur species in aqueous solution. Calibration curves were linear for all the

Table 3
Parameters of the kinetics of reaction (2) according to Eq. (5)

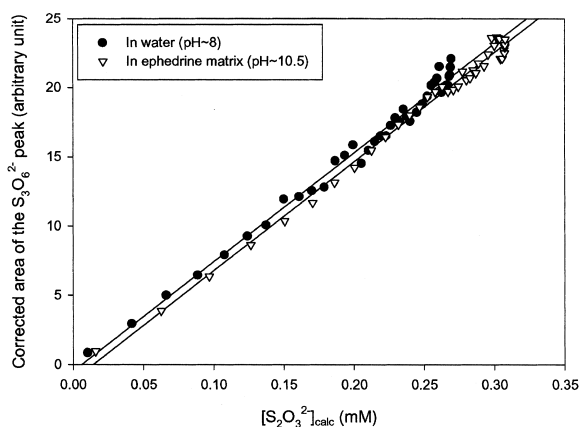| Medium	$[S_4O_6^{2-}]_0$ (mM)	S.E. $[S_4O_6^{2-}]_0$	$[SO_3^{2-}]_0$ (mM)	S.E. $[SO_3^{2-}]_0$	k (mM^{-1} min^{-1})	S.E. k
Water 7.3<pH<8.3	0.270	0.001	0.533	0.002	$1.82 \cdot 10^{-2}$	$0.11 \cdot 10^{-2}$
Ephedrine 10^{-2} M 10.5<pH<10.8	0.308	0.003	0.581	0.002	$2.31 \cdot 10^{-2}$	$0.19 \cdot 10^{-2}$

Fig. 4. Trithionate calibration curves deduced from the kinetic studies of the rearrangement of tetrathionate with sulfite in two different media.

investigated species, including the unstable sulfite and sulfide species, for which the calibration curves were deduced from those of their hydrolysis/oxidation products.

Because of its interesting separation characteristics, this technique was also valuable to monitor the time-dependent concentrations of the reactants and products of the sulfitolysis of tetrathionate. Reaction rate constants could be deduced and are in good agreement with values from the literature.

References

[1] M.B. Goldhaber, Am. J. Sci. 238 (1983) 193.
[2] A.E. Giblin, R.W. Horwarth, Lumnol. Oceanogr. 29 (1984) 47.
[3] H. Fossing, B.B. Jorgensen, Geochim. Cosmochim. Acta 54 (1990) 2731.
[4] K.K. Verma, A.K. Gulati, Analusis 9 (1981) 506.
[5] G. Bondoux, P. Jandik, R. Jones, Spectra 2000 158 (1991) 47.
[6] K. Fukushi, S. Takeda, K. Chayama, S.-I. Wakida, J. Chromatogr. A 834 (1999) 349.
[7] J. Font, J. Gutiérez, J. Lalueza, X. Pérez, J. Chromatogr. A 740 (1996) 125.
[8] D.R. Salomon, J. Romano, J. Chromatogr. 602 (1992) 219.
[9] S. Motellier, K. Gurdale, H. Pitsch, J. Chromatogr. A 770 (1997) 311.
[10] B. Tenberken, P. Ebert, M. Hartmann, M. Kibler, A. Mainka, T. Prokop, A. Röder, K. Bächmann, J. Chromatogr. A 745 (1996) 209.
[11] F. Hissner, J. Mattusch, K. Heinig, J. Chromatogr. A 848 (1999) 503.
[12] W.H. Matchett, W. Winnik, L.O. Betowski, W.C. Brumley, Electrophoresis 18 (1997) 205.
[13] G. Dinelli, A. Vicari, A. Bonetti, P. Catizone, J. Agric. Food Chem. 45 (1997) 1940.
[14] R.A. Walker, D.G. Marangoni, T. Smith-Palmer, Can. J. Chem. 77 (1999) 227.
[15] A. Hilmi, J.H.T. Luong, A.-L. Nguyen, Chemosphere 36 (1998) 3137.
[16] M. Schmidt, in: A. Senning (Ed.), Sulfur in Organic and Inorganic Chemistry, Vol. 2, Marcel Dekker, New York, 1972, p. 106.
[17] M. Pourbaix, A. Pourbaix, Geochim. Cosmochim. Acta 56 (1992) 3157.
[18] H.B. Van der Heidge, Rec. Trav. Chim. 72 (1953) 510.
[19] Gmelin Handbuch der Anorganischen Chemie, Vol. 9B2, Verlag Chemie, Weinheim, 1960, p. 1007.
[20] Von F. Foerster, K. Centner, Z. Anorg. Allg. Chem. 157 (1926) 45.
[21] A. Kurtenacker, M. Kaufmann, Z. Anorg. Chem. 148 (1925) 225.
[22] H. Stamm, M. Goehring, Z. Anorg. Chem. 242 (1939) 413.
[23] A. Fava, S. Bresadola, J. Am. Chem. Soc. 77 (1955) 5792.
[24] O. Foss, I. Kringlebotn, Acta Chem. Scand. 15 (1961) 1608.
[25] L.G. Sillen, Stability Constants of Metal–Ion Complexes, Special Publication No. 17, Chemical Society, London, 1964.