



ELSEVIER

Journal of Chromatography A, 879 (2000) 235–243

JOURNAL OF
CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Capillary electrophoretic determination of thiosulfate and its oxidation products

A. Padarauskas^{a,*}, V. Paliulionyte^a, R. Ragauskas^b, A. Dikčius^b^aDepartment of Analytical and Environmental Chemistry, Vilnius University, Naugarduko 24, LT-2006 Vilnius, Lithuania^bInstitute of Chemistry, A. Gostauto 9, LT-2600 Vilnius, Lithuania

Received 2 December 1999; received in revised form 7 March 2000; accepted 7 March 2000

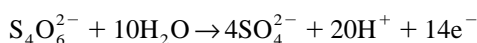
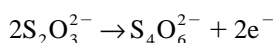
Abstract

Capillary electrophoresis (CE) was developed for the rapid and simple determination of thiosulfate and its oxidation products such as common polythionates, sulfite and sulfate. Direct and indirect UV detection techniques were investigated. The optimized separations of UV absorbing $S_2O_3^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$ and $S_6O_6^{2-}$ anions were carried out in 5 mmol l⁻¹ (NH₄)₂SO₄, 5 mmol l⁻¹ KH₂PO₄ electrolyte at pH 5.0, with direct UV detection at 214 nm. All analytes were well resolved in less than 4 min. Analysis of $S_2O_3^{2-}$, $S_4O_6^{2-}$, SO_4^{2-} and SO_3^{2-} ions can be performed in 5 mmol l⁻¹ H₂CrO₄, 1 mmol l⁻¹ hexamethonium hydroxide electrolyte neutralized with triethanolamine to pH 8.0, using indirect UV detection at 254 nm. However, the detection sensitivity for tetrathionate was poor. Other polythionates can not be detected at all because of their high absorbance even at 254 nm. The developed CE method was applied for the monitoring of sulfur species in spent fixing solutions during the electrolytic oxidation. © 2000 Elsevier Science B.V. All rights reserved.

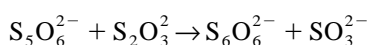
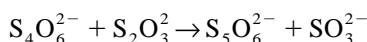
Keywords: Thiosulfate; Inorganic anions; Sulfur compounds

1. Introduction

Large amounts of thiosulfate and $Ag(S_2O_3)_2^{3-}$ anions are present in spent fixing baths. Silver from such solutions is usually recovered electrolytically [1]. In order to minimize unwanted environmental contamination the conversion of thiosulfate to sulfate is necessary. In recent years various anodic oxidation techniques were investigated for this purpose [1–3]. Anodic oxidation of thiosulfate was shown to yield at first tetrathionate and then sulfate, according to the following reactions:



However, sulfur chemistry is complex [4], and intermediates formed in the redox reaction can react with either the starting materials or themselves to yield a number of related products. For example, the tetrathionate formed above can undergo further reaction with the unreacted thiosulfate to yield higher polythionates according to the following equations [5]:



*Corresponding author. Fax: +370-2-630-987.

E-mail address: audrius.padarauskas@chf.vu.lt (A. Padarauskas).

The main problem in the optimization of oxidation procedure is the rapid and simple monitoring of sulfur species, especially polythionates, formed during the oxidation process. The many published papers on analytical methods for polythionate solutions are deficient to various degrees in ability to separate each anion, sensitivity, and simplicity and rapidity of the procedures. Published methods were based mainly on cyanolysis or sulfitolysis of polythionates to form thiocyanate and/or thiosulfate ions which are measured spectrophotometrically [6–8]. In order to determine each species, the authors proposed rather complicated procedures involving, for example, temperature or pH controls, catalytic reaction, and reaction time control. Because the time involved in these procedures is long, the stability of the analytes from the beginning to the end of analysis is in doubt. An alternative basis, the electrochemical behavior of polythionates, was described by several authors [9–11]. However, the polarographic analysis of polythionates is difficult because of their overlapping half-wave potentials. In 1970 Karchmer wrote [12] “There appears to be no satisfactory methods for the determination individual polythionates in the presence of each other.”

In the last two decades different high-performance liquid chromatography (HPLC) techniques were investigated for the separation of common polythionates [13–16]. However, these methods have a lack of selectivity, especially when concentrations of the analytes differ significantly and/or when samples with complicated matrix are analyzed.

In recent years the use of capillary electrophoresis (CE) for the analysis of ionic analytes has grown significantly. The most attractive features of this technique are high resolution, short analysis times, flexibility, ease of implementation, automation capability and low running costs [17]. Several applications of CE were reported for the determination of inorganic sulfur species such as thiosulfate, sulfide, sulfite, sulfate and thiocyanate [18–22] in various aqueous samples but the separation of polythionates was not studied.

In this work CE was investigated for the rapid determination of thiosulfate and its possible oxidation products including common polythionates. The method was applied for the monitoring of sulfur species in spent fixing solutions during the oxidation process.

2. Experimental

2.1. Instrumentation

Separations were performed on a P/ACE 2100 apparatus (Beckman Instruments, Fullerton, CA, USA) equipped with a UV detector with wavelength filters (200, 214, 230 and 254 nm). Fused-silica capillaries (Polymicro Technology, Phoenix, AZ, USA) of 57 cm (50 cm to the detector) \times 75 μ m I.D. were used. The solutes were injected in the hydrodynamic mode by overpressure ($3.43 \cdot 10^3$ Pa, 6 s). System Gold software was used for data acquisition. All experiments were conducted at 25°C.

The oxidation experiments were performed on P-5848 potentiostat (Russia) with flat carbon fiber anode (3.14 cm²). The counterelectrode was a Ti plate (ca. 1 dm²) located in a compartment connected to the working chamber (52 ml) by a cation-exchange membrane.

2.2. Reagents and solutions

All solutions, electrolytes and standards were prepared with ultra-pure water from a Milli-Q system (Millipore, Eschborn, Germany). The sulfur anion standard solutions were prepared from sodium thiosulfate, sodium hydrogen sulfite and sodium sulfate. Thiosulfate and sulfite stock solutions (0.01 mol l⁻¹) were prepared and standardized following the procedures described in Ref. [23]. Working standard solutions were prepared every day in degassed water.

Potassium tetrathionate was purchased from Merck (Darmstadt, Germany). The method described in Ref. [24] was used for the preparation of potassium penta- and hexathionates. Purity of these reagents was checked by chemical analysis [4]. K₂S₅O₆ · 1.5H₂O and K₂S₆O₆ salts were 96.5% and 83.0% pure, respectively. Working standard solutions of polythionates were prepared daily in degassed water.

Triethanolamine (TrEA) was purchased from Sigma (St. Louis, MO, USA). Chromium acid solution (0.1 mol l⁻¹) was prepared by dissolving of CrO₃ (Merck) in water. Tetradecyltrimethylammonium hydroxide (TTAOH) (Merck) and 1,6-bis(trimethylammonium)hexane (Aldrich, Milwaukee, WI, USA) hydroxide were prepared from

bromide salts by conversion using an OH^- form anion-exchange material ARA-12P (Reachim, Russia).

2.3. Procedures

Each day before starting the analysis, the capillary was rinsed with 0.1 mol l^{-1} NaOH and water for 5 min, followed by the used carrier electrolyte for 10 [without electroosmotic flow (EOF) reduction] or 40 min. Between all electrophoretic separations the capillary was rinsed for 2 min with carrier electrolyte. All electrolyte solutions were filtered through a $0.45\text{-}\mu\text{m}$ nylon 66 membrane filter (Supelco, Bellefonte, PA, USA) and degassed by ultrasonication.

Oxidation of thiosulfate was carried out at a constant potential of 1.0 V vs. the standard hydrogen electrode.

3. Results and discussion

3.1. CE with direct UV detection

As mentioned above, the electrolytic oxidation of thiosulfate yields tetrathionate, sulfate and probably higher polythionates $\text{S}_x\text{O}_6^{2-}$ ($x=5, 6$). Thiosulfate and polythionates have relatively strong UV absorbance and this enables the use of more selective direct detection at 214 nm. The choice of carrier electrolyte is extremely important to the success of any CE analysis. An electrolyte optimal for common inorganic anions must have an anion with electrophoretic mobility closely matched to that of the anions of interest if a high-resolution separation is to occur. The electrophoretic mobilities of thiosulfate and higher polythionates differ significantly. For this reason we have chosen a mixed sulfate–phosphate electrolyte with a medium mobility and relatively high buffering capacity over the wide pH range. Thiosulfate is known to decompose in acidic media to elemental sulfur, hydrogen sulfide, and polythionic acids ($\text{H}_2\text{S}_x\text{O}_6$) [12], with subsequent volatilization of H_2S and SO_2 . Therefore, all CE separations were performed in the pH range above 5. In order to reduce the analysis time, the EOF needs to be reduced or reversed to allow the detection all fast and slow anions. Alkyl ammonium salts have been

documented for most CE applications requiring reduction or reversal of EOF [25].

Preliminary investigations were performed using 0.2 mmol l^{-1} TTAOH as EOF-modifier in 5 mmol l^{-1} KH_2PO_4 and 5 mmol l^{-1} $(\text{NH}_4)_2\text{SO}_4$ electrolyte at pH 6.5. However, this electrolyte resulted in very broadened and a poorly shaped peaks of polythionates. Consequently, the accurate quantification of these analytes is impossible under these conditions. The variation of electrolyte pH in the range 5–10 does not improve the peak shapes. Likely, such peak broadening is caused by the formation of neutral ion-pairs between polythionate anions and TTA^+ used as EOF-modifier. For this reason we substituted TTAOH with slightly hydrophobic 1,6-bis(trimethylammonium)hexane (hexamethonium) hydroxide, a C_6 alkyl diquaternary ammonium salt that has higher solubility and lower tendency to form ion-pairs [26]. The peak efficiency of the polythionates in this case significantly increases but the peak of hexathionate anion remains relatively broad. Consequently, all further separations of thiosulfate and polythionates were performed in the electrolyte at pH 5 without EOF-modifier. Due to the slow EOF at this pH its reduction is not necessary.

The electropherograms obtained under optimum conditions for a standard thiosulfate solution at 1 h (a), 3 h (b) and 6 h (c) anodic oxidation process run time are shown in Fig. 1. As can be seen, the major oxidation product is tetrathionate, but some $\text{S}_5\text{O}_6^{2-}$ and $\text{S}_6\text{O}_6^{2-}$ are also formed during the electrolysis. All analytes are well resolved in less than 4 min. In comparison, these analytes can be separated by HPLC in ~ 20 min with very low efficiency [16].

3.2. CE with indirect UV detection

Using the anodic oxidation procedure thiosulfate must be completely converted to sulfate. Consequently, the change in the sulfate concentration also should be monitored during the decomposition procedure. Moreover, according to the reactions given in introduction section sulfite can be formed in such solutions. However both sulfate and sulfite have no UV absorbance. For this reason, indirect UV detection technique was also investigated for the determination of thiosulfate and its oxidation products.

Indirect UV detection in CE is a universal tech-

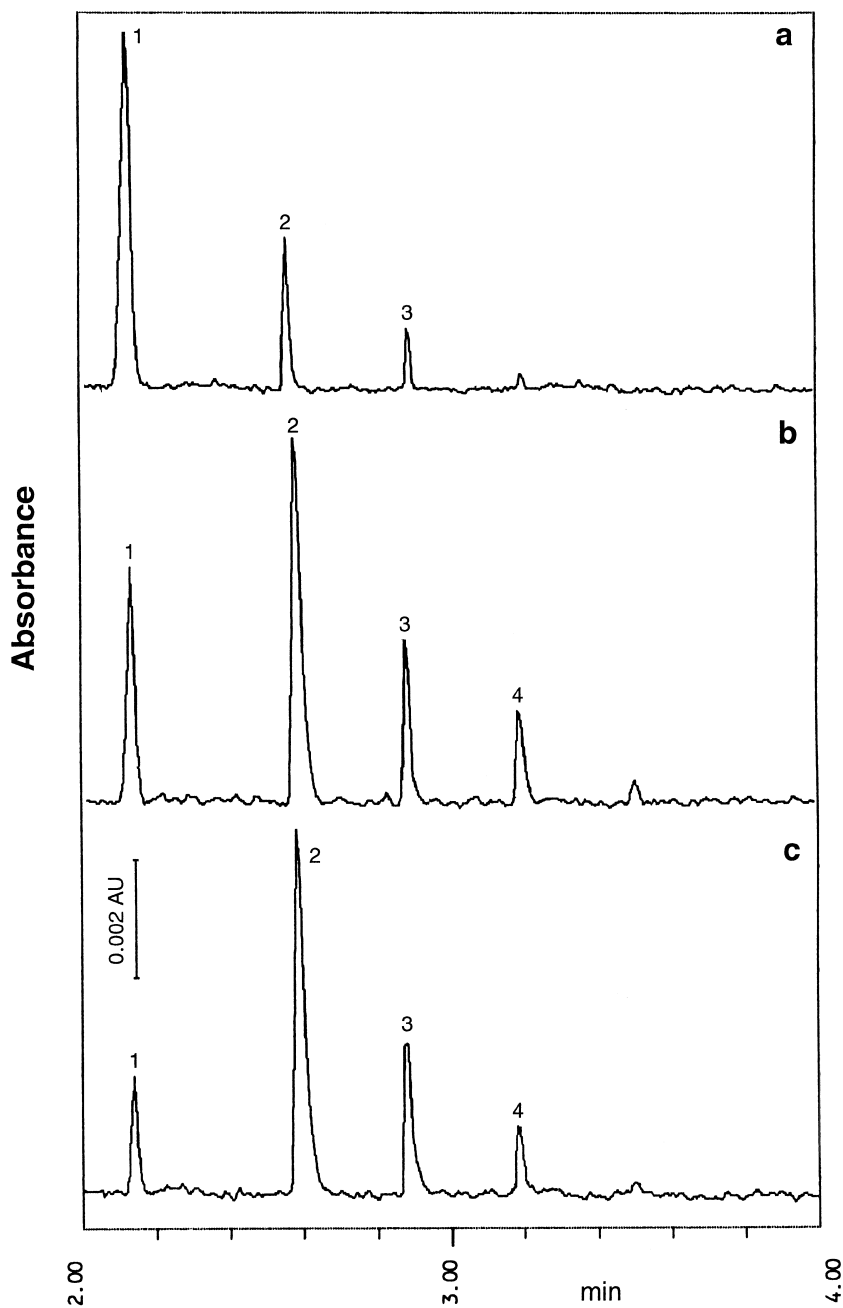


Fig. 1. Electropherograms obtained under optimum conditions for a 0.025 mol l^{-1} standard thiosulfate solution (dilution 1:50) at 1 h (a), 3 h (b) and 6 h (c) anodic oxidation process run time. Electrolyte, $5 \text{ mmol l}^{-1} \text{ KH}_2\text{PO}_4$, $5 \text{ mmol l}^{-1} (\text{NH}_4)_2\text{SO}_4$, pH 5.0; capillary, 57 cm (effective length 50 cm) \times 75 μm ; voltage, -30 kV ; direct UV detection at 214 nm. Peaks: 1 = $\text{S}_2\text{O}_3^{2-}$; 2 = $\text{S}_4\text{O}_6^{2-}$; 3 = $\text{S}_5\text{O}_6^{2-}$; 4 = $\text{S}_6\text{O}_6^{2-}$.

nique to detect non-absorbing ions which requires the presence of a chromophoric co-ion in the carrier electrolyte providing a background signal. Two different UV chromophores were studied: chromate with a high electrophoretic mobility [27] and 1,2-dihydroxybenzene-3,5-disulfonate (Tiron) as a representative of UV chromophores with lower mobility

[28]. Both chromophores at 5 mmol l^{-1} concentration (1 mmol l^{-1} hexamethonium hydroxide, pH 8.0, detection at 254 nm) were compared regarding to the peak shapes obtained for the analytes. However, only $\text{S}_2\text{O}_3^{2-}$, SO_4^{2-} , SO_3^{2-} and $\text{S}_4\text{O}_6^{2-}$ anions were detected with both electrolytes. Moreover, the detection sensitivity for $\text{S}_4\text{O}_6^{2-}$ was poor. Other

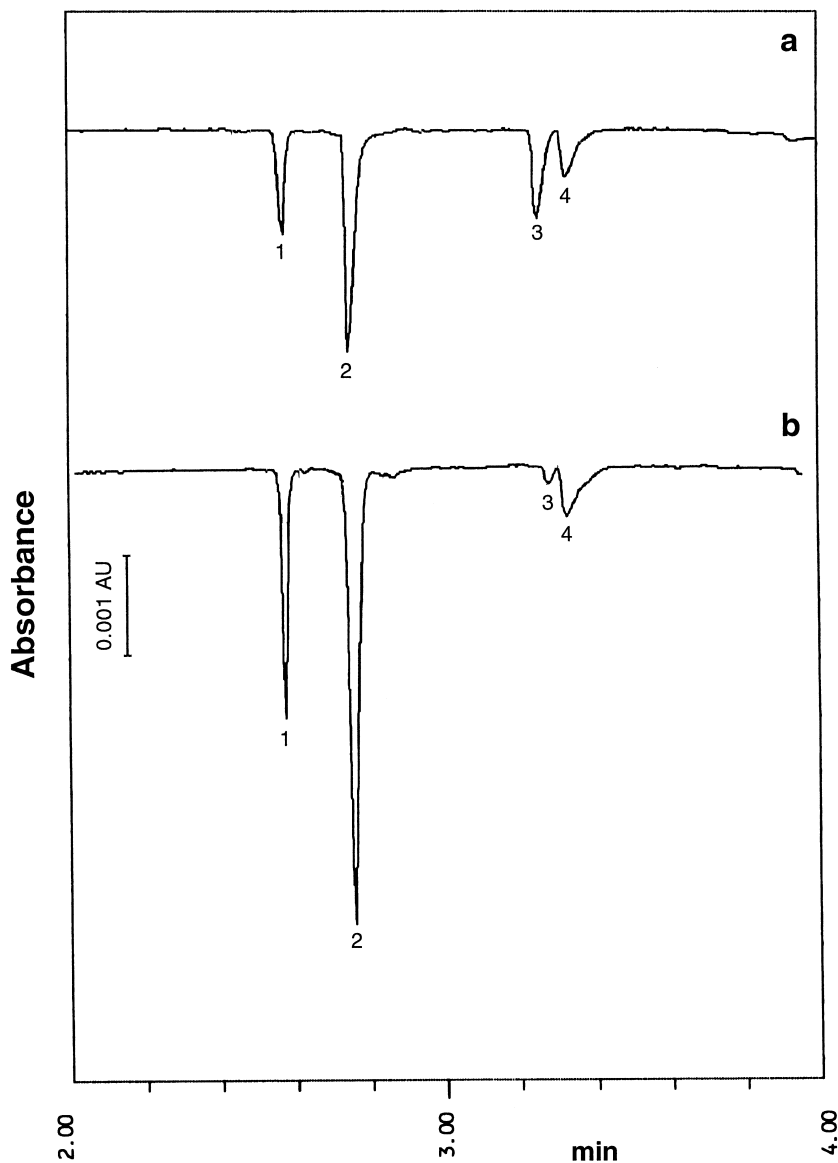


Fig. 2. Electropherograms of a standard ($1 \cdot 10^{-4} \text{ mol l}^{-1}$) anion mixture (a) and 0.025 mol l^{-1} standard thiosulfate solution (dilution 1:50) at 3 h anodic oxidation process run time (b). Electrolyte, $5 \text{ mmol l}^{-1} \text{ H}_2\text{CrO}_4$, 1 mmol l^{-1} hexamethonium hydroxide, pH 8.0 with triethanolamine; indirect UV detection at 254 nm; other conditions as in Fig. 1. Peaks: 1= $\text{S}_2\text{O}_3^{2-}$; 2= SO_4^{2-} ; 3= SO_3^{2-} ; 4= $\text{S}_4\text{O}_6^{2-}$.

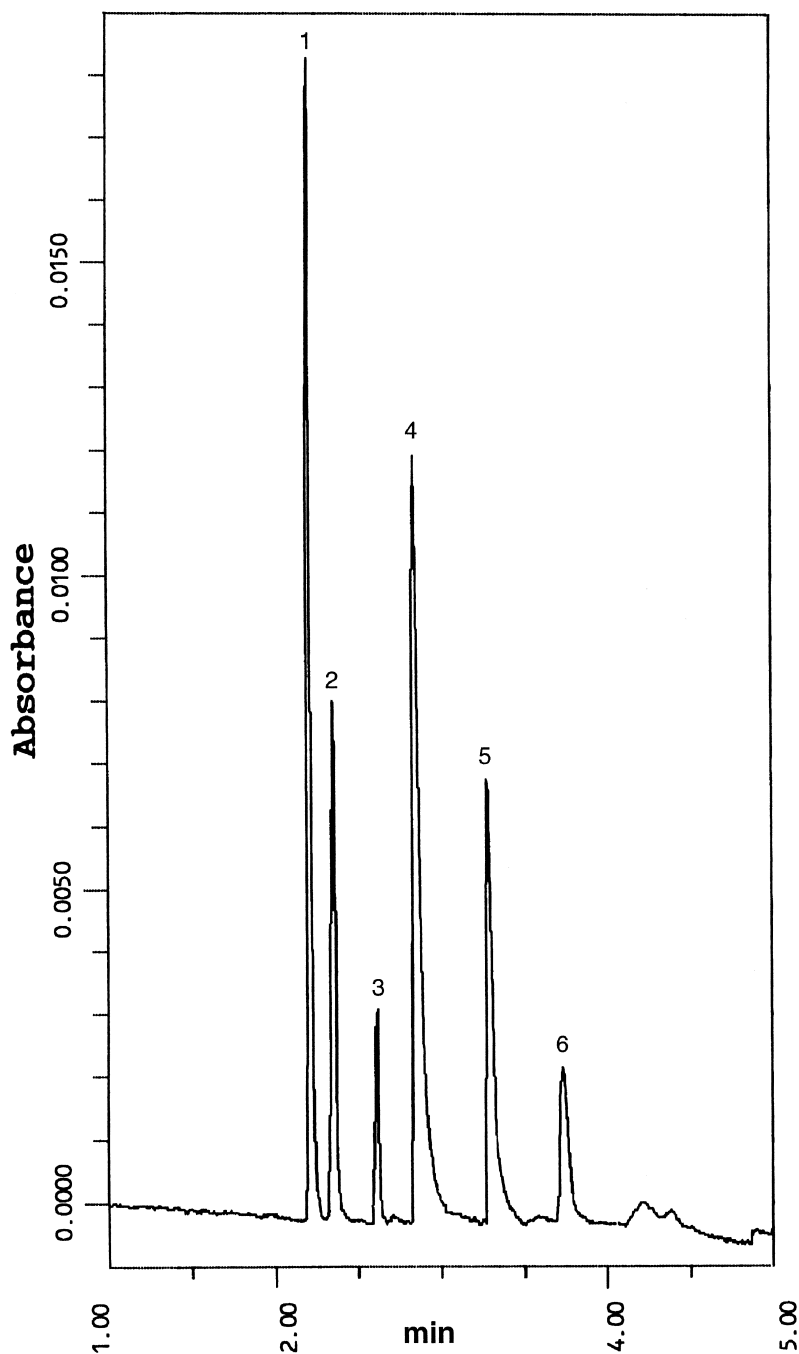


Fig. 3. Electropherogram of 1:200 diluted spent fixing solution sample at 10 h anodic oxidation process run time. Electrolyte, 5 mmol l⁻¹ TBAAc, 5 mmol l⁻¹ (NH₄)₂SO₄, pH 5.0; other conditions as in Fig. 1. Peaks: 1=S₂O₃²⁻; 2=Br⁻; 3=NO₃⁻; 4=S₄O₆²⁻; 5=S₅O₆²⁻; 6=S₆O₆²⁻.

polythionates can not be detected at all because of their high UV absorbance even at 254 nm. Consequently, indirect detection technique can be successfully used only for the determination of $S_2O_3^{2-}$, SO_4^{2-} and SO_3^{2-} anions. Using sodium chromate electrolyte better peak shapes were obtained for all detected anions. Therefore chromate was used for further investigations.

The main disadvantage of sodium chromate elec-

trolyte commonly used in most publications is low (or any) buffering capacity causing pH fluctuations resulting from electrolysis by the separation voltage [29]. That causes changes in the selectivity, problems with reproducibility of migration times and peak areas, and poor baseline stability. Therefore TrEA was added to the carrier electrolyte as the counteranion (instead of sodium) by neutralization a solution of chromic acid with TrEA to pH 8.0. This amine

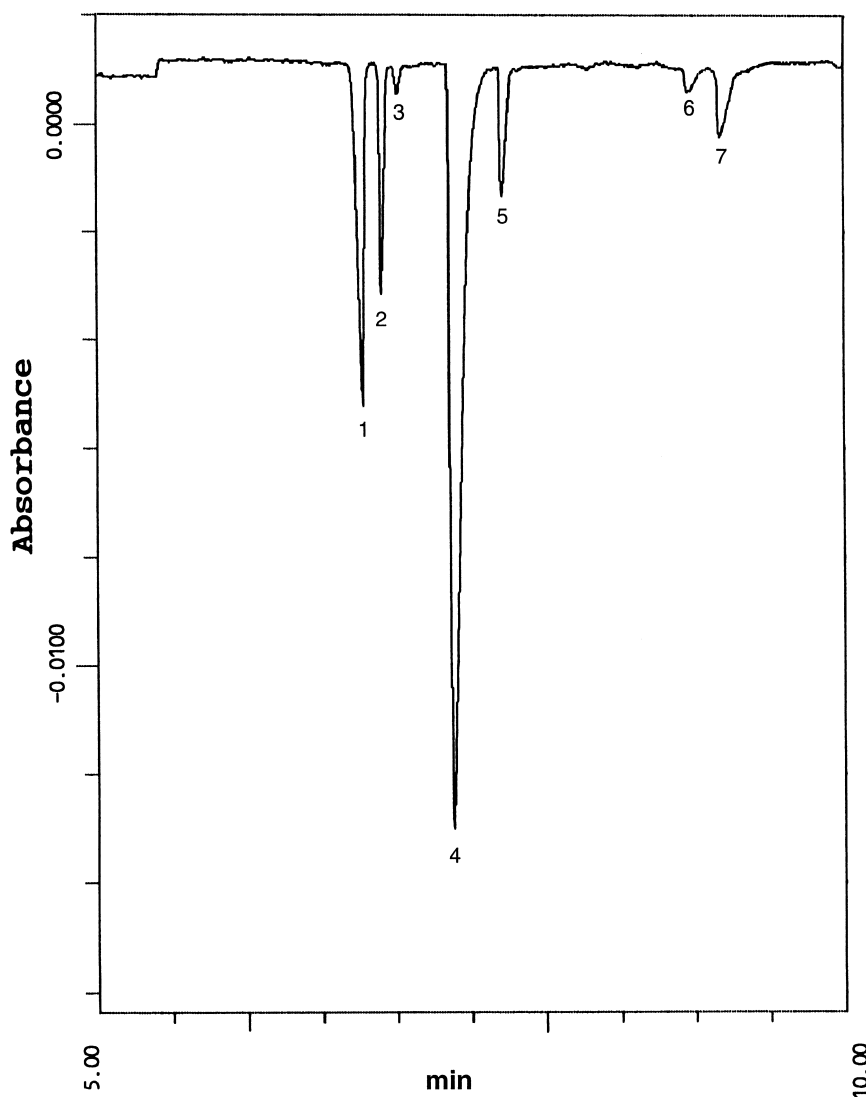


Fig. 4. Electropherogram of 1:200 diluted spent fixing solution sample at 10 h anodic oxidation process run time. Electrolyte, 5 mmol l^{-1} H_2CrO_4 , 1 mmol l^{-1} hexamethonium hydroxide, pH 8.0 with triethanolamine; capillary, 87 cm (effective length 80 cm) \times 75 μm ; other conditions as in Fig. 2. Peaks: 1 = $S_2O_3^{2-}$; 2 = Br^- ; 3 = Cl^- ; 4 = SO_4^{2-} ; 5 = NO_3^- ; 6 = SO_3^{2-} ; 7 = $S_4O_6^{2-}$.

($pK_a=7.9$) has a good buffering capacity in the pH range 7–9 and significantly improves reproducibility of the system.

Fig. 2 shows the electropherograms for a standard $S_2O_3^{2-}$, SO_4^{2-} , SO_3^{2-} and $S_4O_6^{2-}$ solution (a) and for 3 h oxidized standard $S_2O_3^{2-}$ solution (b) obtained by indirect UV detection. Only a very small amount of SO_3^{2-} is detected in the oxidized thiosulfate solution. Since in the real samples sulfite was not stabilized with formaldehyde, such results possibly may be explained by the higher tendency of sulfite to further oxidation with air oxygen.

3.3. Analytical performance

For the assessment of the efficiency of the developed CE systems with direct and indirect detection modes the repeatability (in terms of relative standard deviation, RSD), limit of detection (LOD) and linearity of calibration was determined. Repeatability experiments were performed by making five consecutive runs with standard solutions containing $2 \cdot 10^{-4}$ mol l^{-1} of each anion. The RSDs of migration times and peak areas were in the range from 0.4% for SO_4^{2-} to 1.5% for SO_3^{2-} and from 1.8% for $S_2O_3^{2-}$ to 6.8% for SO_3^{2-} , respectively. The

significantly higher peak area RSD value for SO_3^{2-} probably can be explained by the higher oxidation ability for this analyte.

The detection limits for a signal-to-noise ratio of 3 and 10 s hydrodynamic injections were in the range from $8.0 \cdot 10^{-7}$ mol l^{-1} for $S_4O_6^{2-}$ (direct UV detection) to $8.4 \cdot 10^{-6}$ mol l^{-1} for SO_3^{2-} . The calibration curves were linear in the concentrations ranges $1.0 \cdot 10^{-5}$ – $1.0 \cdot 10^{-3}$ mol l^{-1} for $S_2O_3^{2-}$ and SO_4^{2-} , $1.0 \cdot 10^{-5}$ – $5.0 \cdot 10^{-4}$ mol l^{-1} for $S_5O_6^{2-}$ and $S_6O_6^{2-}$, $1.0 \cdot 10^{-5}$ – $6.0 \cdot 10^{-4}$ mol l^{-1} for $S_4O_6^{2-}$ and $2.0 \cdot 10^{-5}$ – $1.0 \cdot 10^{-3}$ mol l^{-1} for SO_3^{2-} with correlation coefficients ($n=5$) ranging from 0.995 to 0.999.

3.4. Analysis of real samples

The optimized CE systems were applied to the monitoring of sulfur species in spent fixing solutions during the electrolytic oxidation. Large amounts of UV absorbing bromide anions are also present in such solutions. Investigation of Br^- interferences showed, that using both detection techniques thiosulfate partially comigrates with bromide. To avoid such interferences, potassium phosphate in the electrolyte was changed with tetrabutylammonium acetate (TBAAC). In the CE analysis with indirect UV

Table 1
Determination of sulfur anions in spent fixing solution at different oxidation process run times ($n=3$)

Oxidation run time (h)	Analyte	Found (mmol l^{-1})	Added (mmol l^{-1})	Found total (mmol l^{-1})	Recovery (%)
10	$S_2O_3^{2-}$	120	50.0	169	98.0
	$S_4O_6^{2-}$	38.8	50.0	86.6	97.2
	$S_5O_6^{2-}$	11.4	10.0	20.8	94.0
	$S_6O_6^{2-}$	6.22	10.0	15.4	91.8
	SO_4^{2-}	180	100	282	102
20	$S_2O_3^{2-}$	52.4	50.0	102	99.2
	$S_4O_6^{2-}$	24.1	20.0	45.1	105
	$S_5O_6^{2-}$	3.16	5.00	7.90	94.8
	$S_6O_6^{2-}$	1.25	1.00	2.19	94.0
	SO_4^{2-}	260	100	363	103
30	$S_2O_3^{2-}$	9.55	10.0	19.7	101.5
	$S_4O_6^{2-}$	13.2	10.0	23.0	98.0
	$S_5O_6^{2-}$	2.10	2.00	4.02	96.0
	$S_6O_6^{2-}$	NF ^a	5.00	4.76	95.2
	SO_4^{2-}	320	100	419	99.0

^a Not found.

detection a longer capillary (80 cm to the detector) was used. Both these modifications significantly improve the resolution between $S_2O_3^{2-}$ and Br^- without any deterioration of the separation selectivity of other analytes studied.

Fig. 3 shows the electropherogram obtained for a 1:200 diluted spent fixing solution sample at 10 h anodic oxidation process run time using modified carrier electrolyte. The electropherogram for the same sample obtained in chromate electrolyte with indirect UV detection is shown in Fig. 4. As can be seen, matrix components such as Br^- , Cl^- , NO_3^- do not interfere in the determination of sulfur anions. A recovery study was carried out with three samples collected at different oxidation process run time. The results are given in Table 1. The amount of SO_3^{2-} ions in diluted samples was too low to be determined. As can be seen, the method proved to be satisfactory for the determination of $S_2O_3^{2-}$ and its oxidation products in spent fixing solutions with simple sample preparation and with high speed compared with existing analytical techniques.

References

- [1] R. Mina, J.C. Chang, *Photographic Sci. Eng.* 26 (1982) 223.
- [2] C.A.S. Brevett, D.C. Johnson, *J. Electrochem. Soc.* 139 (1992) 1314.
- [3] J. Feng, D.C. Johnson, S.N. Lowery, *J. Electrochem. Soc.* 142 (1995) 2618.
- [4] L. Szekeres, *Talanta* 21 (1974) 1.
- [5] O. Foss, I. Kringlebotn, *Acta Chem. Scand.* 15 (1961) 1607.
- [6] T. Koch, K. Taniguchi, *Anal. Chem.* 45 (1973) 2018.
- [7] D.P. Kelly, L.A. Chambers, P.A. Trudinger, *Anal. Chem.* 41 (1969) 898.
- [8] Y.M. Nor, M.A. Tabatabai, *Soil Sci.* 122 (1976) 171.
- [9] W. Furness, W.C. Dawies, *Analyst* 77 (1952) 697.
- [10] I. Zezula, *Collect. Czech. Chem. Commun.* 35 (1970) 1660.
- [11] O.H. Tuovinen, D.J.D. Nickolas, *Appl. Environ. Microbiol.* 33 (1977) 477.
- [12] J.H. Karchmer (Ed.), *The Analytical Chemistry of Sulfur and Its Compounds, Part I*, Wiley-Interscience, New York, 1970, p. 241.
- [13] J.N. Chapman, H.R. Beard, *Anal. Chem.* 45 (1973) 2268.
- [14] A.W. Wolkoff, R.H. Larose, *Anal. Chem.* 47 (1975) 1003.
- [15] B. Takano, M.A. McKibben, H.L. Barnes, *Anal. Chem.* 56 (1984) 1594.
- [16] R. Steudel, G. Holdt, *J. Chromatogr.* 361 (1986) 379.
- [17] P. Jandik, G. Bonn, *Capillary Electrophoresis of Small Molecules and Ions*, VCH, New York, 1993.
- [18] D.R. Salomon, J. Romano, *J. Chromatogr.* 602 (1992) 219.
- [19] R.G. Kelly, C.S. Brossia, K.R. Cooper, J. Krol, *J. Chromatogr. A* 739 (1996) 191.
- [20] J. Font, J. Gutierrez, J. Lalueza, X. Perez, *J. Chromatogr. A* 740 (1996) 125.
- [21] S. Motellier, K. Gurdale, H. Pitsch, *J. Chromatogr. A* 770 (1997) 311.
- [22] F. Hissner, J. Mattusch, K. Heinig, *J. Chromatogr. A* 848 (1999) 503.
- [23] Y. Miura, K. Fukasawa, T. Koh, *J. Chromatogr. A* 804 (1998) 143.
- [24] M. Goehring, U. Feldman, *Z. Anorg. Allg. Chem.* 257 (1948) 223.
- [25] D. Kaniansky, M. Masar, J. Marak, R. Bodor, *J. Chromatogr. A* 834 (1999) 133.
- [26] M.P. Harrold, M.J. Wojtusik, J. Riviello, P. Henson, *J. Chromatogr.* 640 (1993) 463.
- [27] W.R. Jones, P. Jandik, *Am. Lab.* 22 (1990) 51.
- [28] T. Groh, K. Bächman, *J. Chromatogr.* 646 (1993) 405.
- [29] M. Macka, P. Andersson, P.R. Haddad, *Anal. Chem.* 70 (1998) 743.