



ELSEVIER

Journal of Chromatography A, 848 (1999) 503–513

JOURNAL OF
CHROMATOGRAPHY A

Quantitative determination of sulfur-containing anions in complex matrices with capillary electrophoresis and conductivity detection

Frank Hissner^a, Jürgen Mattusch^{b,*}, Katja Heinig^c

^aUniversity of Leipzig, Department of Biology, Johannisallee 21–23, D-04103 Leipzig, Germany

^bCenter for Environmental Research (UFZ) Leipzig-Halle, Permoserstrasse 15, D-04318 Leipzig, Germany

^cCornell University, College of Veterinary Medicine, Diagnostic Laboratory, Analytical Toxicology, 927 Warren Drive, Ithaca, NY 14850, USA

Received 3 December 1998; received in revised form 30 March 1999; accepted 30 March 1999

Abstract

The analysis of sulfur species in complex matrices, like environmentally related samples, requires selective and sensitive as well as robust determination methods. As many as possible different anions need to be quantified in a reasonable analysis time. Besides ion chromatography, capillary electrophoresis has proven to be a very efficient technique for the separation and determination of ionic compounds. With the advantages of less sample and solvent consumption compared to conventional LC, short separation time, inexpensive and robust capillaries, CE was used to separate the anions sulfate, sulfite, thiosulfate, thiocyanate and sulfide. Detection and injection modes and the composition of the separation buffers have been varied to find the most suitable conditions. Conductivity detection after electrokinetic sample injection and improvement of calibration linearity allowed the determination of sulfur containing anions with low limits of detection (8 to 50 $\mu\text{g/l}$). The developed CE method was applied to the analysis of water from an open-pit mining lake. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Environmental analysis; Water analysis; Inorganic anions; Sulfur compounds

1. Introduction

Sulfur-containing substances play an important role in the metabolism of organism and in environmental cycles, but also in many industrial processes. Some of these compounds show toxic properties (e.g., H_2S). They are related by various oxidation and reduction reactions, syn- and disproportioning processes and affect also the behavior of other ions (e.g., heavy metals) especially in the environment [1,2]. The analysis of sulfur species is of interest to control industrial products, waste water and waste

products, environmental and biological samples. In these complex matrices sulfur-containing anions are often accompanied by other anions, inorganic and organic compounds and occur in low concentrations. For that reason, analytical methods are required that allow specific and sensitive determination for the substances of interests. Separation techniques are preferred because of their selectivity and low detection limits.

A great disadvantage of ion chromatography (IC) commonly used for determination of anions is the impossibility to determine all sulfur compounds in one chromatographic run (with similar sensitivity). Furthermore, columns can suffer from matrix com-

*Corresponding author.

ponents (e.g., humic substances) which requires a careful sample pretreatment.

Therefore, capillary electrophoresis (CE) is increasingly used in routine analysis of inorganic and organic ions in environmental and pharmaceutical samples [3]. This technique has also been applied to sulfur-containing anions. Small anions with high electrophoretic mobility, like the inorganic sulfur ions, migrate strongly to the anodic capillary end and can be detected there (“reversed” polarity, because the detector is normally on the cathodic end). The electroosmotic flow, leading to the cathode, can retard or prevent the migration to the anode and need to be suppressed or reversed. That is usually performed by the addition of modifiers (quaternary ammonium salts [4,5], diethylenetetramine [6–8]) to the separation buffer or by rinsing with this modifiers before the separation. These modifiers adsorb strongly onto the capillary surface (silanol groups) and form a double layer, so that the capillary possesses a positive charge which causes a reversed electroosmotic flow in anodic direction. Separations in permanent coated capillaries are also possible [9]. Some anions, like sulfide and thiocyanate, show absorbance in the UV region and can be detected by direct UV detection [10]. Indirect UV detection [11] in CE is a universal technique to detect non-absorbing anions like sulfate which requires the presence of a chromophoric compound in the separation buffer providing a background signal. For optimal peak shape and sensitivity, background ion and analytes should have a similar electrophoretic mobility. Several buffer substances have been used for CE—indirect UV detection of sulfur-containing anions, including chromate [12,4,10,13], phthalate [14], naphthalenetrissulfonate [6], pyromellitic acid [7,8] and *p*-aminobenzoate [5]. Since commercial conductivity detectors appeared on the market, this technique has been used more and more for the detection of small ions after CE separation. Substances possessing a high charge-to-radius ratio and therefore a high conductivity of their solutions, can be detected directly in buffers with low conductivity, e.g., cyclohexylaminoethanesulfonic acid–tris-(hydroxyethyl)aminomethane [15,16], butyric acid–creatinine [17] or morpholino ethanesulfonic acid–histidine [18] with good sensitivity. Among the sulfur anions, only sulfate has been determined using

conductivity detection [15]. Amperometric detection in CE was used for the determination of sulfite [5] and thiocyanate [14].

To our knowledge, the simultaneous separation of sulfite, sulfate, sulfide, thiosulfate and thiocyanate has not been performed by CE. The potential of conductivity detection need to be developed. In this paper we describe the development of a CE method for the sensitive determination of sulfur-containing anions, the improvement of calibration linearity by conductivity correction and the elimination of matrix interferences by electrokinetic injection. The applicability to the analysis of water from an open-pit mining lake contaminated with humic substances is shown.

2. Experimental

2.1. Instrumentation

For CE experiments UV detection was performed on a 270 A-HT system (PE Applied Biosystems, Weiterstadt, Germany) with a variable-wavelength detector, 900 series interface and data acquisition by personal computer with Turbochrom 4 software. A capillary of 72 cm (50 cm to the detection window)×75 μm I.D. was used. Detection wavelengths were 214 and 254 nm, respectively.

For conductivity detection, a Crystal CE system Model 310 by ATI Unicam (Boston, MA, USA) with Crystal 1000 conductivity detector was applied. The capillary (70 cm×75 μm) was rinsed with 1 mol/l cetyltrimethylammonium bromide (CTAB) for 0.5 min before each analysis. The composition of electrophoretic separation buffers and injection conditions are given in Results and Discussion.

2.2. Reagents and solutions

The sulfur anion standard solutions were prepared from sodium sulfide, thiosulfate, sulfite, sulfate and thiocyanate (Merck, Darmstadt, Germany). Pyromellitic acid, tris(hydroxymethyl)aminomethane (Tris), sodium chromate, hydrochloric acid, sodium hydroxide and lithium hydroxide were also obtained from Merck. CTAB and tetradecyltrimethylammonium bromide (TTAB) were from Aldrich (Steinheim,

Germany). Cyclohexylaminoethanesulfonic acid (CHES) was purchased from Sigma (St. Louis, MO, USA) and Triton X-100 from Riedel-de Hën (Seelze, Germany). All buffer and standard solutions were prepared using triply distilled helium degassed water.

2.3. Samples

Water samples of an open-pit mining lake were taken before and after precipitation of humic substances from different depths from 0.2 to 24 m. The samples containing humic substances were dark-colored, and had an intensive phenolic smell. The samples taken after precipitation were characterized by a light-brown color and no significant smell. The pH had changed from 7.7 to 5.8, the conductivity from 1976 $\mu\text{S}/\text{cm}$ to 2550 $\mu\text{S}/\text{cm}$ because of the addition of Fe(III) salts. Samples were filtered before analysis.

3. Results and discussion

3.1. CE with indirect UV detection

Because indirect photometric detection is the most applied technique in the CE separation of small ions and furthermore, commercial available devices are usually equipped with a UV detector, this mode was also tested for the determination of sulfur-containing anions. Sulfate, sulfite, thiosulfate, thiocyanate and sulfide were separated with a mixture of other inorganic anions, chloride, bromide, nitrite and nitrate. The investigation of a wide spectrum of ions was important, because many “real-world” samples contain a complex mixture of substances. Two different UV absorbing background electrolytes were used: sodium chromate with a high electrophoretic mobility ($0.72 \text{ cm}^2 \text{ kV}^{-1} \text{ s}^{-1}$) and pyromellitic acid (sodium salt) as a representative of buffers with lower mobility ($0.55 \text{ cm}^2 \text{ kV}^{-1} \text{ s}^{-1}$) [19]. In Fig. 1 both electrolytes were compared regarding to the peaks shapes obtained for the analytes. Good resolutions occurred for all peak pairs. The ions sulfite and sulfide, sensitive to oxidation, were not investigated in this experiment. The migration order is determined by the charge-to-size ratio. Sulfate and

thiosulfate possess the same charge, but thiosulfate has a smaller hydrate envelope and migrates faster than sulfate. With chromate buffer, good peak shapes were obtained for the anions with high electrophoretic mobility, like thiosulfate and bromide; the other species showed peak tailing. The pyromellitate buffer provided a high peak symmetry for nitrite and nitrate, whereas the ions with higher mobility (e.g., thiosulfate and bromide) showed a fronting and that with lower mobility (thiocyanate) a tailing. Using chromate a higher baseline stability was obtained, the peak symmetry factors were in general better than in the pyromellitate buffer. Therefore chromate was used for the further investigations. Starting with a 5 mmol/l chromate electrolyte, pH 8 containing 0.5 mmol/l CTAB, the conditions were varied with respect to fast, high resolution separation of the anions. For the determination of species with low pK_a (sulfite and sulfide) the pH was increased to 10. That caused a reduction of migration times leading to a decreased peak resolution. Therefore, a lower CTAB concentration (0.02 mmol/l) was added to the buffer. By this way, a good peak resolution in a separation time of 7 min could be achieved. Using the described electrolyte, sulfite was also separated and appeared in the anion mixture between nitrate and thiocyanate. Sulfide could not be detected because of its high UV absorbance even at 254 nm (compensation of chromate absorbance). Decreasing the wavelength to 214 nm, positive peaks were obtained for sulfide, thiocyanate and thiosulfate but sensitivity was decreased for the non-absorbing compounds, like sulfate.

According to the theory there could occur an oxidation of sulfide and sulfite in the presence of chromate at pH 14, however, no significant changes in peak areas with time could be detected when solutions of these analytes were injected in the alkaline chromate electrolyte of the CE system. The oxidation of stock solutions by standing on air is much more a factor. To prevent substance losses, sulfite was preserved with formaldehyde (formation of methanesulfonic acid, which decomposes in the separation buffer under basic conditions) [13]. Sulfide solutions were prepared in N_2 degassed water.

For the assessment of the efficiency of the developed CE method with indirect UV detection the linearity of calibration, reproducibility (in terms of

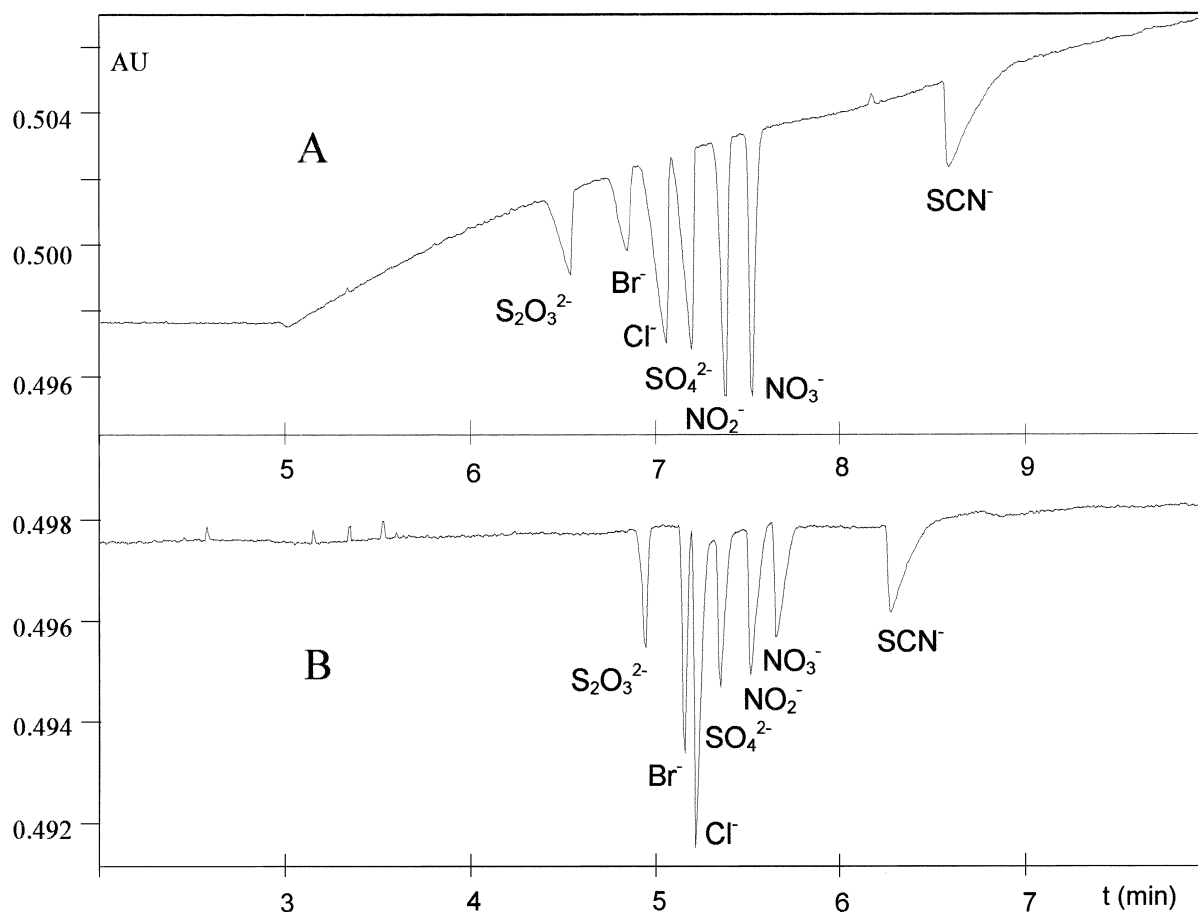


Fig. 1. Comparison of background electrolytes for the separation of anions. (A) 1.5 mmol/l pyromellitic acid, 10 mmol/l Tris, pH 9.15 (rinse capillary with 1 mmol/l CTAB) and (B) 5 mmol/l chromate, 0.5 mmol/l CTAB, pH 8.0. Capillary: 72 cm (effective length 50 cm) \times 75 μ m, voltage: -20 kV, detection: UV 214 nm (A), 254 nm (B), injection: 5 s hydrodynamic 0.5 p.s.i., 10 mg/l standard mixture.

relative standard deviation, RSD) and limit of detection (LOD) was determined. External calibration was carried out using standard solutions containing 1.5, 3, 5, 10 and 15 mg/l of the analytes. The RSD resulted from five times repetition of the analysis of the 10 mg/l standard. LOD has been determined (a) using the threefold baseline noise and slope of the calibration function (statistical) and (b) from experimental observations. Table 1 shows the quantitative parameters measured for the sulfur anions in the chromate buffer.

3.2. CE with conductivity detection

3.2.1. Development of separation conditions

Because with UV detection the simultaneous

determination of all sulfur-containing ions was difficult (high absorbance of sulfide and partly overlapping with chloride), conductivity detection was applied. All anions were supposed to have a sufficient conductivity to give a good response with similar intensity in this alternative detection mode. Using an electrolyte consisting of CHES, LiOH and Triton X-100 (nonionic surface active compound), that has proven to be useful to separate a variety of small inorganic and organic ions [15,16], also a mixture of the sulfur-containing species accompanied by "common" anions could be resolved almost completely (Fig. 2). CHES as an organic buffer provided a low basic conductivity and current. Lithium hydroxide was used to set the pH at 9.2 and to increase the ionic strength of the buffer. Triton X-100 was added

Table 1
 Characterization of CE with indirect UV detection (hydrodynamic injection) and with conductivity detection using electrokinetic or hydrodynamic injection^a

Parameters	Unit	Detection mode	Thiosulfate	Sulfate	Sulfite	Sulfide	Thiocyanate
RSD (peak area)	%	UV	1.7	3.2	4.0		5.0
		Cond./electrokin.	4.1	3.6	4.2	5.1	4.6
		Cond./hydrodyn.	2.6	2.8		3.8	
RSD (migration time)	%	UV	1.2	3.4	2.3		4.1
		Cond./electrokin.	1.43	1.64	1.70	1.83	1.65
		Cond./hydrodyn.					
LOD (3×noise)	mg/l	UV	0.25	0.26	0.42		0.26
		Cond./electrokin	0.012	0.004	0.013	0.013	0.012
		Cond./hydrodyn.	0.5	0.5		0.6	
LOD (experimental)	mg/l	UV	0.17	0.33	0.50		0.40
		Cond./electrokin.	0.01	0.008	0.02	0.05 ^b	0.02
		Cond./hydrodyn.	0.8	0.7		1.0	
Linear slope	AU s/l/mg	UV	662	751	1639		925
	μS s/l/μg	Cond./electrokin.	13 578	12 774	4367	11 308	5111
	μS s/l/mg	Cond./hydrodyn.	20 292	23 750		22 279	
Intercept	AU s	UV	62	188	−340		22
	μS s	Cond./electrokin.		5320	784	27 246	−81 677
	μS s	Cond./hydrodyn.	−1282	−8887		−2572	
R ² (regression coefficient)		UV	0.999	0.998	0.998		0.996
		Cond./electrokin.	0.997	0.998	0.998	0.993	0.996
		Cond./hydrodyn.	0.995	0.998		0.998	

^a Injection conditions: UV: 5 s hydrodynamic 0.5 p.s.i.; conductivity/electrokinetic: 6 s, −5 kV; conductivity/hydrodynamic: 12 s, 25 mbar.

^b Solution with lower concentration not stable (oxidation), high variations.

for influencing the viscosity of the buffer solution. Before each run the capillary was rinsed with CTAB to supply a reversed electroosmotic flow (EOF). CTAB was not added to the buffer to guarantee low conductivity and higher baseline stability. The migration order has been changed in comparison to indirect UV detection due to the different hydration of the analyte ions in different buffers. The peak pairs chloride/thiosulfate and sulfide/sulfate could not be separated with complete baseline resolution. Therefore, the buffer composition had to be varied. Increasing the LiOH content, ionic strength was also increased. That caused a reduction of analyte migration velocity. Due to the pH change, the dissociation behavior (especially of sulfide) has been influenced leading to a shift in migration times of some anions compared to other analytes (migrate faster because of stronger dissociation). Therefore, a higher peak

resolution of the “problem pairs” could be observed. CE with conductivity detection has shown to be well suited for the separation of sulfur-containing species in mixtures of anions. In the following section, investigations of electrokinetic injection are described; the resulting LOD and RSD are compared to hydrodynamic injection.

3.2.2. Electrokinetic injection for sample preconcentration

In the electrokinetic sample injection two problems arose. Using external calibration, the relation of concentration and peak area was not linear. Performing the addition of standards to a sample with high conductivity (mining lake), no changes in peak areas occurred. These effects can be attributed to the dependence of the injected amount from the relation of sample conductivity to conductivity of the electro-

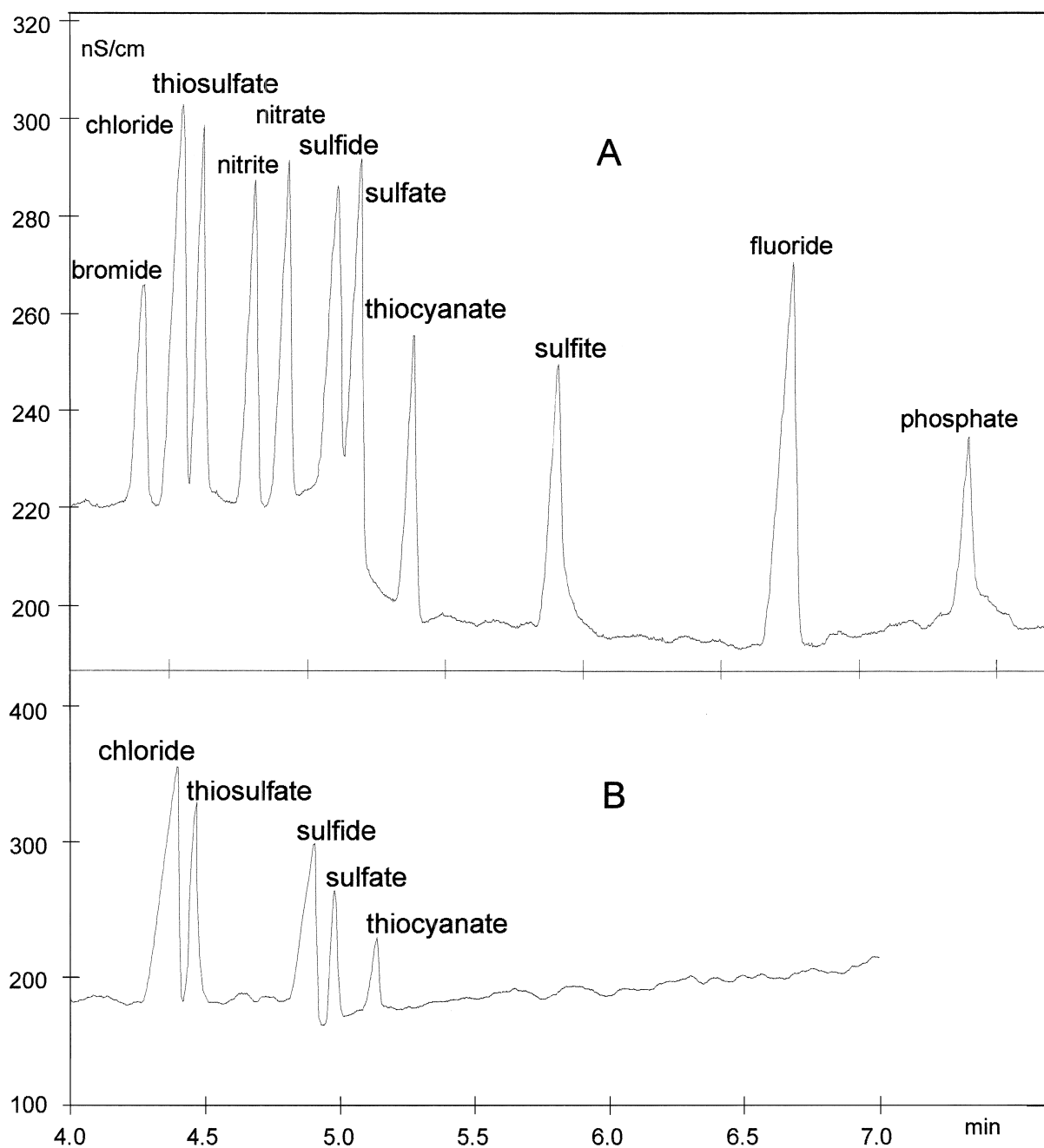


Fig. 2. Separation of anions using conductivity detection. (A) 50 mmol/l CHES, 20 mmol/l LiOH, 0.03% Triton X-100, rinse with 1 mmol/l CTAB. (B) Improved peak resolution by using 35 mmol/l LiOH. Capillary: 72 cm \times 50 μ m, voltage: -25 kV, detection: conductivity 1 μ S/cm FS, injection: 12 s 25 mbar 10 mg/l anion standard mixture.

phoretic buffer, which is of fundamental importance for electrokinetic injection. If the conductivity of the sample solution is lower than that of the buffer in the capillary, the ions migrate after application of a voltage fast into the capillary and form a stacking-front (zone of increased concentration). If the sample concentration increases further on this border layer, the local conductivity in this layer decreases and causes a reduction of field strength. The front of the sample zone migrates slower and the stacking-effect becomes more stronger. This is designated as field amplified sample injection (FASI) [20,21]. Comparing the equations for the sample volume in electrokinetic injection (1) and FASI (2), it can be seen that the FASI equation contains the product of electrophoretic mobility and the relation of buffer to sample conductivity (γ). The lower the sample conductivity, the higher is the injection volume. This applies especially for ions with high electrophoretic mobility.

$$V = \frac{(\mu_e + \mu_{eo})\pi r^2 U t}{L} \text{ (electrokinetic injection)} \quad (1)$$

$$V = \frac{(\gamma\mu_e + \mu_{eo})\pi r^2 U t}{L} \text{ (FASI)} \quad (2)$$

Investigating two sample solutions with the same concentration of analytes but different conductivity, more ions are injected from the solution with lower conductivity in the same time. From a solution of high conductivity and therefore low electric field strength less ions are injected (independent from analyte concentration) than from a solution with low conductivity. That explains the nonlinear calibration function, because the conductivity of the standards increases also with concentration. The problem of standard addition occurred because to low standard concentrations were added to the sample with a high conductivity.

For using the electrokinetic injection with external calibration for quantitation, the relation between sample conductivity and injected sample volume (and therefore signal intensity) has to be determined. With increasing sample concentration conductivity increases linearly, whereas specific resistance decreases exponentially (Fig. 3A). Fig. 3B shows the peak areas resulting from the injection of standards with the same concentration, but different conduc-

tivity (solution of standards in 1:0, 1:1, 1:3, 1:7 diluted buffer). The relation between specific resistance and peak area is linear under constant analyte concentration. If the electrical resistance tends to zero (very high conductivity), peak areas become very small. That means, hydrodynamic injection will lead to better sensitivity in this case. To obtain linear calibration functions it is necessary to multiply the measured peak area with the conductivity of the standard in each case. Another way of solving the linearity problem in FASI is the use of an internal standard during injection [22].

For quantification of the anions in samples the method of addition of known concentrations (standard addition) is very useful. Also in this case the conductivity of the sample has to be determined to estimate the concentration of the standards that will be added. Furthermore it is important to know if the sample conductivity changes highly with the addition of the anionic standards. Using low concentrations in a sample with high conductivity, the changes are negligible and a correction of the calibration function is not necessary.

In Table 1 the conductivity detection with electrokinetic injection is characterized by RSD, LOD and calibration functions. The calibration was done with five standard mixtures in the concentration range 0.1 to 0.5 mg/l. The reproducibility has been determined by five times injecting the 0.1 mg/l standard. Because the injected amount of analytes depends on the matrix conductivity, the LOD is also determined by this parameter, and therefore difficult to determine. The LODs shown in Table 1 are only relevant for a very low sample conductivity (about 4 $\mu\text{S}/\text{cm}$). To estimate the LOD for higher conductivities, the uncorrected calibration curves were differentiated. Using the $3\times$ noise criteria and the conductivity of the sample solution a function for the determination of the detection limit was obtained (Fig. 3C).

Using hydrodynamic injection, the conductivity of the sample matrix has no influence. The detection limit is determined by the sample volume that can be injected without overloading or contaminating the capillary. Hydrodynamic injection is to prefer for samples with high ionic strength. Table 1 characterizes additionally the hydrodynamic injection mode according to LOD, RSD and calibration parameters. The LOD is much higher than with electrokinetic injection for standards with low conductivity.

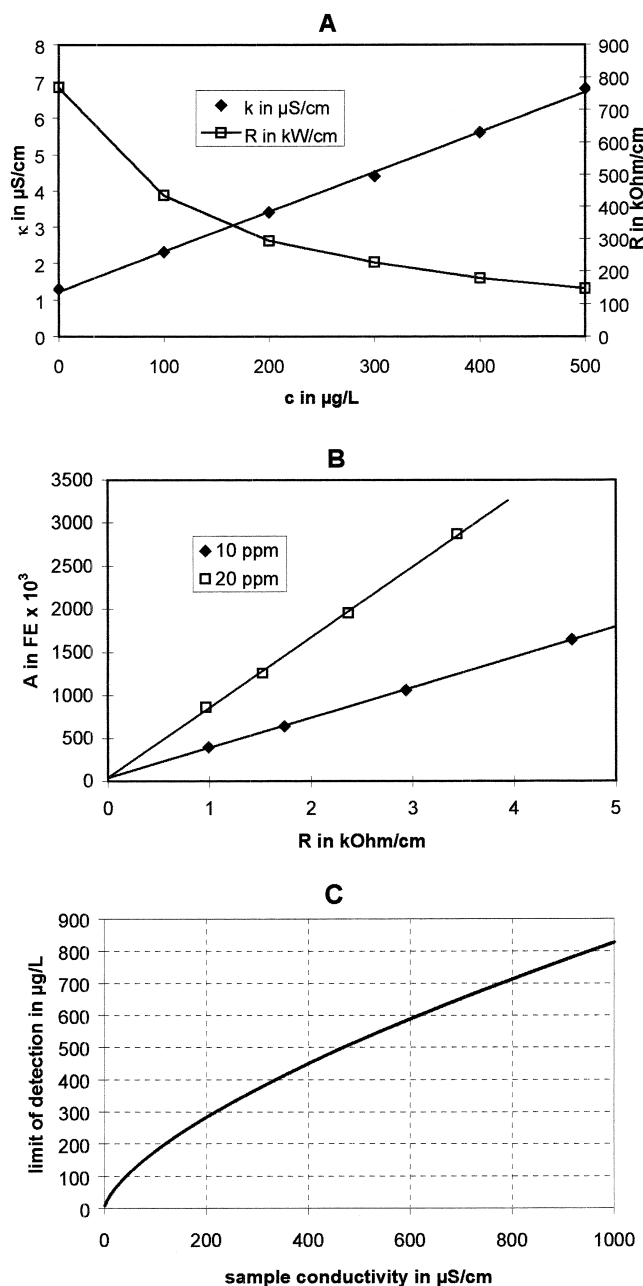


Fig. 3. Influence of matrix conductivity on electrokinetic injection (thiosulfate). (A) Correlation between standard concentration (mixture of all sulfur anions) and conductivity/resistance, (B) influence of matrix conductivity on peak area of thiosulfate with constant anion concentration, (C) dependence of limit of detection on sample conductivity (thiosulfate).

3.3. Analysis of “real-world” samples

The optimized capillary electrophoretic separation

with conductivity detection has been applied to the determination of sulfur-containing anions in contaminated water samples.

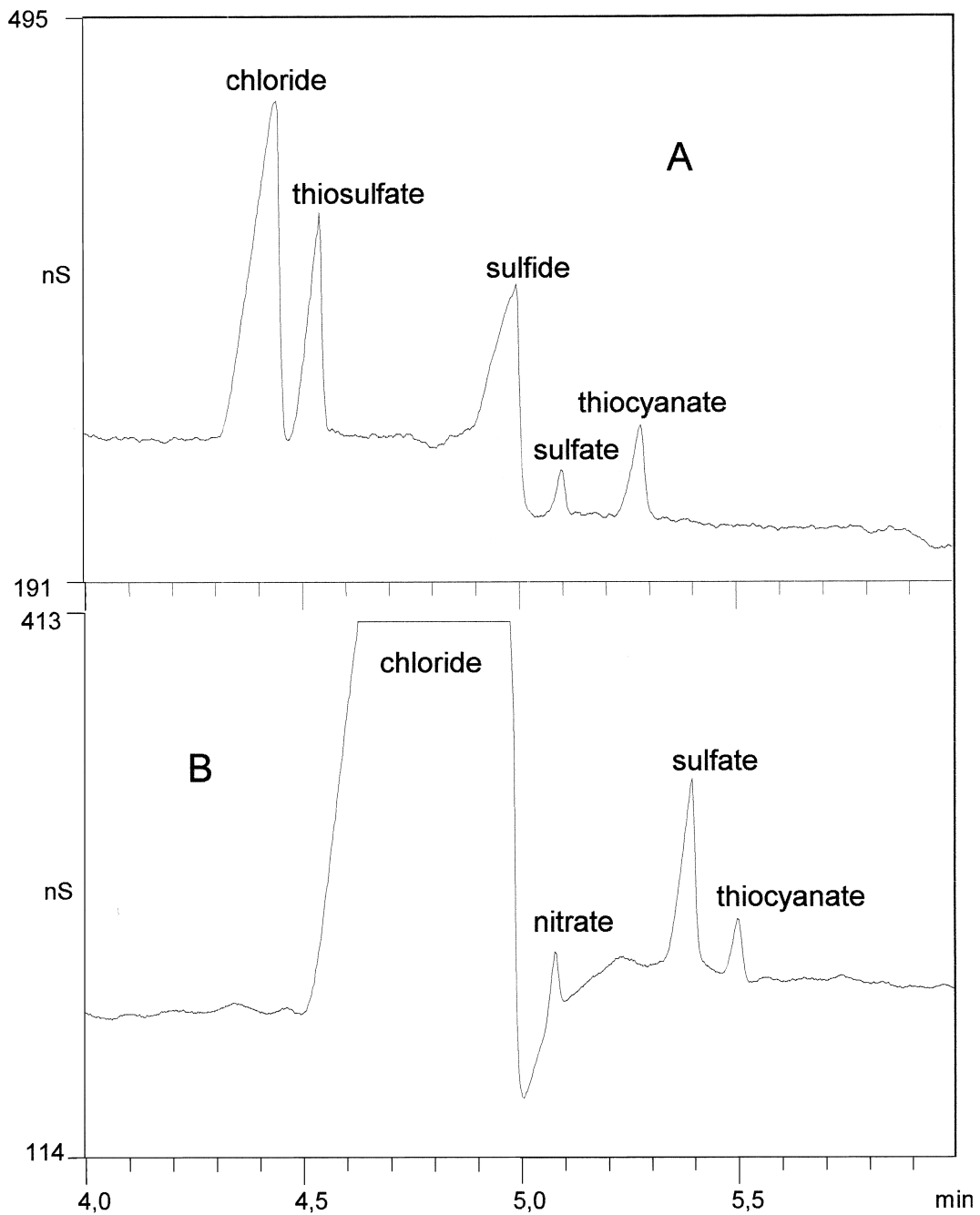


Fig. 4. Determination of sulfur-containing anions in water from an open-pit mining lake by CE-conductivity detection (A) before, (B) after precipitation of humic substances. 50 mmol/l CHES, 35 mmol/l LiOH, 0.03% Triton X-100, rinse with 1 mmol/l CTAB. Capillary: 72 cm \times 75 μ m, voltage: -25 kV, detection: conductivity 1 μ S/cm FS, injection: 6 s, -5 kV, water from 20 m depth.

3.3.1. Determination of sulfur anions in water from an open-pit mining lake

A flooded open-pit mine was used to deposit waste water from a lignite low-temperature carbonization plant. The lake contains organic and inorganic sulfur compounds, which were formed from sulfur containing lignite during the carbonization and were discharged with waste water. H_2S , but also thiosulfate and thiocyanate are formed by this way. These compounds were also produced by chemical and microbiological reactions in the lake. The low oxygen concentration promoted anaerobic processes. For the remediation of the mining lake, a solution of $FeCl_3$ was added to precipitate the phenolic compounds and humic substances [23]. The reduced sulfur species were supposed to be removed during oxidation and precipitation reactions. Therefore, also the analysis of sulfur anions is of importance, because they are indicators for the ecological situation of the lake.

The performance of CE has been evaluated by analyzing samples from the mining lake. To avoid a contamination of the capillary by humic substances, electrokinetic injection was performed. Fig. 4A shows the electropherogram of a water sample from 20 m depth before precipitation. The presence of the ions sulfide and thiosulfate indicates a very low oxygen content. Sulfate and thiocyanate were also found. After precipitation only sulfate and thiocyanate occurs (Fig. 4B). Sulfide and thiosulfate have been removed during the oxidation and precipitation. The sulfate content was increased due to oxidation from the reduced sulfur compounds. The thiocyanate content was not influenced by these processes.

An ion chromatographic determination of sulfur anions in the mining lake was not possible, because the humic substances contaminate the separation column and lead to irreversible performance loss and plugging. Quantification has been performed by standard addition to consider all matrix influences. Because the conductivity of the samples does not change significantly during addition of the standards, a correction of the calibration function in CE was not necessary.

The developed CE method is well suited for determinations of sulfur-containing anions in water samples with humic substances, and can be used for further investigations of the lake to determine the usefulness of remediation processes.

4. Conclusions

The sulfur-containing anions sulfate, sulfite, thiosulfate, thiocyanate and sulfide could be separated effectively by CE together with a variety of other inorganic anions.

Conductivity detection was preferred over indirect UV detection because under the separation conditions for conductivity detection a good peak resolution was obtained and all ions of interest could be detected with a similar sensitivity. The electrophoretic buffer consisted of 20 mmol/l CHES, 35 mmol/l LiOH and 0.03% Triton X-100. The LiOH content was increased to obtain baseline resolution between chloride and thiosulfate, sulfide and sulfate. Using electrokinetic injection from matrices with low conductivity, the detection limits could be increased 20-fold compared to hydrodynamic injection. Because of the strong matrix influence a correction of external calibration curves has to be done. Using the addition of standards, a correction is not necessary. For environmental samples with complex matrices, e.g., humic substances containing water, CE with conductivity detection and electrokinetic injection was successfully applied, because this injection mode is an excellent possibility to avoid contamination by the matrix and to preconcentrate the analytes via stacking processes. CE persuades by its simultaneous determination of all anions in a short separation time.

References

- [1] W. Salomons, W.M. Stigliani, Biogeochemistry of Pollutants in Soils and Sediments, Springer, Berlin, 1996.
- [2] R.W. Howarth, J.W.B. Stewart, M.V. Ivanov, Sulphur Cycling on the Continents, Wiley, New York, 1992.
- [3] J.P. Landers, Handbook of Capillary Electrophoresis, CRC Press, Boca Raton, FL, 1997.
- [4] B. Tenberken, P. Ebert, M. Hartmann, M. Kibler, A. Mainka, T. Prokop, A. Röder, K.J. Bächmann, J. Chromatogr. A 745 (1996) 209–215.
- [5] W. Buchberger, P.R. Haddad, J. Chromatogr. 608 (1992) 59–64.
- [6] Anions with PMA Buffer System, TSP Application MG93-1,-2,-3
- [7] S.A. Shamsi, N.D. Danielson, Anal. Chem. 66 (1994) 3757–3764.
- [8] S. Motellier, K. Gurdale, H.J. Pitsch, J. Chromatogr. A 770 (1997) 311–319.

- [9] K. Srinivasan, G. Pohl, N. Avdalovic, *Anal. Chem.* 69 (1997) 2798–2803.
- [10] C. Bjerregaard, P. Møller, H. Sørensen, *J. Chromatogr. A* 717 (1995) 409–414.
- [11] S.M. Masselter, A.J. Zemann, G.K. Bonn, *J. High Resolut. Chromatogr.* 19 (1996) 131–136.
- [12] D. Volgger, A. Zemann, G. Bonn, *J. High Resolut. Chromatogr.* 21 (1998) 3–10.
- [13] J. Romano, P. Jandik, W.R. Jones, P.E. Jackson, *J. Chromatogr.* 546 (1991) 411–421.
- [14] H. Salimi-Moosavi, R.M. Cassidy, *Anal. Chem.* 67 (1995) 1067–1073.
- [15] S. Valsecchi, G. Tartari, S. Polesello, *J. Chromatogr. A* 760 (1997) 326–332.
- [16] C. Haber, W.R. Jones, J. Soglia, M.A. Surve, M. McGlynn, A. Caplan, J. Reineck, C. Krstanovic, *J. Cap. Electrophoresis* 3 (1996) 1–11.
- [17] F. Foret, M. Deml, V. Kahle, P. Bocek, *Electrophoresis* 7 (1986) 430–432.
- [18] M.J. Gordon, X. Huang, S.L. Pentoney, R.N. Zare, *Science* 242 (1988) 224–238.
- [19] T. Hirokawa, M. Nishino, N. Aoki, Y. Kiso, Y. Sawamoto, T. Yagi, J.I. Akiyama, *J. Chromatogr.* 271 (1983) D1–D106.
- [20] R.L. Chien, D.S. Burgi, *J. Chromatogr.* 559 (1991) 141–152.
- [21] D.S. Burgi, R.L. Chien, *Anal. Chem.* 63 (1991) 2042–2047.
- [22] C. Haber, R.J. Van Saun, W.R. Jones, *Anal. Chem.* 70 (1998) 2261–2267.
- [23] Untersuchungen zur Sanierung des Tagebaurestlochs Vollert-Süd (Schwelvollert), Zwischenbericht, Umweltforschungszentrum Leipzig/Halle, 1995.