ELSEVIER

Journal of Chromatography A, 736 (1996) 341–350

JOURNAL OF CHROMATOGRAPHY A

# Separation of thio- and oxothioarsenates by capillary zone electrophoresis and ion chromatography

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**Abstract**

Capillary zone electrophoresis and ion chromatography were used for the separation of oxomonothioarsenate, oxodithioarsenate, oxotrithioarsenate, tetrathioarsenate and arsenate. The separation by capillary zone electrophoresis was achieved by using an uncoated fused-silica capillary tube and a polyacrylamide-coated capillary tube both filled with phosphate buffers of different pH values, temperatures and, in the case of the uncoated tube, concentrations of the dynamic coating reagent cetyltrimethylammonium bromide. For ion chromatography, a silica gel and a polymer-based anion exchanger with a glyconate borate buffer were used. The capillary zone electrophoresis system showed higher efficiency than ion chromatography with regard to separation capacity, detection limits and reproducibility.

*Keywords:* Thioarsenates; Oxothioarsenates; Arsenates; Inorganic anions; Capillary zone electrophoresis; Ion chromatography

## 1. Introduction

Analyses for arsenic, which occurs in the natural environment as very different species, e.g., arsenate, aresenite, dimethyl- and trimethylarsine, arsenic acids, arsenobetaine and -choline and in sulfide form, requires efficient separation methods. Methods such as chromatography and capillary zone electrophoresis have already been used to separate arsenite, arsenate, monomethyl- and dimethylarsinic acid and arsenobetaine and -choline [1–8]. High-performance liquid chromatography (HPLC) is the most widely used separation method for arsenic species. Atomic absorption spectrometry (AAS) [9–13], inductively coupled plasma mass spectrometry (ICP-MS) [11,14–16] and inductively coupled plasma atomic emission spectrometry (ICP-AES) have been used as element-selective detection methods. In aqueous systems, sulfur- and oxygen-containing arsenic species can also arise from arsenic sulfides in the presence of hydroxyl ions. The aim of this work was to develop suitable separation systems for these species.

## 2. Experimental

The following compounds were used as standard compounds: $Na_3AsO_3S \cdot 7H_2O$, $Na_3AsO_2S_2 \cdot 7H_2O$, $Na_3AsS_4 \cdot 8H_2O$ and the commercially available $NaH_2AsO_4 \cdot 7H_2O$. The

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0021-9673/96/$15.00 
*SSDI* 0021-9673(95)01319-9

characterization of the standard compounds will be described elsewhere [17].

### 2.1. Synthesis of standard compounds

*$Na_3AsO_3S \cdot 7H_2O$*

A 1.44-g amount of sulfur (0.045 mol S) was added to a mixture of 5.00 g of $As_2O_3$ (0.050 mol As) and 6.00 g of NaOH (0.150 mol Na) in 20 ml of water and the solution was heated to 100°C. After 2 h, the excess of sulfur was filtered off and the solution was cooled slowly to 4°C. Colourless needle-shaped crystals were obtained (yield of $Na_3AsO_3S \cdot 7H_2O$: 0.038 mol, 76%). The rest of the solvent was removed under vacuum.

*$Na_3AsO_2S_2 \cdot 7H_2O$*

A 5.76-g amount of sulfur (0.180 mol S) was added to a mixture of 5.00 g of $As_2O_3$ (0.050 mol As) and 6.00 g of NaOH (0.150 mol Na) in 20 ml of water and the solution was heated to 70°C. After 2 days, the excess of sulfur was filtered off and the solution was cooled slowly to 4°C. Colourless rhombic crystals were obtained (yield of $Na_3AsO_2S_2 \cdot 7H_2O$: 0.023 mol, 46%). The crystals were dried under vacuum for 1 h.

*$Na_3AsS_4 \cdot 8H_2O$*

A 5.76-g amount of sulfur (0.180 mol S) was added to a mixture of 5.00 g of $As_2O_3$ (0.050 mol As) and 6.00 g of NaOH (0.150 mol Na) in 20 ml of water and the solution was heated to 100°C. After 3 days, the excess of the sulfur was filtered off and the solution was cooled slowly to 4°C. Yellowish needle-shaped crystals were obtained (yield of $Na_3AsS_4 \cdot 8H_2O$: 0.030 mol, 60%). The attached sulfur was removed by extraction with ethanol and the crystals were dried under vacuum for 1 h.

All compounds were stored in an argon atmosphere at 4°C.

### 2.2. Apparatus

*Ion chromatography*

The instrumentation consisted of an HPLC pump (Model 2200, Bischoff), a Rheodyne injection valve (Bischoff), a Model 690 ion chromatograph conductivity detector (Metrohm) and an integrator (Merck–Hitachi).

The separation columns were Nucleosil 10 Anion II (Macherey–Nagel), 250 mm × 4 mm I.D., capacity 50 mequiv./g, particle diameter 10 μm; and PRP X-100 polymer anion-exchange column (Hamilton), 125 mm × 4 mm I.D., capacity 170 mequiv./g, particle diameter 10 μm.

*Capillary electrophoresis*

A BioFocus capillary electrophoresis system (Bio-Rad) with a programme-controlled UV–Vis detector (190–800 nm) was used. The capillary tubes were an uncoated capillary tube, 50 cm × 50 μm I.D. and a polyacrylamide-coated capillary tube, 24 cm × 25 μm I.D.

### 2.3. Reagents and solutions

*Ion chromatography*

The eluents were prepared by dissolving 1.2 mmol of potassium gluconate, 1.3 mmol of sodium metaborate, 40 mmol of boric acid, 54.2 mmol of glycerine and 0.02 mmol of EDTA in 1 l of deionized water–acetonitrile (85:15, v/v) followed by adjusting the pH to 8.0 (Nucleosil 10 Anion II column) and to pH 7.5 (PRP X-100 column) with 0.1 mol/l potassium hydroxide solution. Before use all eluents were filtered through a 0.45-μm membrane filter and degassed for 30 min in an ultrasonic apparatus.

*Capillary electrophoresis*

The phosphate buffers were prepared by dissolving 2.325 ml of 85% phosphoric acid in 1 l of deionized water followed by adjusting the pH values from 3.0 to 13.0 with a 0.1 mol/l sodium hydroxide solution. Before use all buffers were filtered through a 0.2-μm membrane filter and degassed for 30 min under vacuum. The buffer solutions were stored at 4°C.

### 2.4. Chromatographic conditions

The chromatographic experiments were performed at a flow-rate of 1.2 ml/min and the sample volume was 50 μl. The parameters of the

conductivity detector were set as follows: range 500 $\mu$S/cm, sensitivity 50 and damping 1.

### 2.5. Capillary electrophoresis conditions

For injection the pressure was $1.41 \cdot 10^5$ Pa s, run voltage 15 kV, detection scan range 195–300 nm in 5-nm steps, scan frequency 4 Hz and carousel temperature 5°C.

## 3. Results and discussion

### 3.1. pH-dependent stability of oxothioarsenate and tetrathioarsenate

The pH of the supporting electrolytes or the mobile phases strongly influences the migration or retention time and the separating power. The decomposition of oxothioarsenate and tetrathioarsenate must also be taken into account. In order to determine the stability of the synthesized model compounds, analyses by capillary-zone electrophoresis were carried out in the pH range 3–13. These analyses revealed the oxomonothioarsenate has the greatest stability of the arsenic species examined over the entire pH range (see Fig. 1a–c). Oxodithioarsenate has several maxima of stability, at pH 3, 5–6 and 10 (see Fig. 1b), whereas in solution the unstable tetrathioarsenate remains nearly undecomposed only in the pH range 10–13. The maxima of stability of all arsenic species are located close to the $pK_s$ values [18] of their acids ($H_3AsO_3S$, $pK_{s1}$ 3.3, $pK_{s2}$ 7.2, $pK_{s3}$ 11.0; $H_3AsO_2S_2$, $pK_{s1}$ 2.4, $pK_{s2}$ 7.1, $pK_{s3}$ 10.9; $H_3AsOS_3$, $pK_{s3}$ 10.8; $H_3AsS_4$, $pK_{s3}$ 5.2).

The decomposition of oxomonothioarsenate occurs in favour of oxodithioarsenate, which has one additional sulfur atom. To obtain a material balance, arsenate should also have been created during this decomposition, but it cannot be detected because of its low UV absorption and its low concentration. In the acidic range, oxodithioarsenate is partly decomposed to oxomonothioarsenate and reactive As–SH groups

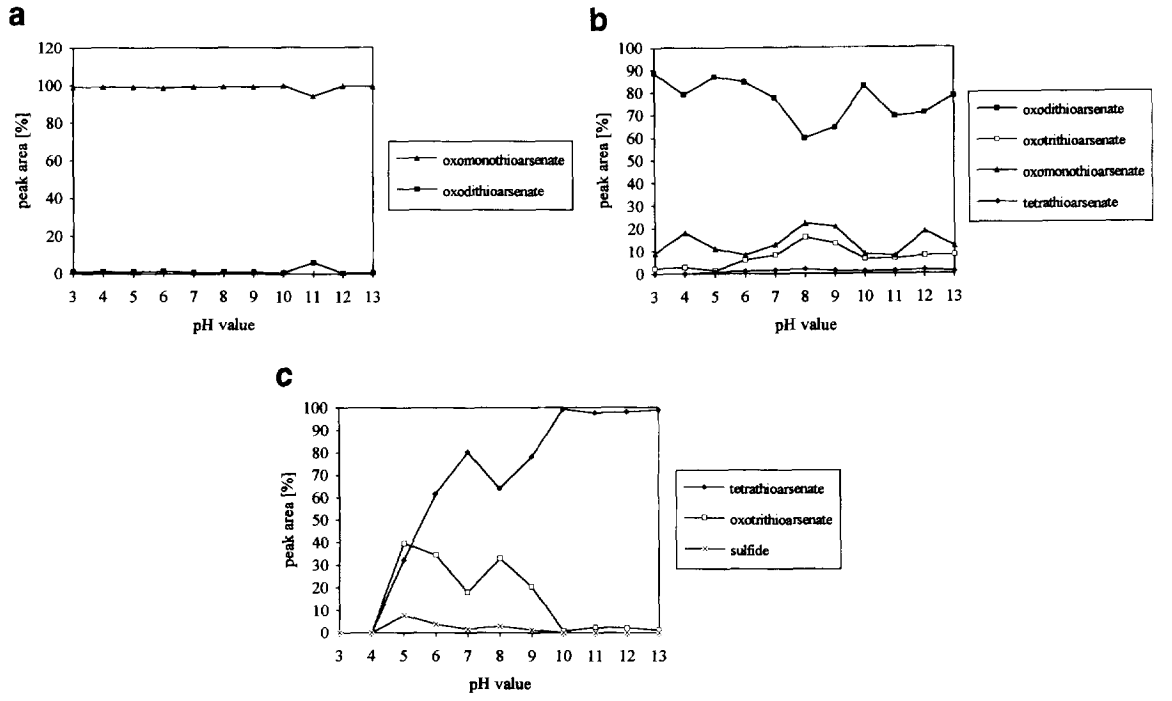


Fig. 1. pH-dependent decomposition of (a) oxomonothioarsenate, (b) oxodithioarsenate and (c) tetrathioarsenate in solution.

cause a splitting off of $H_2S$. In the pH ranges 7–10 and 5–10 oxodithioarsenate is decomposed to oxomonothioarsenate and oxotrithioarsenate, respectively, whereas at the alkaline pH 11 a displacement of equilibrium with almost constant oxotrithioarsenate concentration occurs in favour of oxomonothioarsenate. Tetrathioarsenate is first detectable by capillary zone electrophoresis at pH 5, which indicates a $pK_s$ value in this range. The concentration of tetrathioarsenate increases at the stability peaks at pH 5 and 8 in favour of oxotrithioarsenate and sulfide ions, respectively. The creation of polymeric $(AsS_3)_n$ anions in the acidic hydrolysis of $Na_3AsS_4$ described by Thilo et al. [18] was not observed. The electropherogram in Fig. 2 shows the decomposition of tetrathioarsenate at pH 7 during 30 days. pH 10 is ideal for the simultaneous capillary zone electrophoresis of all arsenic species examined.

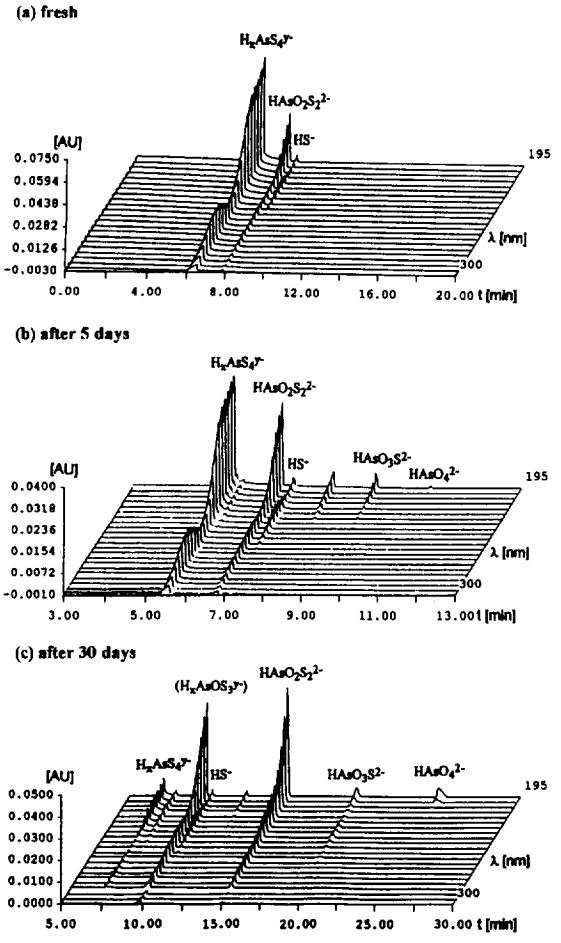


Fig. 2. Electropherograms of time-dependent decomposition of $H_xAsS_4^{x-}$ at pH 7.0.

### 3.2. Separation by capillary zone electrophoresis

Both uncoated and coated capillary tubes were used from consideration of the already determined stabilities of the arsenic species. The samples were applied both with pressure and electrokinetically, but better results were achieved by pressure application. The compounds examined at concentrations of 50–100 mg/l can be well detected in the UV range and also distinguished by their absorption spectra (Fig. 3). For the separation pH 8 was used first because of the limited pH range of the buffers in the case of the coated capillary tube. As was expected from the stability examination, the

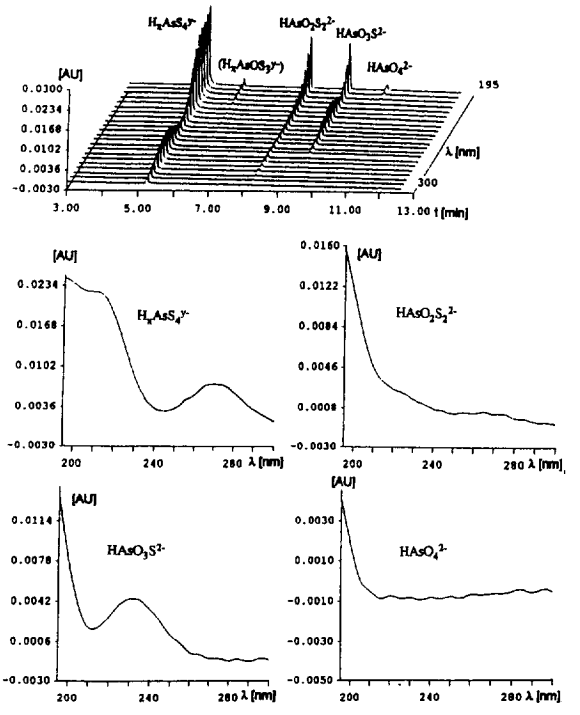


Fig. 3. Electropherogram of $H_xAsS_4^{x-}$ (25 mg/l), $HAsO_2S_2^{2-}$ (ca. 25 mg/l), $HAsO_3^{2-}$ (25 mg/l) and $HAsO_4^{2-}$ (25 mg/l), obtained with an uncoated capillary tube, and absorption spectra.

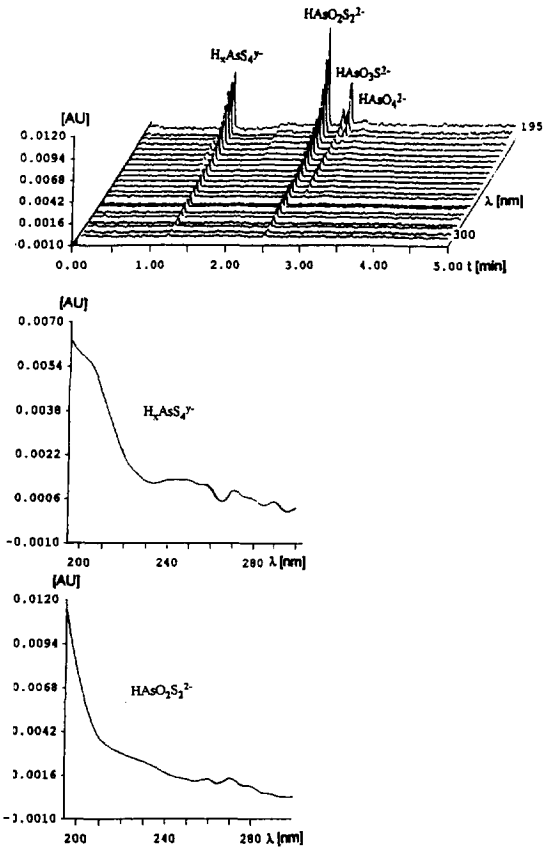


Fig. 4. Electropherogram of $H_xAsS_4^{y-}$, obtained with a coated capillary tube, and absorption spectra from 195 to 300 nm of $H_xAsS_4^{y-}$ and $HAsO_2S_2^{2-}$.

following decomposition products were determined in the coated capillary tube: oxodithioarsenate (47.8% with respect to tetrathioarsenate), oxomonothioarsenate (6.9%) and arsenate (20.1%). In the uncoated capillary tube only the decomposition products oxodithioarsenate (32.4%) and sulfide ions (3.1%) were formed. This shows that not only the pH but also the material of the capillary tubes greatly influence the type and extent of the decomposition. The capillary tube coated with polyacrylamide is only suitable for the analysis of the arsenic species arsenate and oxomonothioarsenate (Fig. 4). The detection limits at 195 nm are 0.5 and 0.1 mg/l, respectively. The uncoated capillary tube at pH 10 is also suitable for the determination of oxodithioarsenate and tetrathioarsenate (see also Fig. 4). The influence of temperature on the migration time was examined as an additional parameter. The results in Table 1 show that shortening of the analysis time due to a rise in temperature can only be achieved at the expense of increased decomposition of tetrathioarsenate. Minimum decomposition occurs at a capillary temperature of 20°C with a total analysis time of 11 min.

A further decrease in the analysis time should be possible with dynamic coating of the capillary tubes with cetyltrimethylammonium bromide (CTAB). The analyses were carried out with

Table 1
Evaluation of the electropherograms of model compounds using an uncoated capillary tube at different capillary tube temperatures

| Compound | Capillary tube temperature (°C) | Migration time (min) | Decomposition (%) |
|---|---|---|---|
| $HAsO_4^{2-}$ | 15 | 11.2 | – |
| | 20 | 10.1 | – |
| | 35 | 7.9 | – |
| $HAsO_3S^{2-}$ | 15 | 10.2 | 1.91 |
| | 20 | 9.1 | 1.20 |
| | 35 | 7.2 | 1.32 |
| $H_xAsS_4^{y-}$ | 15 | 5.4 | 2.22 |
| | 20 | 4.9 | 1.78 |
| | 35 | 4.0 | 2.32 |

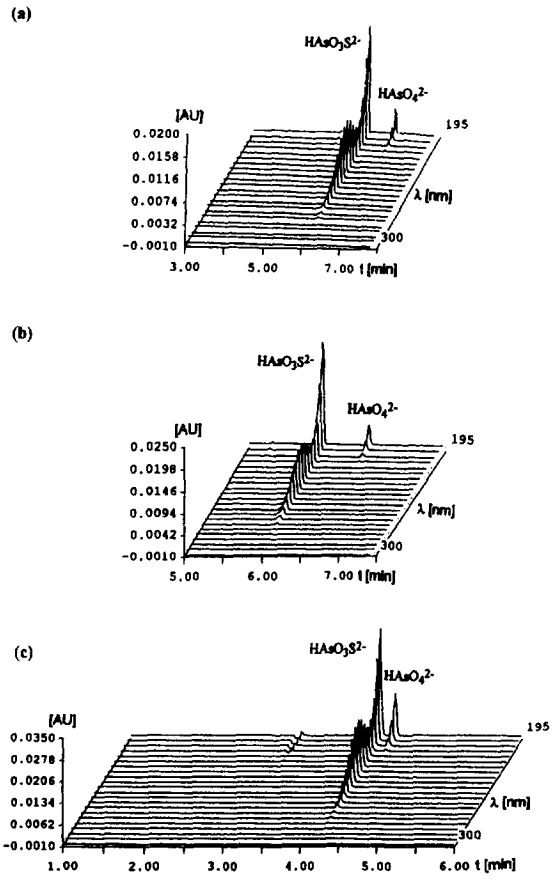


Fig. 5. Electropherograms of $HAsO_4^{2-}$ (50 mg/l) and $HAsO_3S^{2-}$ (50 mg/l) with (a) 0.0125, (b) 0.125 and (c) 1.25 mmol/l CTAB.

different CTAB concentrations in the range 0.0125–1.25 mmol/l. The decomposition of tetrathioarsenate increases with increasing concentration and reaches 100% at 1.25 mmol/l CTAB.

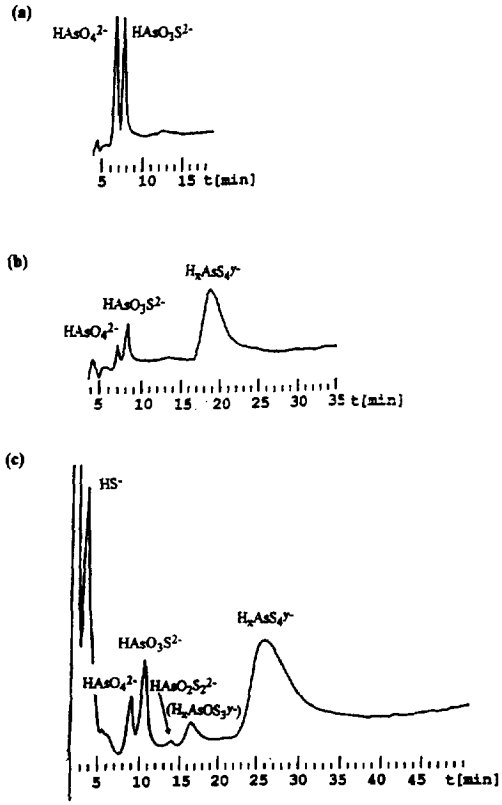


Fig. 6. Chromatograms obtained on a Nucleosil 10 Anion II column of (a) $HAsO_4^{2-}$ and $HAsO_3S^{2-}$ (50 mg/l), (b) $H_xAsS_4^{y-}$ (100 mg/l) and (c) mother liquor of $Na_3AsS_4 \cdot 8H_2O$ synthesis.

The addition of CTAB proved to be very suitable for the separation of arsenate and oxomonothioarsenate (see Fig. 5). The relative standard deviations (R.S.D.s) ($n = 5$) for the migration times were between 0.2 and 0.6%.

Table 2
Influence of pH on the capacity factors of $HAsO_3S^{2-}$ and $HAsO_4^{2-}$ using different separation columns and 15% acetonitrile

| Separation column | Compound | $k'$ | | |
|---|---|---|---|---|
| | | pH 7.0 | pH 7.5 | pH 8.0 |
| Nucleosil 10 Anion II | $HAsO_4^{2-}$ | 1.18 | 1.65 | 2.05 |
| | $HAsO_3S^{2-}$ | 1.18 | 1.65 | 2.50 |
| PRP X-100 | $HAsO_4^{2-}$ | 10.10 | 12.67 | 13.94 |
| | $HAsO_3S^{2-}$ | 10.10 | 25.27 | 25.70 |

An uncoated capillary tube with phosphate buffer (pH 10) is most suitable for the simultaneous determination of all four arsenic(V) species examined (see Fig. 3). However, quantification becomes difficult because of the decomposition of oxodithioarsenate and tetrathioarsenate: the R.S.D.s of the decomposition are 13 and 0.6%, respectively, under constant analysis conditions. Sufficient reproducibility of the quantitative results, therefore, cannot be achieved with oxothioarsenate present. A coated capillary tube at pH 8 and an uncoated tube at pH 10 with CTAB as a modifier can be used for the determination of oxodithioarsenate in addition to arsenate.

### 3.3. Ion chromatography

Mainly highly basic anion exchangers on the basis of both silica gel and polymer have been used in analyses for arsenic species. Good results were achieved with basic anion exchangers on the basis of styrene–divinylbenzene with a low

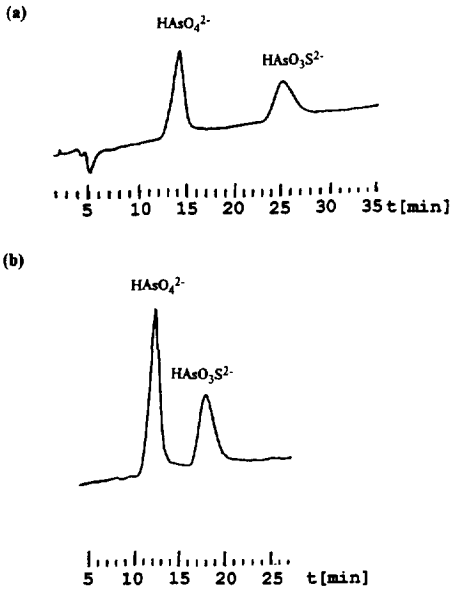


Fig. 7. Chromatograms obtained on a PRP X-100-column of (a) $HAsO_4^{2-}$ and $HAsO_3S^{2-}$ (50 mg/l), mobile phase pH 8.0, and (b) $HAsO_4^{2-}$ and $HAsO_3S^{2-}$ (50 mg/l), mobile phase pH 7.

Table 3
Evaluation of the chromatograms of model compounds

| Column | Compound | Retention time (min) | $k'$ | Resolution | Asymmetry |
|---|---|---|---|---|---|
| Nucleosil 10 Anion II | $HAsO_4^{2-}$ | 6.9 | 2.05 | | 0.67 |
| | | | | 3.13 | |
| | $HAsO_3S^{2-}$ | 7.9 | 2.50 | | 1.36 |
| | | | | 5.42 | |
| | $HAsO_2S_2^{2-}$ | 13.9 | 5.10 | | 1.00 |
| | | | | 1.86 | |
| | $(H_xAsOS_3^{y-})$ | (16.5) | (6.25) | | (2.00) |
| | | | | 2.89 | |
| | $H_xAsS_4^{y-}$ | 25.7 | 10.32 | | 2.40 |
| PRP X-100 | $HAsO_4^{2-}$ | 12.6 | 12.67 | | 1.00 |
| | | | | 12.08 | |
| | $HAsO_3S^{2-}$ | 18.4 | 25.27 | | 1.25 |
| | | | | 3.67 | |
| | $HAsO_2S_2^{2-}$ | Not elutable | – | – | – |
| | $(H_xAsOS_3^{y-})$ | – | – | | – |
| | | | | – | |
| | $H_xAsS_4^{y-}$ | Not elutable | – | | – |

Table 4
Comparison of the separating systems

| Parameter | IC | | CE | | |
|---|---|---|---|---|---|
| Column/capillary tube | Nucleosil 10 Anion II | PRP X-100 | Polyacrylamide-coated capillary tube | Uncoated capillary tube | |
| Buffer/eluent | Gluconate–borate (pH 8.0), conductivity 304 $\mu$S/cm | Gluconate–borate (pH 7.5), conductivity 195 $\mu$S/cm | 20 mmol/l phosphate buffer (pH 8.0) | 20 mmol/l phosphate buffer (pH 10.0) | 20 mmol/l phosphate buffer, (pH 10.0)–1.25 mmol/l CTAB |
| Detection limit (mg.l) | $HAsO_4^{1-}$ 25.0<br>$HAsO_3S^{3-}$ 25.0 | $HAsO_4^{3}$ 2.5<br>$HAsO_3S^{3-}$ 5.0 | $HAsO_4^{3}$ 0.5<br>$HAsO_3S^{3-}$ 0.1 | $HAsO_4^{3}$ 0.25<br>$HAsO_3S^{3-}$ 0.10<br>$AsS_4^{3}$ 0.10 | $HAsO_4^{3}$ 0.10<br>$HAsO_3S^{3-}$ 0.05 |
| Decomposition (%) | $HAsO_4^{2-}$ –<br>$HAsO_3S^{2-}$ –<br>$HAsO_2S_2^{3}$ –<br>$H_xAsS_4^{y-}$ 13.73 | $HAsO_4^{3}$ –<br>$HAsO_3S^{3-}$ –<br>$HAsO_2S_2^{3}$ not elutable<br>$H_xAsS_4^{y-}$ not elutable | $HAsO_4^{3}$ .<br>$HAsO_3S^{3-}$ 2.53<br>$H_xAsS_4^{y}$ 74.10 | $HAsO_4^{3}$ .<br>$HAsO_3S^{3-}$ 0.76<br>$H_xAsS_4^{y}$ 1.08 | $HAsO_4^{3}$ –<br>$HAsO_3S^{3-}$ –<br>$H_xAsS_4^{3}$ 100 |
| Time of intake | 5 h | 5 h | – | – | 5 min (rinse time of buffer) |
| Sample volume | 5–50 $\mu$l | 5–50 $\mu$l | 5–50 nl | 5–50 nl | 5–50 nl |

capacity especially for the determination of arsenic species in biological matrices and sea water with their high chloride contents [19]. The low reversed-phase character of the exchange matrix has a positive effect [20]. The selection of the eluent for the non-suppressed conductivity was oriented to the separation of sulfur species (sulfur anions, sulfite, sulfate and thiosulfate) for which a glyconate–borate eluent had proved successful [21]. For the determination of the influence of the pH in the range 7–8 the capacity factors of arsenate and oxomonothioarsenate as the most stable arsenic species were determined. The results are summarized in Table 2.

pH 8.0 was found to be the optimum for the Nucleosil 10 Anion II column (Fig. 6). A higher pH is not suitable for this column because of the sensitivity to hydrolysis of the silica gel matrix and because of poor detection limits caused by the strongly increasing conductivity of the eluent, dependent on pH. The shortest retention time with good resolution was given by an eluent with a pH of 7.5 for the separation of arsenic species on the PRP X-100 column (Fig. 7).

The good reproducibility of the capacity factors ($k'$) is shown by the 3.8% R.S.D. for arsenate and oxomonothioarsenate using the Nucleosil 10 Anion II column and 1% using the PRP X-100 column. Table 3 shows that all arsenic species examined can be separated with the Nucleosil 10 Anion II column. However, it is not suitable for quantification on account of the poor reproducibility compared with analysis using the PRP X-100 column and on account of the decomposition of tetrathioarsenate into arsenate (0.44%) and oxodithioarsenate (13.3%). A further substance was detected in the analysis of a mother liquor from the synthesis of tetrathicarsenate, with a retention time of 16.46 min. This compound is probably oxotrithionate, but its synthesis was not successful.

The strength of this separation system lies in the analysis of all oxothioarsenic species. The bad peak symmetry with the silica gel column compared with the polymer column is caused by the slow pH-dependent hydrolysis of the silica gel matrix. The high asymmetry factor of tetrathicarsenate is caused by the long retention time and decomposition. Only the species arsenate and oxomonothioarsenate can be separated with the polymer column; the remaining arsenic species are not eluted with the eluent used.

### *3.4. Comparison between capillary zone electrophoresis and ion chromatography*

The comparison between the tested separation systems shows that the greatest difficulties with the two methods arise from the pH-dependent decomposition of the arsenic species and from the correlations with the separation materials. Ion chromatography is only suitable for the determination of arsenate and oxomonothioarsenate, and the system with the PRP X-100 polymer column has better detection limits and reproducibility than that with the Nucleosil 10 Anion II column. The best results with the three separation systems for capillary zone electrophoresis were achieved with the use of an uncoated quartz capillary with phosphate buffer (pH 10.0). This separation system also showed higher efficiency than ion chromatography with regard to separation capacity and reproducibility. The detection limits with both systems are not directly comparable because different detectors were used. Table 4 shows a comparison between all the separation systems examined with regard to the extent of decomposition, time requirement and sample amount.

## References

[1] J.F. López-Sánchez, M.B. Amran, M.D. Lakkis, F. Lagarde, G. Rauret and M.J.F. Leroy, Fresenius' J. Anal. Chem., 348 (1994) 810.
[2] P. Morin, M.B. Amran, S. Favier, R. Heimburger and M. Leroy, Fresenius' J. Anal. Chem., 342 (1992) 357.
[3] R. Rubio, A. Padro, J. Alberti and G. Rauret, Anal. Chim. Acta, 283 (1993) 60.
[4] R. Rubio, A. Padro, J. Alberti and G. Rauret, Mikrochim. Acta, 109 (1992) 39.
[5] E.H. Larsen and S.H. Hansen, Mikrochim. Acta, 109 (1992) 47.
[6] P. Morin, M.B. Amran, S. Faver, R. Heimburger and M. Leroy, Fresenius' J. Anal. Chem., 339 (1991) 504.
[7] F.T. Henry and T.M. Thorpe, Anal. Chem., 52 (1980) 80.

[8] B.S. Sheppard and A.J. Caruso, Analyst, 107 (1992) 971.
[9] J.S. Blais, G.-M. Momplaisir and W.D. Marshall, Anal. Chem., 62 (1990) 1161.
[10] L. Ebdon, S. Hill, A.B. Walton, G.E. Millward and M. Whitfield, Analyst, 113 (1988) 1159.
[11] J.J. Thompson and R.S. Houk, Anal. Chem., 58 (1986) 2541.
[12] D.G. Iverson, M.A. Anderson, T.R. Holm and R.R. Stanforth, Environ. Sci. Technol., 13 (1979) 1491.
[13] C.T. Tye, S.J. Haswell, O. O'Neil and K.C.C. Bancroft, Anal. Chim. Acta, 169 (1985) 195.
[14] D. Beauchemin, M.E. Bednas, S.S. Berman, J.W. McLaren, K.W.M. Siu and R.E. Sturgeon, Anal. Chem., 60 (1988) 2209.
[15] S. Branch, P. O'Neil, K.C.C. Bancroft and L. Ebdon, Anal. Proc., 26 (1989) 73.
[16] J.J. Thompson and R.S. Houk, Anal. Chem., 58 (1986) 2541.
[17] G. Schwedt, M. Rieckhoff and F. Menzel, in preparation.
[18] E. Thilo, K. Hertzog and A. Winkler, Z. Anorg. Allg. Chem., 373 (1970) 111.
[19] G.K. Low, G.E. Batley and S.J. Buchmann, Chromatographia, 22 (1987) 292.
[20] D.P. Lee, J. Chromatogr. Sci., 22 (1984) 327.
[21] R.E. Poulson, J. Chromatogr. Sci., 25 (1987) 409.