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Effect of electrolyte composition in the capillary electrophoretic separation of inorganic/organic anions in the presence of cationic polymers

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Abstract

Electrolyte modification with two cationic polyelectrolytes has been investigated for the separation of inorganic anions, aliphatic and aromatic carboxylic acids, and sulphonic acids. Changes in migration rates and separation selectivity, arising from hydrophobic interactions, ion exchange, and changes in electroosmotic flow were studied for benzoate, chromate and phosphate + chloride counter-ions as a function of pH, and for the addition of methanol and acetonitrile. Large changes in separation selectivity, for aliphatic and sulphonic acids, were observed with benzoate electrolytes as compared to chromate electrolytes. In addition, electroosmotic flow was faster in the former separation electrolytes by about 65%. Changes in selectivity as a result of hydrophobic interactions were investigated with a series of aromatic acids where shifts in migration order were observed as function of polyelectrolyte concentration. For inorganic anions, in chromate electrolytes at a constant concentration of polyelectrolyte, the addition of methanol or acetonitrile decreased migration rates by as much as 67%. The analytical merits of the methodology were examined for a potash (concentrated KCl) sample and a simulated decontamination solution containing EDTA, Fe^{3+}(EDTA) and oxalate.

1. Introduction

The analysis of small organic and inorganic anions is of interest to a wide range of industries such as food and detergent industries [1–6] and electronic components manufacturing industries [7]. In recent years, ion chromatography (IC) has been used to analyze for organic [1–5,8–13] and inorganic anions [14–17] of widely differing valency and hydrophilicity. Capillary electrophoresis (CE) offers a separation mechanism complementary to IC, but in addition, has minimal sample and reagent requirements [18], faster analysis times [19], and superior separation efficiency and peak capacity [20]. Manipulation of selectivity in the CE separation of small organic and inorganic anions has primarily involved: (i) changes in the composition of the separation electrolyte (i.e. choice of type and/or concentration of electrolyte [21–23], addition of organic solvents [24,25] and changes in pH [23,24]); (ii) use of cationic surfactants (non-micellar) of relatively short chain lengths either alone [26–29] or in the presence of organic modifiers [30–32]; and

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(iii), employment of micelles for aliphatic [32] and aromatic acids [33] and for less hydrophilic anions [34]. An alternative approach for selectivity control is the use of cationic polyelectrolytes, which has been examined briefly for the separation of organic ions [35,36] and more recently, in our laboratories, for inorganic anions [37]. Since our studies with inorganic anions gave encouraging results, this approach for control of selectivity has been studied further for a series of aliphatic carboxylic and sulphonic anions with both sodium benzoate and sodium chromate electrolytes. The use of polyelectrolytes was also examined for the separation of a series of aromatic acids to ascertain the effect of hydrophobic interactions on selectivity. Organic modifiers, methanol (1–65%, v/v) and acetonitrile (1–35%, v/v), were also employed to investigate their effects on separation selectivity. Finally, the polyelectrolyte systems were applied to samples of potash (concentrated KCl), and a simulated decontamination solution.

2. Experimental

2.1. Instrumentation

The CE instrument was a Quanta 4000 (Waters Chromatography Division of Millipore, Milford, MA, USA) with a Maxima 820 data station (version 3.30 Dynamic Solutions); data acquisition rate was 20–25 points/s. Power supply (30 kV) polarity was reversed (cathode at injection end). Fused-silica capillaries (Polymicro Technologies, Phoenix, AZ, USA) were 60 cm (53 cm to detector) × 365 μm O.D. × 77 μm I.D.; unless otherwise noted. Analyte zones were detected in the indirect mode by absorbance at 254 nm (Hg lamp) with the exception of the aromatic acids, which were detected via direct absorbance at 214 nm (Zn lamp). Samples were introduced hydrostatically by elevation of the sample vials to 10 cm for 15 s. All pH values were measured with a Fisher Accumet pH meter (Model 805) calibrated immediately prior to use.

2.2. Reagents and procedures

Deionized and then distilled water (Corning, Mega-Pure, MP-6A and D2, NY, USA) was used to prepare all solutions, and all reagents were reagent grade unless noted otherwise. Sodium chromate tetrahydrate (99 + %; Aldrich, Milwaukee, WI, USA) was used to prepare separation electrolyte solutions (0.005 *M*) as described previously [41]. Sodium benzoate electrolyte (0.005–0.02 *M*) was prepared by adding stoichiometric amounts of sodium hydroxide (BDH, Toronto, Canada) to benzoic acid (BDH). Analytical-grade methanol and acetonitrile were purchased from BDH. Tetramethylammonium hydroxide (25%, w/w; Aldrich) was used for pH adjustment of the sodium benzoate polypyrrolidinium electrolytes. NICE-Pak OFM Anion-BT (registered trademark of Waters Chromatography Division of Millipore) was used as an electroosmotic flow modifier. The polyelectrolytes poly(1,1-dimethyl-3,5-dimethylenepiperidinium chloride) (PDDPiCl; Polysciences, Warrington, PA, USA) and poly(1,1-dimethyl-3,5-dimethylenepyrrolidinium chloride) (PDDPyCl, Aldrich) were converted to the chromate and benzoate forms as described elsewhere [37]. Stock sample solutions (0.02 *M*) were diluted to 10^{-4} *M* (carboxylic and sulphonic acids) and $5 \cdot 10^{-5}$ *M* (aromatic acids and inorganic anions) prior to injection.

2.3. Capillary preparation

Capillaries were conditioned with the separation electrolyte for 30 min before the first run and for 2 min between runs, which has been shown to result in improved migration time reproducibility [38]. Prior to switching to a new electrolyte system, capillaries were purged by application of pressure (15 mmHg; 1 mmHg = 133.322 Pa) in the following sequence: water (5 min), 0.1 *M* HCl (10 min), water (5 min), 0.1 *M* NaOH (10 min) and water (5 min). Electrolyte pH adjustments were done with 0.001 *M* chromium(VI) oxide or 0.1% (v/v) of a 25%

(w/w) solution of tetramethylammonium hydroxide.

2.4. Calculations

Electroosmotic flow (μ_{eos}) was determined for each one of the runs of both standards and mixtures from the expression $\mu_{eos} = \nu_{eos}/E$, where ν_{eos} is the neutral marker (water) migration velocity (cm/s), μ_{eos} is electroosmotic mobility ($cm^2\ V^{-1}\ s^{-1}$), and E is the field strength (V/cm). The water peak was about 0.4 min wide (base width) and migration time was measured at the peak minimum (negative peak). Electroosmotic mobility has been given a positive sign when it was directed towards the detector. Analyte electrophoretic mobility (μ_{ep}) was calculated from the expression $\mu_{ep} = (\mu_{mig}/E) - \mu_{eos}$, where μ_{mig} is the *net migration* velocity of an analyte zone. The number of theoretical plates (N) was calculated from, $N = 5.54\ (t_{mig}/w_{0.5})^2$ where t_{mig} is zone *net* migration time (s) and $w_{0.5}$ is the width (in time units) at 50% maximum peak height. Resolution (R_s) was calculated from $R_s = 2\Delta t_{mig}/(w_1 + w_2)$, where Δt_{mig} is the difference in net migration time between zones 1 and 2, and w_1 and w_2 are their respective base widths in time units.

3. Results and discussion

3.1. Choice of polyelectrolyte

During this and previous investigations [37] of PDDPy, PDDPi, polybrene and diethylaminoethyldextran polyelectrolyte systems we found that PDDPy and PDDPi systems gave better electroosmotic flow stability and higher separation efficiencies. Consequently, this report focuses on the use of these two polyelectrolytes. These five- and six-membered ring heterocyclics have quite similar average molecular masses (200 000 to 300 000), and in these studies it was found that their CE behaviour was very similar.

3.2. Electroosmotic flow studies

In our previous studies with polyelectrolytes [37] a chromate counter-ion was used in the electrolyte since this permitted both indirect detection of a wide range of species and allowed direct comparison with a standard commercial system. To permit a wider range of interactions between the polyelectrolyte and the analytes, the monovalent and more hydrophobic anion benzoate was also included in the present study. Results of studies of the dependence of the electroosmotic mobility (μ_{eos}) on sodium benzoate concentration (0.005–0.02 M) in the pH range 6–10 are shown in Fig. 1 for 0.08% (w/v) PDDPybenzoate. These results show that μ_{eos} decreased slightly with increasing sodium benzoate concentration. This decrease in μ_{eos} can be

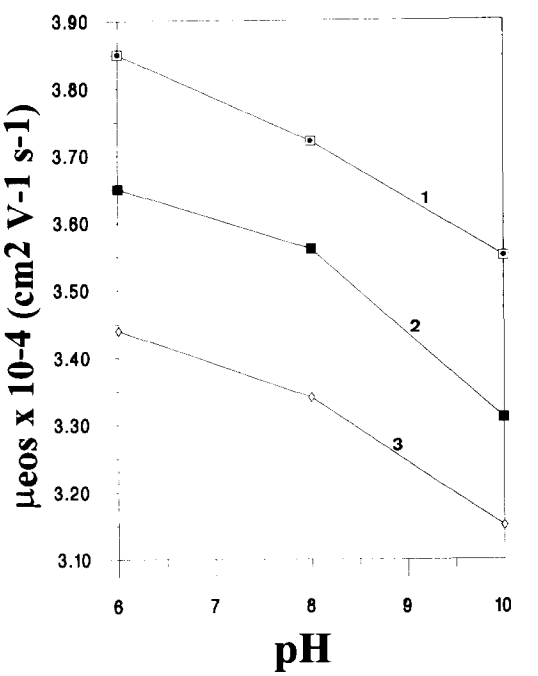

Fig. 1. Plot of electroosmotic mobility versus pH for PDDPybenzoate. Curves 1, 2 and 3: 0.005, 0.01 and 0.02 M sodium benzoate, respectively, in the presence of 0.08% (w/v) PDDPybenzoate. Experimental conditions: neutral marker, water; capillary end-to-end length 68.7 cm; injection-to-detection window length 61.4 cm; field strength 291 V/cm; direction of electroosmotic flow is towards the anode.

attributed to ionic strength effects on the silica–electrolyte double layer, which result in a decrease of the ζ potential [39], but other parameters such as counter-ion charge, hydrated radius, and hydrophilicity also appear to play a role in the way the counter-ion affects the magnitude of μ_{eos} [39,40]. To examine the effect of polyelectrolyte concentration, electroosmotic flow was studied in benzoate and chromate electrolytes containing PDDPy at pH 8 over the concentration range of 0.01–0.1% (w/v). These studies showed that electroosmotic mobility was larger for benzoate electrolytes by approximately 65%. This difference in μ_{eos} can be explained in the way chromate and benzoate interact with the positively charged layer. Divalent chromate is highly associated with the adsorbed polymer [41] in contrast to the monovalent and bulkier benzoate. This will result in a higher ζ potential for the benzoate electrolyte, and thus a faster electroosmotic flow (assuming no significant changes in dielectric constant or viscosity at the capillary–electrolyte interface). A weaker association of the benzoate counter-ion with the polyelectrolyte might also explain the decreasing μ_{eos} (as a function of pH) in comparison to the fairly constant μ_{eos} vs. pH profiles observed with the chromate system [37]. Exchange of benzoate by the smaller more hydrophilic hydroxide would cause changes in the double layer structure and charge, and consequently changes in μ_{eos} would be expected. Since the use of organic modifiers, such as methanol and acetonitrile, is known to decrease μ_{eos} and improve resolution and selectivity [39,42–47], the effects of these modifiers was examined for a polyelectrolyte system. The results in Fig. 2 show that μ_{eos} decreased with concentration of CH_3OH or CH_3CN for PDDPichromate at pH 8. This behaviour could provide a means to control μ_{eos} as well as separation selectivity in electrolytes containing polyelectrolytes. The trends in Fig. 2 are similar to those observed in bare fused-silica capillaries [39,42–47], and have been explained in terms of changes in medium dielectric constant [46], in the properties (charge, hydration) of the double layer [44], and in the solid–electrolyte interfacial viscosity [45].

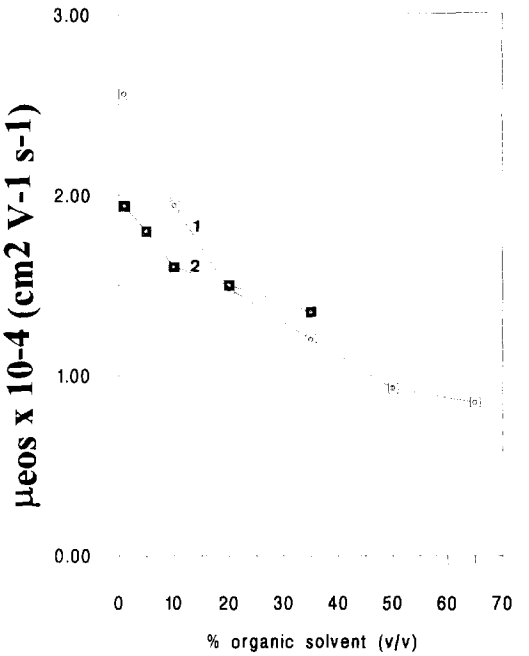

Fig. 2. Plot of electroosmotic mobility versus percent organic solvent. Curves 1 and 2: methanol and acetonitrile, respectively, with 0.1% (w/v) PDDPichromate at pH 8. Experimental conditions: neutral marker, water; capillary end-to-end length 58.2 cm; injection-to-detection window length 50.8 cm; field strength 344 V/cm; direction of electroosmotic flow is towards the anode.

3.3. Changes in migration rates and selectivity

Migration rates of organic acids (formate, acetate, oxalate, citrate, ethanesulphonate, butanesulphonate, pentanesulphonate and octanesulphonate) were measured in 0.08% (w/v) PDDPybenzoate as a function of pH (6–10) and sodium benzoate concentration (0.005–0.02 *M*). These studies showed that generally the anions had a higher μ_{ep} at higher concentrations of sodium benzoate for a given pH. Values of μ_{ep} at 0.005 *M* benzoate were in the range of $1 \cdot 10^{-4}$–$4 \cdot 10^{-4}$ $cm^2\ V^{-1}\ s^{-1}$ and increased by ca. 20% at the higher concentrations. These observations suggest an ion-exchange mechanism of interaction between the anions and the polycation where counter-ion displacement by analyte becomes less favourable at the higher concentrations of the benzoate. Changes in selectivity

were only significant for ions of different charge. For example, oxalate migrated prior to all anions at 0.02 *M* sodium benzoate (pH 8), but after ethanesulphonate, butanesulphonate and citrate at 0.01 *M* benzoate. Citrate and oxalate could not be detected at pH 6 (both divalent at this pH) irrespective of electrolyte concentration (0.005–0.02 *M*), even at sample concentrations as high as $5 \cdot 10^{-4}$ *M*. The low detection sensitivity for these species is not clear to us at the moment but might be due to a strong interaction with the polyelectrolyte resulting in migration of these anions away from the detector.

The effects of polyelectrolyte counter-ion on anion migration rates were examined in 0.005 *M* sodium chromate and 0.01 *M* sodium benzoate for PDDPy over the concentration range 0.01–0.08% (w/v) at pH 8. Although baseline resolution of all eight organic anions was achieved in 0.01% (w/v) PDDPychromate, their separation was not possible with the benzoate system presumably due to its more rapid μ_{eos}. Interestingly, the changes in μ_{ep} as a function of polyelectrolyte concentration were larger in the benzoate system. Electrophoretic mobilities decreased by 51% (citrate, oxalate) and by about 40% for the other monovalent analytes in the PDDPybenzoate concentration range 0.01–0.08% (w/v). Over the same concentration range with PDDPychromate, μ_{ep} decreased by about 17% for oxalate and only a few percent for the monovalent acids. These observations are consistent with a more effective analyte displacement of the monovalent benzoate counter-ion by the analyte as compared to chromate, which is in accordance with established eluotropic series in ion chromatographic separations [48]. The greater changes in μ_{ep} observed for the monovalent acids in benzoate relative to the ones observed in chromate polyelectrolytes may offer an advantage in manipulating separation selectivity for these species in view of the rather small changes in selectivity seen when ion-pairing reagents are used for their CE separation [26]. Separation efficiencies for the chromate system ranged between 35 545 and 397 608 theoretical plates and were consistently lower than the ones observed with the benzoate system (281 688–906 282 theoretical plates). The better efficiency for the benzoate electrolyte is due to a zone asymmetry effect associated with the more mobile (compared to most of the analytes) chromate ion as compared to the less mobile benzoate, which more closely matches analyte electrophoretic mobilities [21].

Organic solvents have been used to optimize CE separations of organic [43,46] and to a lesser extent inorganic species [30,31], and observed changes in selectivity have been attributed to changes in analyte effective charge and solvation [30,43,46]. Since the primary goal of this study was to evaluate polyelectrolytes for selectivity modification, the separation of a series of inorganic anions (bromide, chloride, iodide, fluoride, nitrate, thiocyanate, perchlorate and sulfate) was examined in methanol and acetonitrile. The results of this study are shown in Figs. 3 and 4; concentrations higher than those shown in Figs. 3 and 4 were not used because of precipitation of the polyelectrolyte. Fig. 3 shows that values of

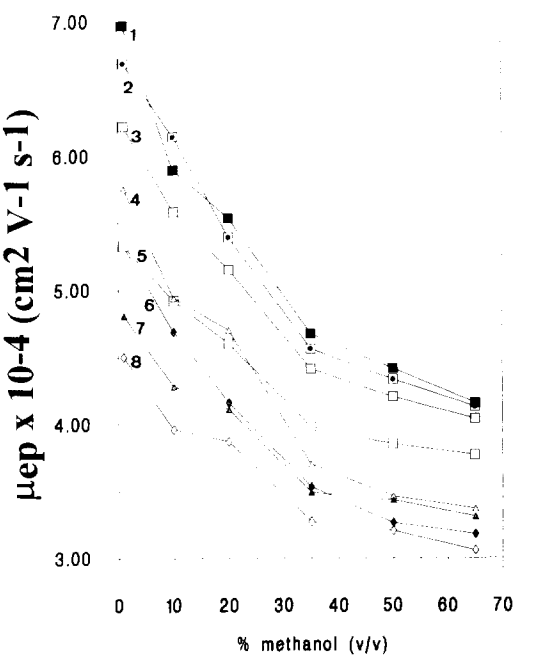

Fig. 3. Plot of electrophoretic mobility versus % CH_3OH. Curves: 1 = chloride; 2 = bromide; 3 = nitrate; 4 = sulfate; 5 = iodide; 6 = fluoride; 7 = thiocyanate; 8 = perchlorate. Other experimental conditions as for Fig. 2.

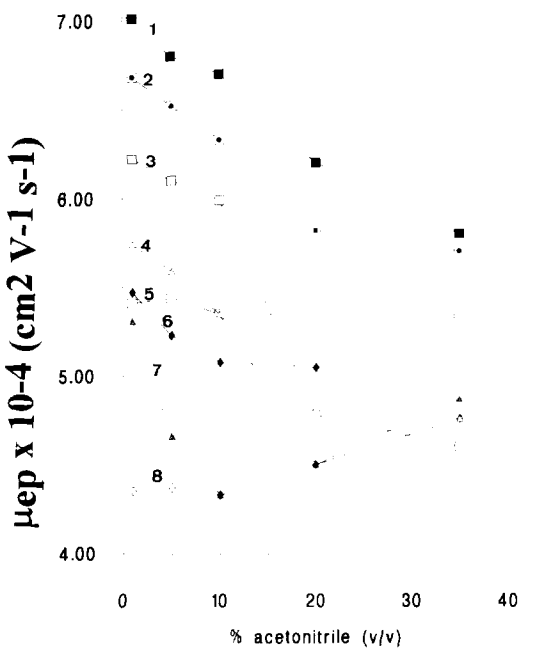

Fig. 4. Plot of electrophoretic mobility versus % CH_3CN. Curve designations and experimental conditions as for Fig. 3.

μ_{ep} decrease upon addition of methanol, and these changes, which are similar to those observed for simple aqueous electrolyte systems, can be of use for minor adjustments of selectivity. The variations in μ_{ep} in Fig. 3 are most likely a result of changes in analyte solvation [24,30,43,46] and changes in the dipole–anion interactions which are quite strong when methanol is used as the solvating medium [49]. When CH_3CN is used however, the anions show distinctly different behaviour with some anions exhibiting a minimum or increasing values of μ_{ep} (see Fig. 4). This difference in selectivity patterns observed in the two organic solvents can perhaps be attributed to their different solvation properties. Methanol is capable of solvating anionic species to a greater extent compared to acetonitrile and the former solvent offers a more structured medium (H-bonding network) as compared to acetonitrile. In addition, solvation of the polyelectrolyte, which prefers the aqueous phase, may play a more important role here, possibly due to the formation of water rich domains and/or the formation of different polymer configurations. The selectivity trends observed in the case of acetonitrile modifier plus polyelectrolyte are unique in comparison to the ones observed with acetonitrile plus OFM (surfactant) [31]. This is an indication that polyelectrolyte properties such as solvation and structural conformation play an important part in adjustment of relative migration and the observed selectivity patterns can not be exclusively attributed to changes in analyte solvation. Undoubtedly such changes in μ_{ep} could prove very useful for certain analytical problems. Since analyte peaks had between 94 244 and 523 218 theoretical plates, separation efficiency should not be a limiting factor in further development of these systems for chemical analysis.

3.4. Hydrophobic interactions

While the main mode of interaction between the polyelectrolytes and anions is expected to be ion exchange, polyelectrolytes should also be capable of interacting with analytes via hydrophobic interactions [50,51]. To investigate this possibility, the separation of a series of aromatic carboxylic acids (benzoic, 3,5-dihydroxybenzoic, salicylic, methylsalicylic and phthalic) was examined for polyelectrolyte (PDDPiCl) concentrations between 0.0075–0.2% (v/v) in a 0.005 *M* phosphate buffer at pH 6.8. Fig. 5 shows that baseline resolution of all five acids was easily achieved, but of more interest was the order of migration with respect to the neutral marker. Up to 0.2% (v/v) PDDPiCl, the anions benzoate, salicylate and 3-methylsalicylate migrated prior to the neutral marker (at about 4.7 min in Fig. 5), but phthalate and 4-hydroxybenzoate migrated after the neutral marker. Migration after the neutral marker, which was not observed with inorganic anions and aliphatic acids, indicates interactions other than ion exchange (possibly hydrophobic). Evidence of such interactions has been found in physico-chemical studies of polyelectrolyte solutions [50,51]). Although polyelectrolyte additives have been previously examined for the separation of aromatic acids [36], these changes in migration order were not reported.

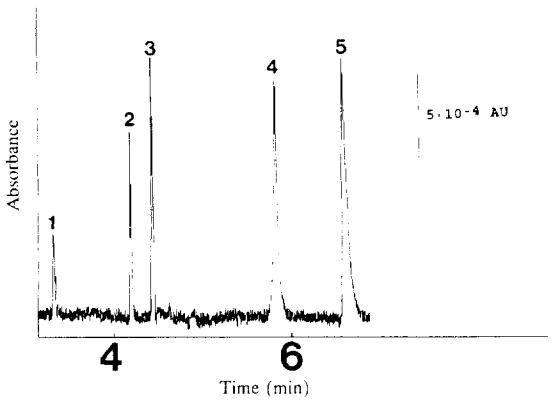

Fig. 5. Electropherogram for five aromatic acids in PDDPichloride. Peaks: 1 = benzoate; 2 = salicylate; 3 = 3-methylsalicylate; 4 = 3,5-dihydroxybenzoate; 5 = phthalate. Experimental conditions: 0.005 *M* sodium phosphate buffer plus 0.2% PDDPichloride (v/v) at pH 6.8. hydrostatic injection from 10 cm for 15 s; field strength 417 V/cm; direct UV detection at 214 nm.

Consequently, polyelectrolyte additives may offer significant advantages for the analysis of charged hydrophobic analytes in view of the poor selectivity often associated with the micellar electrokinetic separation of these compounds [52] and the prolonged analysis times observed in aqueous electrolytes modified with organic solvents under counter-electroosmotic conditions [24]. As for other polyelectrolyte systems, separation efficiencies (with the exception of phthalic acid) were in the range of 100 000–300 000 plates.

3.5. Applications

To evaluate the potential of the polyelectrolyte systems for chemical analysis, these systems were applied to samples that were known to be difficult to analyze by conventional IC methods. The first sample examined was a simulated decontamination solution that contained EDTA, Fe^{3+}(EDTA), citrate and oxalate. The analysis of these species is of importance to the power generating industry where they are used to remove corrosion products on heat transport systems. IC methods for these components are time consuming and prone to interference from metal ions other that iron [11]. It is anticipated that the ability to change the selectivity patterns via changes in electrolyte concentration, organic solvent content, and pH could prove useful for real decontamination solutions where the samples often contain a number of other metal complex species. Fig. 6 shows that with a polyelectrolyte system resolution of all four compounds was possible in about 4.6 min; IC analysis requires preliminary sample treatment and a separation time of up to 30 min. Another sample type examined was potash fertilizer brines. A potash (concentrated KCl) sample was diluted 100-fold and injected without any sample pretreatment. The electropherogram (Fig. 7) showed baseline resolution of bromide and sulfate from the large excess of chloride, which could not be achieved without the polyelectrolyte (0.005 *M* sodium chromate plus 2.5 m*M* OFM at pH 8). Calibration was linear (R^2 = 0.9998) for bromide and sulfate in the concentration range $5 \cdot 10^{-5}$–$5 \cdot 10^{-3}$ *M* (five concentration points); sensitivity plots [53] indicated maximum changes in sensitivity of about 23% for bromide ($1 \cdot 10^{-4}$–$5 \cdot 10^{-3}$ *M*) and 5% for sulfate ($5 \cdot 10^{-4}$–$5 \cdot 10^{-3}$ *M*). The acid profile of homemade white wine was also obtained (Fig. 8) without performing any quantitation. The sam-

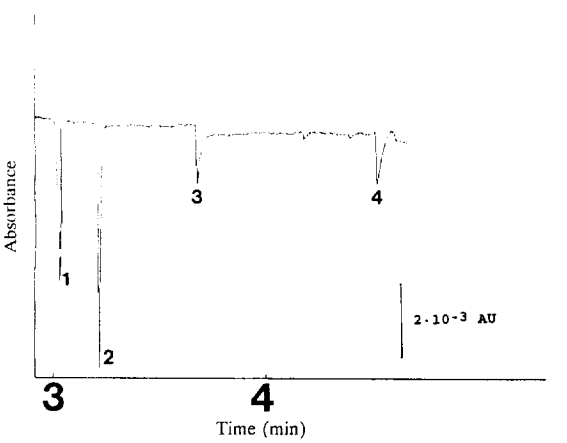

Fig. 6. Electropherogram of a simulated decontamination solution. Peaks: 1 = Fe^{3+}(EDTA); 2 = oxalate; 3 = citrate; 4 = EDTA. Experimental conditions: 0.005 *M* sodium chromate plus 0.23% (w/v) PDDPichromate at pH 8.4; field strength, 333 V/cm.

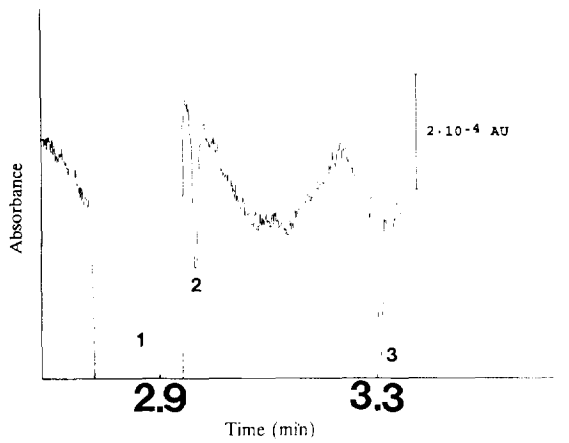

Fig. 7. Electropherogram of potash sample. Peaks: 1 = chloride; 2 = bromide; 3 = sulfate. Experimental conditions: 0.005 *M* sodium chromate plus 0.154% (w/v) PDDPichromate at pH 8.00; field strength 333 V/cm; capillary end-to-end length 60 cm; injection-to-detection window length 54 cm; potash concentration, 0.1007% (w/v).

ple was diluted 100-fold and injected. Identification of the various components was done by comparison of retention times with various acid standards. The migration order observed was substantially different compared to a CE separation of these acids in white wine previously reported [54]. This novel migration order may offer advantages in terms of resolution and quantitation of a minor acid migrating close to one present in excess.

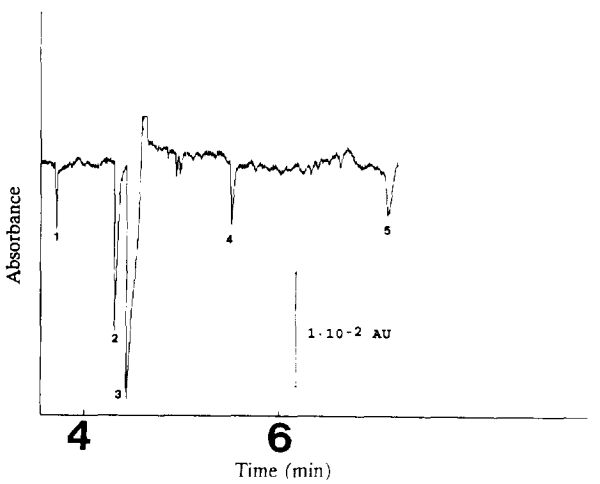

Fig. 8. Electropherogram of home-made white wine. Peaks: 1 = malate; 2 = lactate; 3 = acetate; 4 = succinate; 5 = citrate. Experimental conditions: sample dilution, 1:100 dilution; electrolyte, 0.005 *M* sodium chromate plus 0.154% (w/v) PDDPichromate at pH 8; field strength 417 V/cm.

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References

[1] D.P. Lee, *J. Chromatogr. Sci.*, 20 (1982) 203–208.
[2] D.P. Lee and A.D. Lord, *LC·GC*, 5 (1986) 261–266.
[3] D. Murawski, *J. Chromatogr.*, 546 (1991) 351–367.
[4] D. Zhou and D.J. Pietrzyk, *Anal. Chem.*, 64 (1992) 1003–1008.
[5] P.E. Shaw and C.W. Wilson III, *J. Sci. Food Agric.*, 34 (1983) 1285–1288.
[6] D.P. Lee, *J. Chromatogr. Sci.*, 22 (1984) 327–331.
[7] L.J. Anthony and E. Delgado, presented at the *International Ion Chromatography Symposium 1993, Baltimore, MD, September 1993.*
[8] T.A. Walker, T.V. Ho and N. Akbari, *J. Liq. Chromatogr.*, 14 (1991) 1351–1366.
[9] T.A. Walker, T.V. Ho and N. Akbari, *J. Liq. Chromatogr.*, 12 (1989) 1213–1230.
[10] P.G. Rigas and D.J. Pietrzyk, *Anal. Chem.*, 59 (1987) 1388–1393.
[11] R.M. Cassidy and S. Elchuk, *Anal. Chem.*, 57 (1985) 615–620.
[12] D. Grosjean, A. Van Neste and S.S. Parmar, *J. Liq. Chromatogr.*, 12 (1989) 3007–3017.
[13] P. Walser, *J. Chromatogr.*, 439 (1988) 71–81.
[14] R.M. Cassidy and S. Elchuk, *J. Chromatogr. Sci.*, 21 (1983) 454–459.
[15] A. Siriraks and J. Stillian, *J. Chromatogr.*, 640 (1993) 151–160.
[16] W. Shotyk, *J. Chromatogr.*, 640 (1993) 309–316.
[17] N. Chauret and J. Hubert, *J. Chromatogr.*, 469 (1989) 329–338.
[18] J. Romano, P. Jandik, W.R. Jones and P.E. Jackson, *J. Chromatogr.*, 546 (1991) 411–421.
[19] M.V. Pickering, *LC·GC*, 7 (1989) 752–754.

[20] W.R. Jones and P. Jandik, *J. Chromatogr.*, 608 (1992) 385–393.
[21] P. Jandik and W.R. Jones, *J. Chromatogr.*, 546 (1991) 431–443.
[22] L. Kelly and R.J. Nelson, *J. Liq. Chromatogr.*, 16 (1993) 2103–2112.
[23] F. Foret, M. Deml, V. Kahle and P. Boček, *Electrophoresis*, 7 (1986) 430–432.
[24] S. Fujiwara and S. Honda, *Anal. Chem.*, 59 (1987) 487–490.
[25] F. Foret, S. Fanali, L. Ossicini and P. Boček, *J. Chromatogr.*, 470 (1989) 299–308.
[26] W.R. Jones and P. Jandik, *J. Chromatogr.*, 546 (1991) 445–458.
[27] X. Huang, J.A. Luckey, M.J. Gordon and R.N. Zare, *Anal. Chem.*, 61 (1989) 766–770.
[28] E.L. Pretswell, A.R. Morrisson and J.S. Park, *Analyst*, 118 (1993) 1265–1267.
[29] X. Huang, M.J. Gordon and R.N. Zare, *J. Chromatogr.*, 480 (1989) 285–288.
[30] M.P. Harrold, M. Jo Wojtusik, J. Riviello and P. Henson, *J. Chromatogr.*, 640 (1993) 463–471.
[31] W. Buchberger and P.R. Haddad, *J. Chromatogr.*, 608 (1992) 59–64.
[32] R. Szucs, J. Vindevogel and P. Sandra, *J. High. Resolut. Chromatogr.*, 14 (1991) 692–693.
[33] W.C. Brumley and C.M. Brownrigg, *J. Chromatogr.*, 646 (1993) 377–389.
[34] T. Kaneta, S. Tanaka, M. Taga and H. Yoshida, *Anal. Chem.*, 64 (1992) 798–801.
[35] S. Terabe and T. Isemura, *Anal. Chem.*, 62 (1990) 650–652.
[36] S. Terabe and T. Isemura, *J. Chromatogr.*, 515 (1990) 667–676.
[37] C. Stathakis and R.M. Cassidy, *Anal. Chem.*, 66 (1994) 2110–2115.
[38] S.C. Smith, J.K. Strasters and M.G. Khaledi, *J. Chromatogr.*, 559 (1991) 57–68.
[39] K. Salomon, D.S. Burgi and J.C. Helmer, *J. Chromatogr.*, 559 (1991) 69–80.
[40] H.J. Isaaq, I.Z. Atamna, G.M. Muschik and G.M. Janini, *Chromatographia*, 32 (1991) 155–161.
[41] F. Osawa, *Polyelectrolytes*, Marcel Dekker, New York, 1971.
[42] B.B. VanOrman, G.G. Liversidge, G.L. McIntire, T.M. Olefirowicz and A.G. Ewing, *J. Microcol. Sep.*, 2 (1990) 176–180.
[43] C. Stathakis, P.L. Warburton and R.M. Cassidy, *J. Chromatogr. A*, 659 (1994) 443–447.
[44] W. Schutzner and E. Kenndler, *Anal. Chem.*, 64 (1992) 1991–1995.
[45] C. Schwer and E. Kenndler, *Anal. Chem.*, 63 (1991) 1801–1807,
[46] K. Salomon, D.S. Burgi and J.C. Helmer, *J. Chromatogr.*, 549 (1991) 375–385.
[47] J.C. Reijenga, G.V.A Aben, Th.P.E.M. Verheggen and F.M. Everaerts, *J. Chromatogr.*, 260 (1983) 241–254.
[48] P.R. Haddad and P.E. Jackson, *Ion Chromatography —Principles and Applications* (*Journal of Chromatography Library*, Vol. 46), Elsevier, Amsterdam, 1990, Ch. 2, p. 23.
[49] R.G. Bates, in J.F. Coetzee and C.D. Ritchie (Editors), *Solute–Solvent Interactions*, Marcel Dekker, New York, 1969, Ch. 2, pp. 74–78.
[50] N.J. Turro and I.F. Pierola, *J. Phys. Chem.*, 87 (1983) 2420–2423.
[51] T. Itaya, K. Ueda, H. Ochiai and A. Imamura, *Polymer J.*, 25 (1993) 545–552.
[52] S. Terabe, Y. Miyashita, O. Shibata, E.R. Barnhart, L.R. Alexander, D.G. Patterson, B.L. Karger, K. Hosoya and N. Tanaka, *J. Chromatogr.*, 516 (1990) 23–31.
[53] M. Janoski and R.M. Cassidy, *LC · GC*, 10 (1992) 692–696.
[54] X. Huang, J.A. Luckey, M.J. Gordon and R.N. Zare, *Anal. Chem.*, 61 (1989) 766–770.