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Method development approaches for capillary ion electrophoresis

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ABSTRACT

Capillary ion electrophoresis (CIE) is a capillary electrophoretic technique optimized for rapid determination of low-molecular-mass inorganic and organic ions. CIE predominantly employs indirect UV detection since the majority of the analytes lack specific chromophores. Described are three methods for detection and electrolyte optimization. The first method discussed approaches for optimizing sensitivity, selectivity and peak confirmation using a chromate electrolyte and selected detection wavelengths. Peak confirmation is aided by using both direct and indirect detection of analytes. The second and third methods involve an unattended electrolyte development approach for instruments that only provide fresh electrolyte on the injection side of the capillary. The electrolyte composition is changed in both the injection side vial and in the capillary before each sample injection while leaving the receiving side electrolyte vial constant at the initial electrolyte composition. In one mode, the concentration of the electroosmotic flow (EOF) modifier used to induce anodic flow is varied while keeping the background electrolyte composition constant. In a second experiment, the background electrolyte co-ion is sequentially changed from high mobility to low mobility while keeping the EOF modifier concentration constant. The end effect is to achieve a broad range of controlled peak symmetry for analytes in a sample matrix. The results are compared to separations obtained when the injection side and receiving side electrolytes are manually matched.

INTRODUCTION

Capillary ion electrophoresis (CIE) (Water's tradename: Capillary Ion Analysis, CIA), introduced in the beginning of this decade, is finding solutions to a number of difficult and challenging problems ranging from sulfur specification of Kraft black liquors in the pulp and paper industry to determining trace impurities in the presence of percent level of ionic material to routine analysis of parts per billion (ppb) level contaminants in high purity water [1–11]. The rapid growth of this technique is due to the inherent simplicity of the hardware and because the nature of the fused-silica capillary's inner wall surface can be altered by the choice of electrolyte. In essence the electrolyte and the polarity of the applied voltage programs the capillary to separate anionic, cationic or neutral species. This represents a substantial economy over established ion analysis techniques such as ion chromatography where separations are wholly dependent on dedicated specialized analytical columns that cost as much as 100 times more than the fused-silica capillaries.

To date, photometric detection in CIE has been dominated by the indirect ultraviolet mode [12,13] as an "universal" detection approach, with some applications of direct UV having been reported. Other reported detection modes include indirect fluorometry [14], direct conductometry [15,16] and suppressed conductometry [17,18]. However, UV detection, offers more versatility over bulk property detectors such as conductivity; there is more flexibility in optimizing sensitivity through a proper selection of the electrolyte co-ions and measurement wavelength. This is especially important when analyzing samples containing disparate concentration levels of the analyte [9]. Also, there is a greater selection of UV absorbing co-ions with mobilities similar to the inorganic anions of interest than there are fluorescent or suppressible co-ions.

In CIE separations of anions, a quaternary amine EOF modifier is used in the electrolyte. This dy-

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namically coats the inner wall of the fused-silica capillary. The modifier imparts a positive charge on the wall and changes the EOF towards the anode hence augmenting the mobility of the anions. Since the analysis time is short (3 to 5 min), high sample throughput is achievable through automation. Electrolytes containing the EOF modifier equilibrate rapidly in the capillary. An unused 60 cm × 75 μm fused-silica capillary is stabilized in less than 2 min by drawing electrolyte into the capillary via a 15 p.s.i. (1 p.s.i. = 6894.76 Pa) vacuum. Generally 2 capillary volumes (less than 6 μl) of electrolyte is adequate when varying electrolyte parameters such as pH or ionic strength. To minimize electrolyte solubility incompatibilities and baseline drift, extra steps involving flushing with water and then with the next electrolyte are required when changing the electrolyte co-ion.

With such short periods needed for analysis and electrolyte interchange, several electrolyte compositions can be evaluated in less than an hour. Due to the constraint of having the receiving side electrolyte stationary, automated methods development typically requires leaving the receiving electrolyte unchanged throughout the experiments. Recent work by Bocek and co-workers [19,20] showed that analyte selectivity can be changed through careful selection of the receiving side electrolyte composition (anodic chamber) as delivered by either a step-change or a transient pulse during the analysis. CIE anion separations are not sensitive to receiving side composition unless the electrolyte is substantially different in composition. The anodic EOF prevents large cationic species from reaching the cathodic electrolyte and even impedes the migration of the faster alkali metal ions to the injection side. However, baseline perturbations and drift were observed when the receiving electrolyte was very dilute or when the pH was highly acidic. In these situations, it is recommended that the electrolyte injection and receiving side electrolytes are the same.

EXPERIMENTAL

Instrumentation

The CE system employed was the Quanta 4000 (Waters Chromatography Division of Millipore Corporation, Milford, MA, USA) with a negative power supply. A Hg lamp was used for 185, 254, 313, 365, 405, 436 and 546 nm detection. A Zn lamp and a Cd lamp were used for 214 and 229 nm detection respectively. Waters AccuSep polyimide coated fused-silica capillaries was used throughout this work. The capillary dimensions are 75 μm I.D. × 375 μm O.D. with the detection window placed 8 cm from the receiving electrolyte end to the detector cell. Capillary lengths used were 40 and 60 cm.

Data acquisition was carried out with a Waters 860 data station with SAT/IN and LAC/E modules connecting the CE system to the data station with signal polarity inverted. Detector time constant was set at 0.1 s and data acquisition rate was 20 Hz. Collection of electropherographic data was initiated by a signal cable connection between the Quanta 4000 and the SAT/IN module.

UV spectra was generated using a Waters Model 990 photodiode-array detector in a flow-injection analysis made using a Rheodyne (Colati, CA, USA) Model 7010 injector.

Preparation of electrolytes

Background electrolyte solutions were prepared from various salts: sodium chromate tetrahydrate (99+%, Aldrich, Milwaukee, WI, USA), potassium hydrogenphthalate, *p*-hydroxybenzoic acid and potassium sorbate (all 99%, Sigma, St. Louis, MO, USA). The electroosmotic flow modifier was prepared from Waters CIA-Pak OFM Anion-BT [21] obtained as a 20 m*M* concentrate. Adjustment of electrolyte pH was done with either sulfuric acid (J. T. Baker, Phillipsburg, NJ, USA) or lithium hydroxide monohydrate (Aldrich). Solutions of 100 m*M* of the acid or base were used for the adjustment of electrolyte pH. The 100 m*M* lithium hydroxide solution was also used in the first of a three-stage capillary conditioning rinse cycle. Milli-Q reagent grade water (Millipore, Bedford, MA, USA) was used throughout.

Standard analyte solutions

All standard solutions were prepared by a dilution of 1000 ppm stock solutions containing a single anion. The stock solutions were prepared fresh every six months and were stored in 2000 ml polycarbonate tissue culture flasks (Corning Glass Works, Corning, NY, USA). All mixed anion standards were prepared freshly for each of the experiments. Milli-Q water and polymethylpentene containers

(Nalgene, Rochester, NY, USA) were used throughout.

System operation

Two sample carousel configurations were employed for the CE system. The 20 sample carousel used 600 μl polypropylene centrifuge tubes (Waters) for sample vials and 20 ml high density poly-ethylene (HDPE) sample side electrolyte vials (Waters). The six-sample carousel used 4 ml (15 × 45 mm) polypropylene Sunvials (Sunbrokers, Wilmington, NC, USA) for electrolytes and samples. Receiving side electrolyte vials were 20 ml glass scintillation vials (Waters) for both carousels. All vials were rinsed with Milli-Q water and dried prior to use.

RESULTS AND DISCUSSION

Indirect UV detection optimization for chromate background electrolyte

The use of chromate as a co-ion was first reported by Jones and Jandik in 1990 [22] and has been used extensively for anion analysis due to its unique combination of UV absorbtion characteristics and high electrophoretic mobility [1–10,22–26]. Fig. 1 shows a UV absorption spectra of chromate from 200 to 400 nm superimposed with lines indicating the measurement wavelengths commonly available

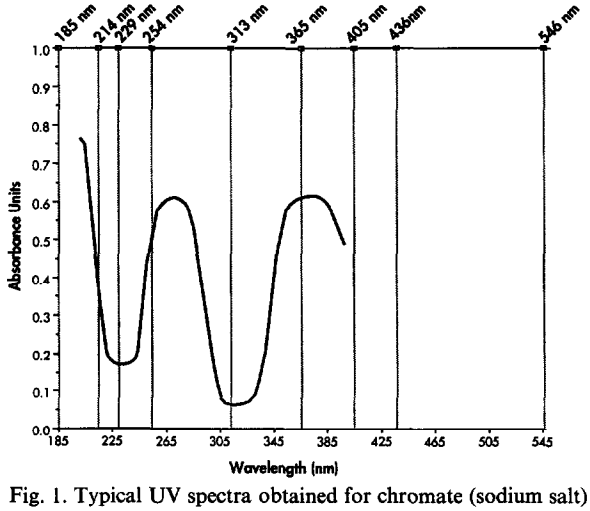

Fig. 1. Typical UV spectra obtained for chromate (sodium salt) using a photodiode-array detector in the range 200–400 nm. Superimposed on UV spectra are lines representing the wavelengths used for detection of analytes on a chomate electrolyte described in Table I.

from Hg, Zn and Cd light sources. There are three UV maxima for chromate at 200, 272 and 370 nm. The largest signal generated for indirect UV detection is found where chromate absorbs most strongly and the analytes absorbs least. From Fig. 1, the strongest background signal for chromate is 185 nm, assuming that chromate continues to absorb strongly below 200 nm. The next strongest signal is found at 365 nm which is near chromate's third UV maxima. Finally another convenient monitoring wavelength is 254 nm, near the second UV maxima. Table I shows peak height ratios of 11 inorganic anions with respect to 254 nm for nine wavelengths using a 5-m*M* chromate–0.5 m*M* OFM Anion-BT electrolyte. Consistent with the UV spectra, 185 nm produced the largest signal for 9 of the 11 anions while 365 nm and 254 nm had the second and third largest signal for 7 anions respectively. Large detector signals alone do not always provide the most sensitivity, lamp energy effects detector performance since the higher lamp energies provides more photons per unit time resulting in reduced short noise [27,28]. The measured lamp output defined as the difference between the sample and reference side photodiode currents is 0.40, 1.55 and 0.08 nA for 185, 254 and 365 nm respectively. The high Hg lamp current found at 254 nm provides the best detection limits for the 11 analytes. Using the fluoride anion for comparison, the detection limit (defined here as 3 times the baseline noise) is 80 ppb for 254 nm compared to 190 ppb at 185 nm and 220 ppb at 365 nm. Table I also lists the detection limits for the 11 anions at the various wavelengths. In all three wavelengths discussed, Fig. 2, the peaks are detected indirectly except for bromide at 185 nm which absorbs sligthly more than chromate. The poor sensitivity for bromide is ideal for samples where excessive bromide is a matrix intererence masking proper identification and quantitation of adjacent peaks. The 185 nm wavelength has also been shown to be suited for the detection of sulfide which absorbs similarly to chromate at 254 nm [5].

Direct UV detection for chromate background electrolyte

At 214 and 229 nm, the UV absorption of chromate is at a minimum: this does not permit universal indirect detection. However, these wave-

TABLE I

PEAK HEIGHT RATIO WITH RESPECT TO 254 nm FOR EIGHT DIFFERENT WAVELENGTHS USING AN ELEVEN INORGANIC ANION MIXTURE AND DETECTION LIMITS DEFINED AS 3× NOISE IN ppm

Negative numbers indicate the analyte is more absorbing than the background electrolyte. The terms dl and np stand for detection limit and no peak respectively. Concentrations (ppm): All anions are at 4 ppm except for chloride (2); molybdate and tungstate (10); fluoride (1). The electrolyte is 5 m*M* 0.5 m*M* OFM Anion-BT adjusted to pH 8.0. Applied potential is 20 kV (negative polarity). Capillary dimensions are 60 cm (52 cm to detector) × 75 μm I.D. fused-silica. UV detection (wavelengths listed in table). Injection is hydrostatic (10 cm for 30 s). Capillary flushed with fresh electrolyte for 2 min prior to loading of sample.

No.	Anion	Wavelength (nm)								
		185	214	229	254	313	365	405	436	546
Peak height ratio (with respect to 254 nm)										
1	Thiosulfate	3.55	−0.58	−0.61	1.00	dl	1.67	0.57	0.14	np
2	Bromide	−0.18	−0.08	0.21	1.00	dl	1.56	0.54	0.14	np
3	Chloride	2.71	0.51	0.20	1.00	dl	1.52	0.52	0.12	np
4	Sulfate	4.04	0.53	0.20	1.00	dl	1.51	0.52	0.13	np
5	Nitrite	2.87	−2.29	−0.92	1.00	dl	1.55	0.53	0.11	np
6	Nitrate	2.26	−2.94	−0.38	1.00	dl	1.49	0.53	0.14	np
7	Molybdate	5.10	−2.44	−1.74	1.00	dl	2.19	0.75	0.19	np
8	Tungstate	2.64	0.12	0.16	1.00	dl	1.53	0.54	0.12	np
9	Fluoride	4.03	0.52	0.21	1.00	dl	1.57	0.51	0.15	np
10	Phosphate	3.79	0.60	0.25	1.00	dl	1.44	0.49	0.12	np
11	Carbonate	3.93	0.49	0.17	1.00	dl	1.55	0.58	0.12	np
Detection limit (3× noise in ppm)										
1	Thiosulfate	0.71	−1.32	−1.39	0.25	6.00	0.70	2.68	3.05	np
2	Bromide	−10.17	−6.84	2.62	0.18	6.00	0.55	2.05	2.21	np
3	Chloride	0.38	0.60	1.52	0.10	3.00	0.31	1.17	1.40	np
4	Sulfate	0.30	0.69	1.84	0.12	6.00	0.38	1.42	1.63	np
5	Nitrite	0.51	−0.19	−0.48	0.15	6.00	0.44	1.65	2.15	np
6	Nitrate	0.95	−0.22	−1.72	0.22	6.00	0.67	2.42	2.48	np
7	Molybdate	1.13	−0.71	−1.00	0.58	15.00	1.23	4.64	5.15	np
8	Tungstate	2.31	15.61	11.25	0.61	15.00	1.85	6.74	8.52	np
9	Fluoride	0.19	0.43	1.09	0.08	1.50	0.22	0.88	0.86	np
10	Phosphate	0.78	1.49	3.55	0.30	6.00	0.96	3.63	4.29	np
11	Carbonate	0.84	2.02	5.74	0.33	6.00	1.00	3.41	4.72	np

lengths are aids for confirming peak identity for UV absorbing anions such as thiosulfate, nitrite, nitrate and molybdate as shown in Fig. 3. Good candidates for background electrolytes for indirect UV detection at 214 nm are the strongly absorbing nitrite, nitrate and molybdate ions while only nitrite and molybdate are optimal as background electrolytes at 229 nm. Selection of a UV absorbing analyte as the electrolyte co-ion for purposes of indirect UV detection is optimal if it has a similar mobility to the analytes of interest for best peak symmetry and also if the sample matrix has an excess of the ion used as the electrolyte co-ion, which is therefore not necessary to quantitate. In the experiments that follow, 254 nm detection provides the best overall performance and is the wavelength used throughout the rest of this paper.

Successive increase in EOF modifier concentration

In earlier work, a linear correlation was obtained with adjusted ionic equivalent conductance values from the literature for individual analytes plotted against reciprocal migration times of 27 inorganic and organic anions [24]. Three anions did not fit the linear relationship, iodide, thiocyanate and perchlorate which all had significantly longer migration times than predicted. It was suspected that the mobility difference was due to hydrophobic interac-

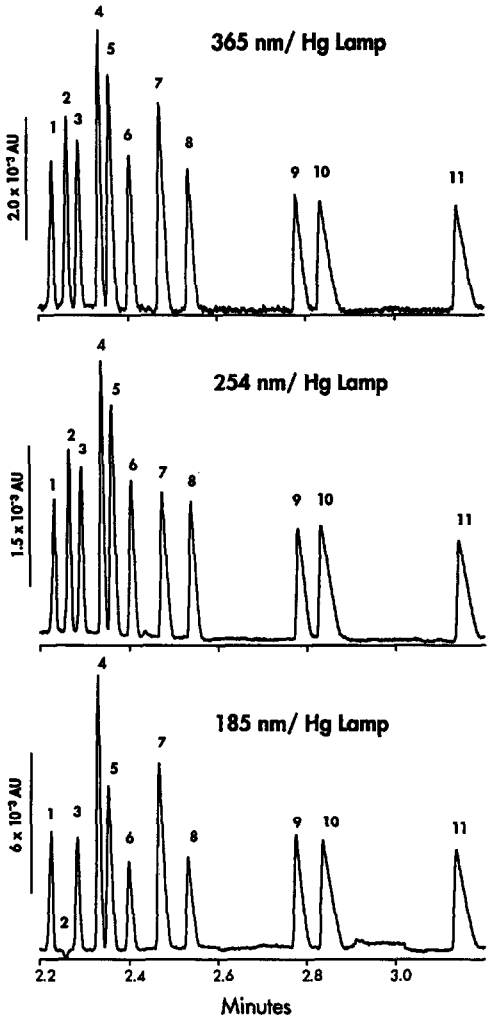

Fig. 2. Separations of 11 inorganic anions listed in Table I using Hg lamp detection at or near chromate UV maxima. Electrolyte and running conditions described in Table I. All peaks are visualized indirectly except for negative bromide (peak 2) at 185 nm.

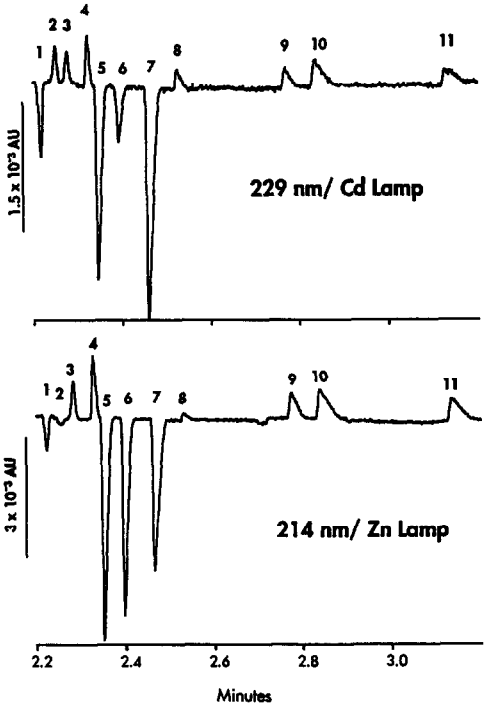

Fig. 3. Separations of 11 inorganic anions listed in Table I using a Cd lamp for 229 nm and a Zn lamp for 214 nm detection. Chromate is at a UV minima at two of these wavelengths, all positive peaks are visualized indirectly. Running conditions listed in Table I.

tion of the analytes with 0.5 m*M* EOF modifier in a 5-m*M* chromate electrolyte. These 3 anomalous analytes included in a 13 anion test mixture were evaluated for effects on selectivity in a 5-m*M* chromate electrolyte with respect to the EOF modifier ranging from 0.25 m*M* to 1.5 m*M*. A six-electrolyte carousel was used for the evaluation. Each electrolyte vial is used with a specific sample vial. Therefore each sample vial was filled with the same test mixture. The receiving side electrolyte is not automated and remains constant with the initial electrolyte composition unless manually changed. To reduce running time a 60-cm capillary was shortened by 20 cm from the injection end. The applied field strength (kV/cm) was kept constant by reducing the applied voltage to prevent overheating conditions in the capillary. This permitted a proportional reduction in the programmed running parameters consisting of data acquisition, injection and capillary flush times. The result was 5.7 min per sample with a total experiment time of less than 35 min for the evaluation of 6 electrolytes. The migration time data was normalized with respect to nitrite for improved visualization in changes in selectivity. The graph generated from the automated sequence of unmatched electrolytes is shown in Fig. 4A. The 3 polarizable anions are highlighted with bold lines. As evident from the increasing migration time ra-

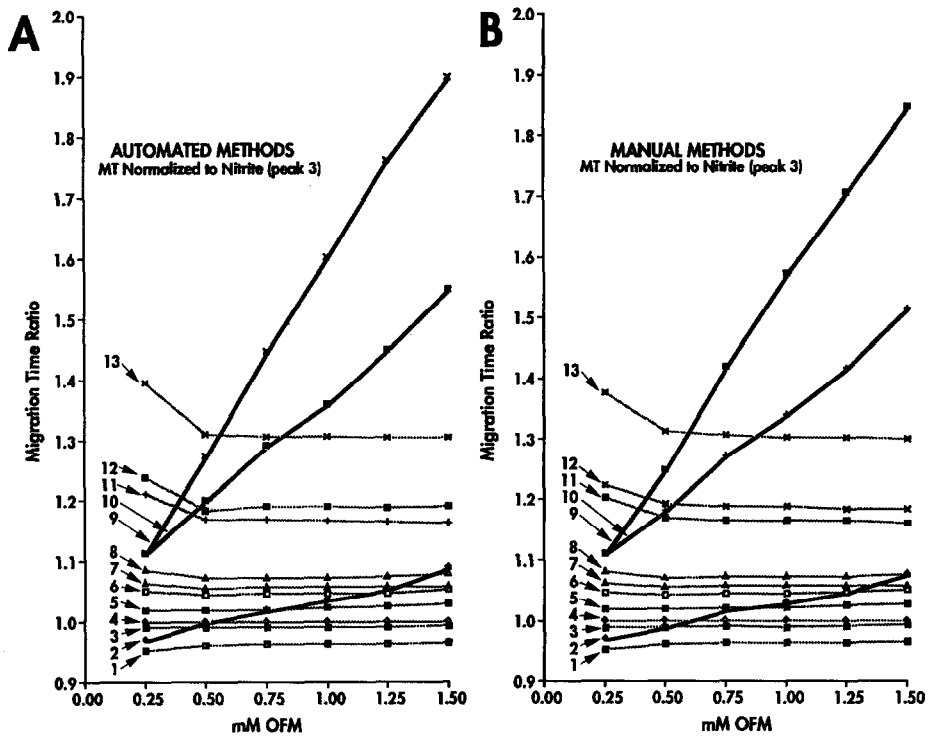

Fig. 4. Selectivity changes obtained from automated electrolyte changing where the receiving side electrolyte remains constant with the first electrolyte composition. Selectivity changes obtained from manual electrolyte changing where the receiving side electrolyte matches the injection side. Concentrations (ppm): 1 = bromide (4); 2 = iodide (5); 3 = sulfate (4); 4 = nitrite (4); 5 = nitrate (4); 6 = molybdate (10); 7 = azide (4); 8 = tungstate (10);9 = perchlorate (4); 10 = thiocyanate (4); 11 = fluoride (1); 12 = phosphate (4); 13 = carbonate (4). The EOF modifier, OFM Anion-BT, concentration is increased from 0.25 m*M* to 1.5 m*M* in 6 discrete electrolytes all containing 5 m*M* sodium chromate adjusted to pH 8.0. Applied potential is 13.3 kV (negative polarity). Capillary dimensions are 40 cm (32 cm to detector) × 75 μm I.D. fused-silica. UV detection at 254 nm. Injection is hydrostatic (10 cm for 20 s). Capillary flushed with fresh electrolyte for 1.4 min prior to loading of sample.

tios, these anions show a high sensitivity to minor changes in EOF modifier concentration. Further experiments have to date placed iodide after peak 13 (bicarbonate) using 3 m*M* EOF modifier.

The same experiment was repeated using a fresh capillary except this time the receiving electrolyte is identical to the injection side electrolyte (Fig. 4B). Comparing the graphs in Fig. 4A and B we see that the data is virtually identical. Since migration times are inversely related to the ionic equivalent conductance Fig. 5 shows the data from Fig. 4A as reciprocal normalized migration times for each analyte under the different electrolyte conditions. The ionic equivalent conductance (IEC) obtained from the literature [29] are adjusted (IEC_{adj}) according to reference [24]. A linear curve fit is obtained for the 0.5 m*M* OFM Anion-BT data with iodide, thiocyanate and perchlorate data points omitted. A correlation coefficient of $r^2 = 0.982$ is obtained. From this graph it can be seen that as the EOF modifier concentration approaches zero, the observed mobility of polarizable anions approach the value calculated from IEC_{adj}. Deviations from the line for the 0.25 m*M* data for the slower anions carbonate, phosphate and fluoride is not due to interaction with the EOF modifier but due to a slower EOF obtained using less modifier. An improved curve fit for this data is obtained when the normalized migration times reflect the electrophoretic mobilities rather than the apparent mobility. To do this correctly it is necessary to subtract the contribution due to the EOF, *e.g.* as measured with a neutral

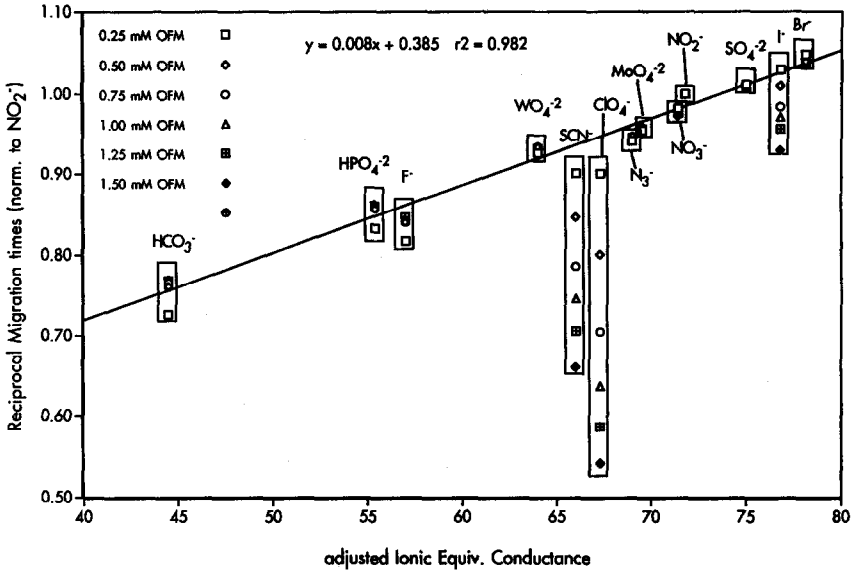

Fig. 5. Plot of reciprocal migration times normalized to nitrite anion from data obtained in Fig. 4A. This graph illustrates the deviation from predicted mobility IEC_{adj} due to EOF modifier concentration. See text for details.

marker. In order to accurately predict the mobility of the polarizable anions in the electrolyte, a hydrophobic factor (defined as a function of the EOF modifier concentration) must be included to the adjustments.

Successive change in electrolyte co-ion mobility

In situations where different electrolytes offer improved sensitivity and peak symmetry for specific analytes, it may be advantageous to analyze a sample under different electrolyte conditions. Three background electrolytes were selected with strong UV absorbtion around 254 nm, chromate, *p*-hydroxybenzoate and sorbate. Chromate is optimum for highly mobile inorganic anions through fluoride and phosphate. At an elevated pH *p*-hydroxybenzoate becomes a moderately mobile divalent anion through ionization of the hydroxyl group. The sorbate anion absorbs more strongly than *p*-hydroxybenzoate and is a low mobility electrolyte optimized for anions migrating after the bicarbonate ion. A four-quadrant electrolyte carousel with two sample vials that alternate as capillary conditioning rinse vials was used in the experiment. Again, the receiving side electrolyte is not automated and remains constant with the initial electrolyte composition unless manually changed. A three-stage rinse cycle consisting of a dilute base, water rinse and the next electrolyte composition described elsewhere [9] was used to simulate a situation where removal of sample excipients retained on the inner wall necessitates on-line clean-up of the capillary. A 15 anion mixture was injected with the three different mobility electrolyte systems. All electrolytes were 5 m*M* in co-ion concentration and 0.5 m*M* in EOF modifier. The automated and manual sequence of electrolyte changing all included a three-cycle capillary conditioning step described earlier. The manually balanced injection and receiving side electrolyte was run after the automated sequence using the same capillary. Fig. 6A shows the three electropherograms obtrained with the 15 anion mixture injected and the three different electrolytes, using the automated method. The chromate electrolyte (top) separation shows all the anions fully resolved with increased tailing for the later peaks. The *p*-hydroxybenzoate electrolyte shows improved peak symmetry for the 8 through 11 but fails to resolve peaks 1 through 5. The sorbate electrolyte shows best sensitivity and selectivity for peaks 11 through 15 but does not resolve peaks 1 through 7. In terms of the standard, the chromate electrolyte is sufficient for

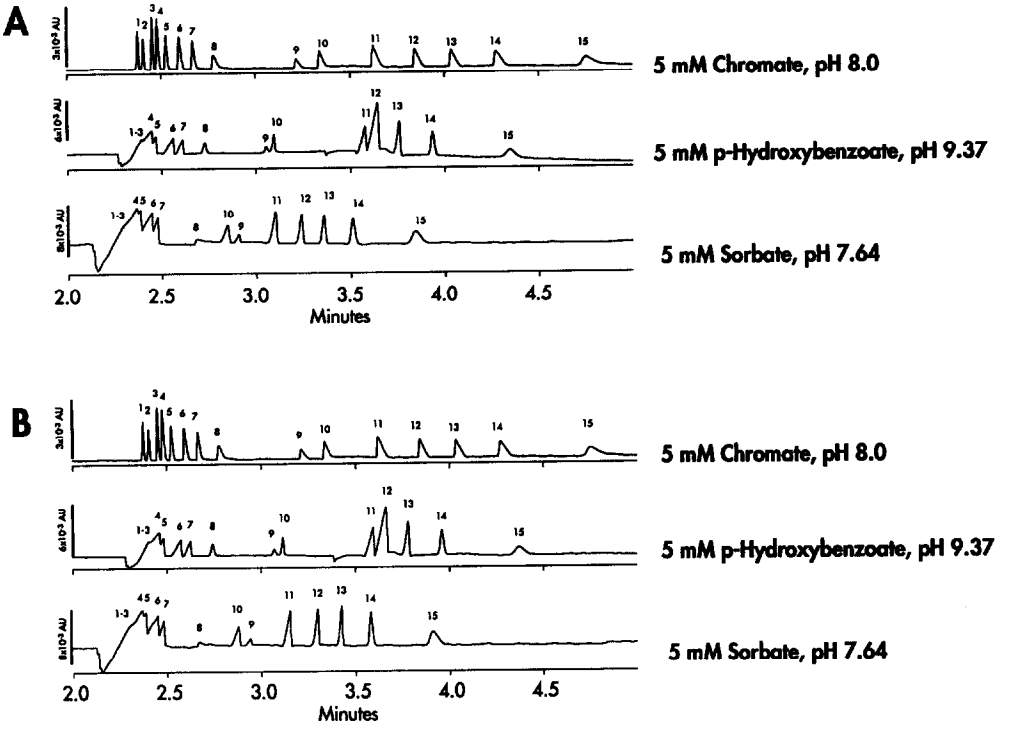

Fig. 6. Selectivity changes obtained from automated electrolyte changing where the receiving side electrolyte remains constant with the first electrolyte composition. Selectivity changes obtained from manual electrolyte changing where the receiving side electrolyte matches the injection side. Concentrations (ppm): 1 = bromide (4); 2 = chloride (2); 3 = sulfate (4); 4 = nitrite (4); 5 = nitrate (4); 6 = molybdate (10); 7 = tungstate (10); 8 = citrate (4); 9 = phthalate (4); 10 = carbonate (4); 11 = ethanesulfonate (5); 12 = propanesulfonate (5); 13 = butanesulfonate (5); 14 = pentanesulfonate (5); 15 = hexanesulfonate (5). All electrolyte contain 0.5 m*M* OFM Anion-BT. Applied potential is 20 kV (negative polarity). Capillary dimensions are 60 cm (52 cm to detector) × 75 μm I.D. fused-silica. UV detection at 254 nm. Injection is hydrostatic (10 cm for 30 s). Capillary flushed with fresh electrolyte for 2 min with dilute base, 1 min with Milli-Q water and 2 min with next electrolyte composition prior to loading of sample.

separating all 15 components. In real world situations the late migrators may contain more complex mixtures which the chromate electrolyte may not fully resolve due to peak assymmetry [1,9].

The manually matched electrolyte separations found in Fig. 6B show that the results are again virtually identical to those obtained with the automated method.

CONCLUSIONS

CIE provides a rapid and highly efficient analysis approach for small ions that extends into facilitating methods development. In this paper the versatility of UV detection using properly selected wavelengths with respect to electrolyte chemistry was demonstrated. This technique offers means for universal, selective or confirmational determination of analytes. The simplicity of using an open tubular fused-silica capillary permits rapid conversion from one electrolyte composition to another in 1–2 min and less than 5 minutes if on-line capillary clean-up is required. The data obtained for a selectivity chart which maps the changes in analyte mobility with respect to six discrete changes of a single electrolyte parameter was accomplished automatically under 35 min. In a second variation, rapid electrolyte conversion in the capillary permitted full optimization of peak symmetry and sensitivity for highly mobile inorganic anions to less mobile organic acids.

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