Journal of Chromatography, 608 (1992) 385–393
Elsevier Science Publishers B.V., Amsterdam

CHROM. 24 176

Various approaches to analysis of difficult sample matrices of anions using capillary ion electrophoresis

William R. Jones and Petr Jandik

Applied Technology Group, Waters Chromatography Division of Millipore, 34 Maple Street, Milford, MA 01757 (USA)

ABSTRACT

Capillary ion electrophoresis is a capillary electrophoretic technique optimized for the analysis of low-molecular-mass inorganic and organic ions. Sensitive detection is based predominantly on indirect UV since the majority of the ions lack specific chromophores. Rapid separations with efficiencies approaching 1 000 000 theoretical plates are a result of directing the electroosmotic flow towards the detector in combination with an appropriately mobile background electrolyte co-ion. Selectivity of separations can easily be predicted with the aid of readily available ionic equivalent conductances.

Described in this paper are the optimized separations of several types of samples considered until recently to be beyond the capabilities of capillary electrophoresis. These include samples of disparate concentration levels, reactive anions and trace ion analysis with detection limits in the low parts per trillion (10^{12}) concentration range.

INTRODUCTION

Capillary ion electrophoresis (CIE) (Waters' trade name: Capillary Ion Analysis, CIA) is an emerging separation technique which is rapidly expanding to encompass the various classes of ions that were once the domain of ion chromatography (IC) [1,2]. The ions characterized in our laboratory and reported in the literature include inorganic and organic anions, small chain anionic surfactants, group I and II metals, the majority of fourth period metals, Cd, Hg and the lanthanides [3–11]. Table I lists the 129 ionic species found analyzable by CIE to date. The original list reported in mid-1990 contained only 53 anions [3]. All ions were separated in fused-silica capillaries and detected at either 185, 214 or 254 nm wavelengths. The open tubular capillary provides a versatile user definable separation media which is solely dependent upon the electrolyte chemistry and polarity of the power supply. This combination controls the selectivity and mode of separation. In contrast, IC separation selectivities are determined by type of columns which are generally specific for either anionic or cationic species. Selectivity for IC is based predominantly on the composition of the column's stationary phase and the ion-exchange moieties either covalently bound or dynamically coated to the surface, with selectivity refinements provided by the eluent [12]. IC requires more than one detection mode to visualize the ions listed in the Table I. Conductivity detection, the universal IC detection is suitable for the majority of them. Unfortunately, the less efficient separations by ion exchange (ranging from 1000 to 10 000 plates) frequently require more specific detection schemes, such as photometry with post column reaction for transition metals and amperometric detection for electroactive species such as cyanide and sulfide.

CIE achieves a very high peak capacity [13–15] for both anions and cations with rapid analysis times. Control of the electroosmotic flow (EOF) which originates from polarity and magnitude of the zeta potential [16,17] is accomplished controlling the electrolyte pH for cations and with special electroosmotic flow modifiers which dynamically coat the inner wall of the fused-silica capillary for anions.

Correspondence to: Mr. W. R. Jones, Applied Technology Group, Waters Chromatography Division of Millipore, 34 Maple Street, Milford, MA 01757, USA.

0021-9673/92/$05.00

TABLE I

ANIONS AND CATIONS THAT HAVE BEEN CHARACTERIZED BY CIE WITH UV DETECTION

The anions are divided into two categories, inorganic and organic, and are listed alphabetically. The cations are listed according to their class and in order of increasing atomic number.

Inorganic anions	*Organic anions*	*Organic anions (continued)*	*Alkali metals*
Arsenate	Acetate	Isocitrate	Lithium
Arsenite	*trans*-Aconitate	α-Ketoglutarate	Sodium
Azide	Ascorbate	Lactate	Potassium
Borate	*dl*-Aspartate	Maleate	Rubidium
Bromate	Benzoate	Malonate	Cesium
Bromide	Butanesulfonate	Methanesulfonate	
Carbonate	Butyrate	Nonanesulfonate	*Alkaline earths*
Chlorate	4-Carboxybenzaldehyde	Octanesulfonate	Beryllium
Chloride	Chloroacetate	Orotate	Magnesium
Chlorite	Citrate	Oxalacetate	Calcium
Chromate	Crotonate	Oxalate	Strontium
Cyanide	Decanesulfonate	Pentanesulfonate	Barium
Fluoroborate	Dodecanesulfonate	*o*-Phthalate	
Fluoride	Dichloroacetate	Propanesulfonate	*Transition metals*
Hypochlorite	Ethanesulfonate	Propionate	Manganese
Iodide	Formate	Pyridinedicarboxylate	Iron
Metasilicate	Fumarate	Pyruvate	Cobalt
Metavanadate	Galactarate	Quinate	Nickel
Molybdate	*d*-Galacturonate	Salicylate	Copper
Monofluorophosphate	*d*-Gluconate	Shikimate	Zinc
Nitrate	Glucuronate	Sorbate	Cadmium
Nitrite	*l*-Glutamate	Succinate	Mercury
Orthovanadate	Glutarate	Tartarate	Lead
Perchlorate	Glycerate	Terephthalate	
Persulfate	Glycolate	Trichloroacetate	*Lanthanides*
Phosphate	Glyphosate	Trifluoroacetate	Lanthanum
Phosphite	Heptanesulfonate	Trimesate	Cerium
Selenate	Hexanesulfonate	*p*-Toluate	Praseodymium
Selenite	α-Hydroxybutyrate	Valerate	Neodymium
Sulfate	Hydroxymethylbenzoate		Samarium
Sulfide	2-Hydroxyvalerate		Europium
Sulfite			Gadolinium
Thiocyanate			Terbium
Thiosulfate			Dysprosium
Tungstate			Holmium
			Erbium
			Thulium
			Ytterbium
			Lutetium
			Non-metal cation
			Ammonium

The EOF is made to flow towards the detector in the majority of the CIE applications. The polarity of the power supply is selected to direct electromigration of anions towards the detector as well [3]. Two important examples of EOF and analyte mobility being directed toward the detector are the simultaneous separation of alkali, alkaline earths and lanthanide cations on one hand and the separation of 30 inorganic and organic anions on the other hand. The total run times are 1.8 and 3.1 min, respectively [4,10]. Further improvements in peak capacity are illustrated in the 36-anions electropherogram Fig. 1. The concentration range of the anions in this standard mixture is 0.3 ppb[a] to 3.3 ppm. The

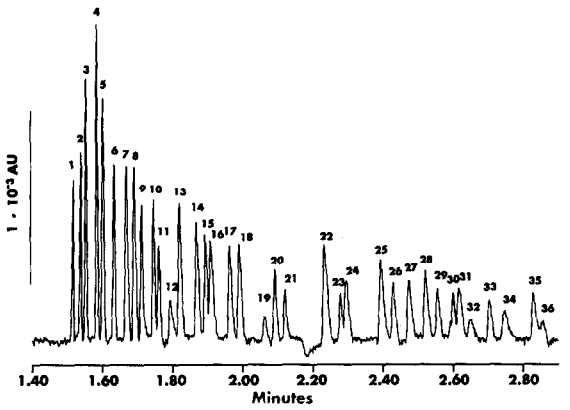

Fig. 1. Electropherogram (83-s section) of 36 anions. Peaks concentrations [ppm]: 1 = thiosulfate [1.3]; 2 = bromide [1.3]; 3 = chloride [0.7]; 4 = sulfate [1.3]; 5 = nitrite [1.3]; 6 = nitrate [1.3]; 7 = molybdate [3.3]; 8 = azide [1.3]; 9 = tungstate [3.3]; 10 = monofluorophosphate [1.3]; 11 = chlorate [1.3]; 12 = citrate [0.7]; 13 = fluoride [0.3]; 14 = formate [0.7]; 15 = phosphate [1.3]; 16 = phosphite [1.3]; 17 = chlorite [1.3]; 18 = glutarate [1.7]; 19 = *o*-phthalate [0.7]; 20 = galactarate [1.3]; 21 = carbonate [1.3]; 22 = acetate [1.3]; 23 = chloroacetate [0.7]; 24 = ethanesulfonate [1.3]; 25 = propionate [1.3]; 26 = propanesulfonate [1.3]; 27 = *dl*-aspartate [1.3]; 28 = crotonate [1.3]; 29 = butyrate [1.3]; 30 = butanesulfonate [1.3]; 31 = valerate [1.3]; 32 = benzoate [1.3]; 33 = *l*-glutamate [1.3]; 34 = pentanesulfonate [1.7]; 35 = *d*-gluconate [1.7]; 36 = *d*-galacturonate [1.7]. The electrolyte is 5 m*M* chromate and 0.4 m*M* OFM Anion-BT adjusted to pH 8.0. Applied potential is 30 kV (negative polarity). Capillary dimensions are 60 cm (52 cm to detector) × 50 μm I.D. fused silica. Indirect UV detection. Injection by electromigration at 1 kV for 15 s.

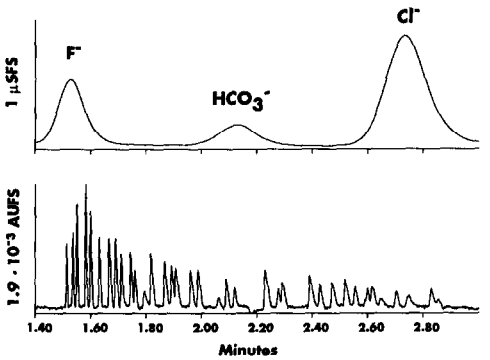

Fig. 2. Comparison of an IC separation and a CIE separation. The top plot (anion-exchange chromatogram) shows only three anions (fluoride, carbonate and chloride) using a Waters IC-Pak A, borate–gluconate eluent at 1.2 ml/min and Waters 431 conductivity detection. This separation is fully described in refs. 28 and 29. The bottom separation (CIE electropherogram) shows the 36-anion separation under conditions given in Fig. 1.

standard was introduced into the capillary by electromigration. Comparing the peak capacity of a conventional anion-exchange separation, we observe only three anions, fluoride, carbonate and chloride being resolved during the same time interval Fig. 2. Using the migration time data from the 36-anion electropherogram of Fig. 2, reciprocal migration times are plotted against published values of ionic equivalent conductances [18,19] adjusted to reflect the charge of the respective analyte anion found at the pH of the electrolyte [4] (Fig. 3). A good linear correlation is found with a correlation coefficient of 0.987. This is consistent with eqn. 1, where the apparent mobility, μ_{app}, of the analyte is equal to the sum of the electrophoretic mobility, μ_{ep}, and the electroosmotic mobility, μ_{eof} and with $\mu = \lambda F$, where λ is the ionic equivalent conductance and F is the Faraday constant. The apparent mobility is also

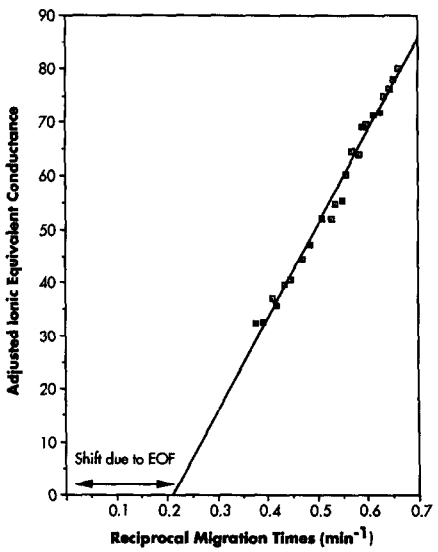

Fig. 3. Reciprocal migration times of some anions from Fig. 2 plotted against their respective values of ionic equivalent conductance for the prevalent ionic form at pH 8.0. The ionic equivalent conductances were also adjusted (□) according to valence state as described in ref. 4. $y = -36.817 + 174.90x$; $R^2 = 0.987$.

[a] Throughout this article, the American billion (10^9) and trillion (10^{12}) are meant.

equal to the analyte velocity, (L_d/t_m) divided by the field strength (V/L_t) (eqn. 2, where L_d is the length of the capillary to the detector, t_m is the migration time, V is the applied potential and L_t is the total length of the capillary.

$$\mu_{app} = \mu_{ep} + \mu_{eof} \quad (1)$$

$$\mu_{app} = (L_d/t_m)/(V/L_t) \quad (2)$$

From Fig. 3 the apparent electroosmotic mobility, μ_{eof}, can be obtained from the x-intercept value and the electrophoretic mobility, μ_{ep}, can be calculated from eqn. 1. This approach is more accurate for determining this parameter than using the water component of the sample as the neutral marker of the separation. The water peak is very broad and is measured in fractions of a minute as compared to analytes being measured in fractions of a second. Also, its apex is irregularly shaped and dependent on the sample matrix. For practical purposes, the analysis is over when the last analyte of interest has passed through the detector window, whereupon the capillary is usually purged with fresh electrolyte to remove the neutral components including the water peak and prepare for loading of the next sample.

EXPERIMENTAL

Instrumentation

The capillary electrophoresis (CE) system employed was the Quanta 4000 (Waters Chromatography Division of Millipore, Milford, MA, USA). Both positive and negative power supplies were employed. A Hg lamp was used for 185 and 254 nm detection and Zn lamp was used for 214 nm. Waters AccuSep polyimide-coated fused-silica capillaries are used throughout this work. The capillary dimensions ranged from 40 to 60 cm total length with the detection window placed 8 cm from the receiving electrolyte end to the detector cell. Both 50 and 75 μm I.D. capillaries were employed. 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. 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.

Preparation of electrolytes

The electrolytes were prepared from various salts. For indirect UV detection $Na_2CrO_4 \cdot 4\,H_2O$ 99 + % (Aldrich, Milwaukee, WI, USA) was used exclusively. Direct UV detection electrolytes used sodium chloride (Sigma, St. Louis, MO, USA) or hexanesulfonic acid, sodium salt 98% (Aldrich). Adjustment of electrolyte pH was done with various acids and bases depending on the application. In the first step the acid and base solutions were prepared in concentrations of 100 m*M* from lithium hydroxide monohydrate, H_2SO_4 (Ultrex grade), glacial acetic acid. (J. T. Baker, Phillipsburg, NJ, USA). Waters CIA-Pak OFM Anion-BT[a] a 20 m*M* EOF modifier concentrate was added to some electrolytes in the 0.4–0.5 m*M* concentration range in order to reverse the direction of EOF when using negative power supply. The OFM modifier was converted to the chloride form for low-UV work at 214 nm and the hydroxide form for certain disparate concentration level samples. In both cases conversion of the OFM modifier was accomplished through replacement of the OFM anion with anion-exchange resin in the chloride (AG1-X8, 200–400 mesh) and hydroxide form (AG1-X8), respectively. (Bio-Rad Labs., Richmond, CA, USA). All resins were precleaned by soaking resin in 18 MΩ water for 24 h prior to use. A 5-ml volume of cleaned resin bed was packed into in a Pharmaseal Stylex 10-ml Luer tip syringe (American Pharmaseal Labs., Glendale, CA, USA) with a Millex-HV 0.45-μm filter unit (Millipore, Bedford, MA, USA) to contain the resin. The resin was rinsed once with 5 ml of 18 MΩ water prior to placing the OFM concentrate through for conversion. Milli-Q reagent-grade water (Millipore) was used for rinsing and dilution. Sodium octanesulfonate used as an additive to samples prior to preconcentration was purified by recrystallization in 18 MΩ water (Kodak, Rochester, NY, USA).

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 200-ml polycarbonate tissue culture flasks (Corning Glass Works, Corning, NY, USA). All mixed anion standards were

[a] Patents pending.

prepared freshly for each of the experiments. Milli-Q water and polymethylpentene containers (Nalgene, Rochester. NY, USA) were used throughout. For electromigrative injections, low-ppb samples were prepared by adding ppm concentrations of sodium octanesulfonate according to the procedure described elsewhere [5].

System operation

The CE system incorporates two modes of sample entry into the capillary—hydrostatic and by electromigration. Two sample carousel configurations were employed. For hydrostatic mode of injection a 20-sample carousel was used with 600-μl polypropylene centrifuge tubes (Waters) for sample vials. Electromigration injections utilized a 6-sample carousel with 2-ml polypropylene VersaVial (Sun Brokers, Wilmington, NC, USA) vials for trace analysis samples.

RESULTS AND DISCUSSION

Actual samples and standards

Of the various types of samples, Kraft Black liquor from pulp and paper production is one of the more difficult samples for IC. Its high-pH matrix containing reactive sulfur species and polyphenolic compounds poisons IC columns [6]. However, open tubular capillaries are not prone to fouling as is the case with IC columns, since it does not contain any packing material that could be affected. A thousandfold dilution in water prior to injection into the CE system is the only sample preparation required [10,20].

Certain types of samples, however, do interact with CE capillaries. A sample that was found to modify the wall of a capillary was brewed coffee. Increased migration times were observed after every injection of the sample. This migration time shift could be eliminated with an automated three-stage rinse cycle of 100 m*M* lithium hydroxide for 2 min, 18 MΩ water (Milli-Q water) for 1 min and running electrolyte for 2 min, performed between sample injections. Fig. 4A shows four consecutive injections of a coffee sample with only a 2-min purge of electrolyte before each sample loading. Fig. 4B shows four consecutive injections of a coffee sample with the three-stage rinse cycle performed before each sample loading as described above.

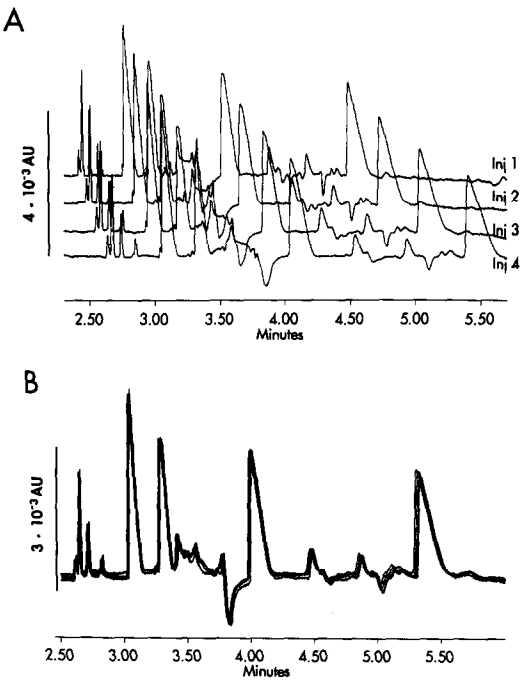

Fig. 4. (A) Four consecutive injections overlaid of a brewed coffee sample using only a 2-min purge electrolyte purge before each sample loading. (B) Four consecutive injections overlaid of a brewed coffee sample using a three-stage rinse cycle consisting of 100 m*M* lithium hydroxide for 2 min, 18 MΩ water (Milli-Q water) for 1 min and running electrolyte for 2 min, performed between sample injections. The electrolyte is 5 m*M* chromate and 0.5 m*M* OFM Anion-BT, pH 8. Applied potential is 20 kV (negative polarity). Capillary dimensions are 60 cm (L_t), 52 cm (L_d) and 50 μm I.D. Injection is hydrostatic (10 cm for 30 s).

The monitoring of anionic disinfection byproducts in drinking water can be accomplished by the separation shown in Fig. 5. Eight common inorganic anions with inorganic oxyhalides and halogenated organic acids can be analyzed in about 4.2 min. This is another example of how selectivity inherent to CIE permits separations that are traditionally difficult by IC. Three difficult problems encountered in IC are solved by this CIE method: (1) resolution of chlorate from nitrate, (2) separation of fluoride from acetate and other monovalent organic acids and (3) determination of perchlorate which is a very highly retained anion on resin-based IC columns. A 5 m*M* chromate with 0.3 m*M* OFM Anion-BT electrolyte at pH 8.0 was used for the separation. The reduced conentration of OFM, 0.3 m*M* rather than 0.5 m*M*,

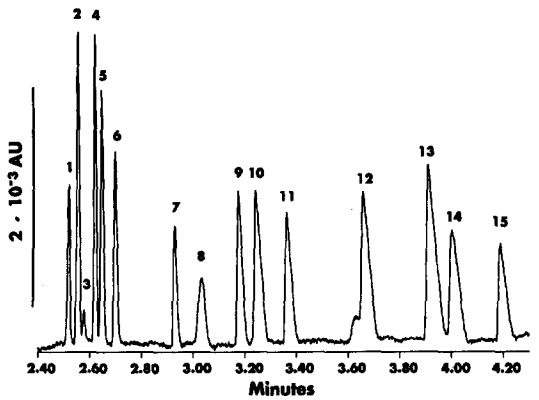

Fig. 5. Separation of fifteen inorganic and organic halides. Peaks and concentrations [ppm]: 1 = bromide [4]; 2 = chloride [2]; 3 = iodide [4]; 4 = sulfate [4]; 5 = nitrite [4]; 6 = nitrate [4]; 7 = chlorate [4]; 8 = perchlorate [4]; 9 = fluoride [1]; 10 = phosphate [4]; 11 = chlorite [4]; 12 = carbonate [4]; 13 = acetate [5]; 14 = monochloroacetate [5]; 15 = dichloroacetate [5]. The electrolyte is 5 m*M* chromate and 0.3 m*M* OFM Anion-BT adjusted to pH 8.0. Applied potential is 20 kV (negative polarity). Capillary dimensions are 60 cm (L_t), 52 cm (L_d) and 75 μm I.D. Injection is hydrostatic (10 cm for 30 s).

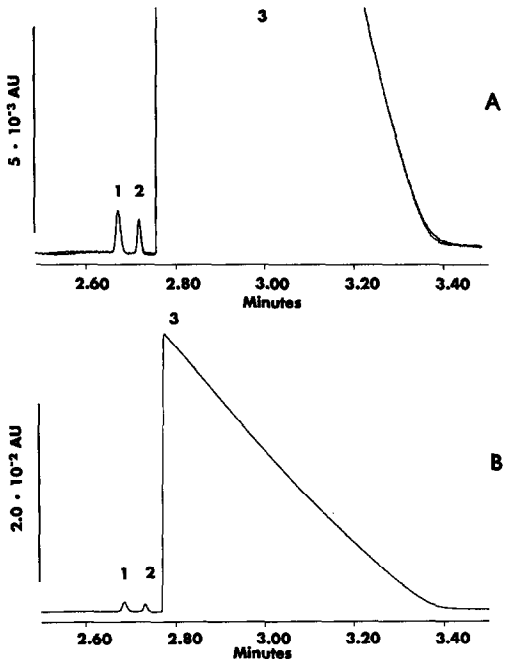

Fig. 6. (A) An expanded view of citrate sample for chloride and sulfate. Peaks and concentrations [ppm] injected: 1 = chloride [1]; 2 = sulfate [1]; 3 = citrate [1500]. (B) The same separation as in the top plot, but at a different sensitivity to show fully the citrate peak. The electrolyte is 5 m*M* chromate, 0.5 m*M* OFM Anion-BT (converted to hydroxide form), pH adjusted to 8.0 with acetic acid. Applied potential 20 kV negative polarity, detection at 254 nm, 60 cm × 75 μm fused-silica capillary with 10 cm for 30-s hydrostatic injection.

used in most applications placed the hydrophobic perchlorate anion before fluoride. At 0.5 m*M* OFM the perchlorate has a reduced mobility and comigrates with carbonate. This is assumed to be a result of ion-pairing of perchlorate and OFM.

Disparate concentrations (analysis of fine chemicals)

Samples that contain an excess of one ion with respect to another ion often make it difficult to resolve the excess concentration from the trace constituent. Dilution of the sample solves the problem of the excess ion at the expense of lowering the concentration of the trace constituent below its detection limits. In IC, considerations must be given not only to the selectivity of the analytes, but also to total ion-exchange capacity of the column [21]. Moderate ion-exchange capacity columns reduce the risk of sample overloading at the sacrifice of short analysis times. The reequilibration time alone can exceed 1 h after a column overloading. Shown in Fig. 6A is an electropherogram of 1500 ppm citrate solution prepared from its trisodium salt. The sample was spiked with 1 ppm of chloride and sulfate. Detection limits, defined as 2 × the baseline noise, for chloride and sulfate are 48 ppm and 25.7 ppm respectively in the trisodium citrate dihydrate solid. Reproducibility is also illustrated in Fig. 6A by the overlay of four consecutive injections of the sample. Using a chromate background electrolyte with OFM Anion-BT for electroosmotic flow control the analysis time is under 3.5 min, including the citrate. The 0.5 m*M* OFM Anion-BT EOF modifier was converted to the hydroxide form via hydroxide form anion-exchange resin and electrolyte pH adjusted with acetic acid.

By comparison this analysis would require a 1 h runtime using isocratic elution in IC since citrate is a highly retained trivalent anion on IC columns. Viewing the citrate peak in its entirety (Fig. 6B) reveals that it rapidly reaches its apex and then tails. For analytes that migrate after the major peak, the separation may suffer with peaks rising off the

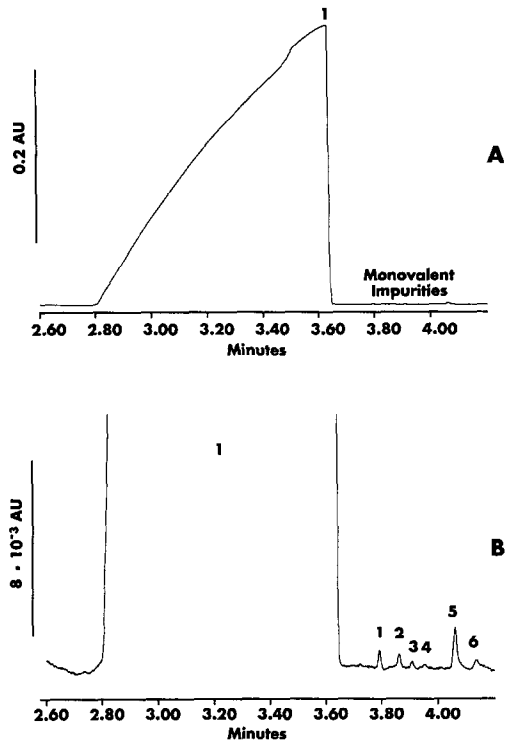

Fig. 7. Top plot is an electropherogram of a 99.9% pure terephthalic acid sample, the separation is scaled to show the complete terephthalate peak. Bottom plot is the same separation as in the top plot but at a different sensitivity to show the trace impurities. Peaks and concentrations [ppm] injected: 1 = terephthalate [5000]; 2 = unknown; 3 = benzoate [not quantitated]; 4 = unknown; 5 = toluate [0.56]; 6 = unknown. The electrolyte is a 25 m*M* hexanesulfonate, 0.5 m*M* OFM Anion-BT (converted to chloride form), pH adjusted to 10 with lithium hydroxide. Applied potential 25 kV (negative polarity), detection at 185 nm, 60 cm (L_t), 52 cm (L_d) and 75 μm I.D. fused-silica capillary with 10 cm for 30-s hydrostatic injection.

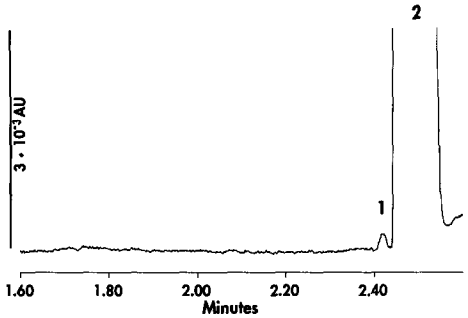

Fig. 8. Separation of chloride in the presence of excess sulfate. Peaks and concentration [ppm] injected: 1 = chloride [1]; 2 = sulfate [1000]. The electrolyte is 5 m*M* chromate, 1.5 m*M* OFM Anion-BT. Applied potential 20 kV (negative polarity), detection at 254 nm, 60 cm (L_t), 52 cm (L_d) and 75 μm I.D. fused-silica capillary with 10 cm for 15-s hydrostatic injection.

downward sloping baseline created by the major constituent. Peak asymmetry is a result of electrodiffusional processes described in the literature and can be easily manipulated [22,23]. The asymmetry of a peak, created by the differences in the mobility of the electrolyte co-ion and the analyte, can be easily controlled through the proper selection of various mobility of co-ions in electrolytes. Fig. 7A shows traces of UV absorbing anions following a massive 5000 ppm terephthalate peak. In Fig. 7B the terephthalate peak is again shown completely and we can see that it is fronting with a dramatic vertical drop immediately after it reaches its apex. Here a less mobile electrolyte co-ion, hexanesulfonate, is utilized to optimize the peak symmetry of the analytes of interest. The impurities are those usually found in a 99.9% pure solid terephthalic acid. Sample preparation consists of adding 1 g of lithium hydroxide monohydrate together with 0.5 g of the acid into a 100-ml volumetric flask. Additional sensitivity is achieved through utilization of direct UV detection at 185 nm.

When disparate levels of ion concentrations include ions having a small difference in selectivity, such as chloride and sulfate, the approach is to maximize the resolution between the two peaks. Sulfate exibits decreased mobility with respect to chloride as the OFM Anion-BT concentration of the electrolyte increases [4]. Fig. 8 shows a separation of 1 ppm chloride in the presence of 1000 ppm sulfate with an analysis time under 2.8 min.

Reactive anions

Analyzing reactive anions such as hypochlorite and persulfate by IC have long been a problem especially if quantitative results were the objective. Strong oxidating agents frequently react with the stationary phase of anion-exchange columns, resulting in both a decrease in column life and poor recoveries. A literature search of IC methodologies reveals that from 1975 until today only one method is found for persulfate [24] and one method for hypochlorite [25]. The IC method for hypochlorite uses amperometric detection before the anion-ex-

change column making it actually a flow injection analysis (FIA) technique. Since no separation has taken place prior to detection, the method works only if there are no other electroactive species augmenting the hypochlorite signal. The IC method for persulfate requires excessive run times (37 min), especially if weakly retained species such as chloride have to be separated in its presence.

In the development of a CIE method, the major consideration is selecting the appropriate electrolyte that prevents degradation of the reactive analytes. From the literature, persulfate with the highest ionic equivalent conductance value with respect to the 36-anions separation, would be predicted to migrate before thiosulfate and bromide. No peak for persulfate was found in the predicted region of the electropherogram running under the same conditions as in Fig. 1. A badly shaped peak observed very late in the separation occurred only when more than 500 ppm of persulfate were injected. It was suspected that a reaction was occurring between the persulfate and the OFM Anion-BT. Removal of the OFM from the electrolyte required reversing the polarity of injection and elevating the 5 m*M* chromate electrolyte to pH 11.0 with lithium hydroxide. The high pH of the electrolyte generates a μ_{eof} greater than that of the μ_{ep} of the analytes of interest. Hence the analytes are drawn towards the detector rather than being pushed as in the former case. The result is a reversed selectivity of anions in comparison to the earlier figures, the lower-mobility anions reach the detector first followed by higher-conductivity anions. Fig. 9A shows the persulfate migrating last and after the bromide anion as expected from its ionic equivalent conductance. The same electrolyte used for persulfate is applicable also for the hypochlorite anion Fig. 9B. Chlorite, carbonate, chlorate, perchlorate and chloride all migrate after the hypochlorite peak.

Decomposition of hypochlorite occurs rapidly with a 10% reduction in area from a 31 ppm solution

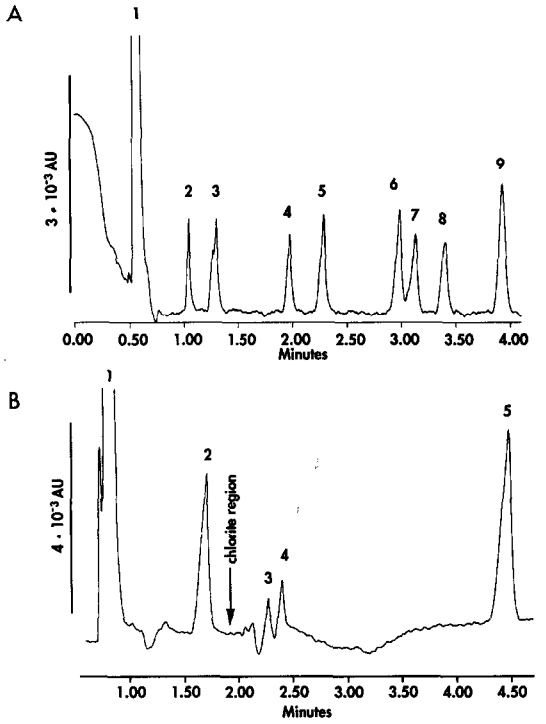

Fig. 9. (A) A separation of a reactive ion persulfate. Peaks and concentration [ppm] injected: 1 = water [not quantitated]; 2 = fluoride [1]; 3 = carbonate [not quantitated]; 4 = nitrate [4]; 5 = nitrate [4]; 6 = sulfate [4]; 7 = chloride [2]; 8 = bromide [4]; 9 = persulfate [10]. (B) Separation of hypochlorite. Peaks and concentration [ppm] injected: 1 = water [not quantitated]; 2 = hypochlorite [31]; 3 = carbonate [not quantitated]; 4 = chlorate [not quantitated]; 5 = chloride [not quantitated]. The electrolyte for both plots is 5 m*M* chromate with pH adjusted to 11.0 using lithium hydroxide. Applied potential (A) 30 kV and (B) 25 kV (positive polarity), detection at 254 nm, 40 cm (L_t), 32 cm (L_d) and 75 μm I.D. fused-silica capillary with a 10 cm at 30-s hydrostatic injection.

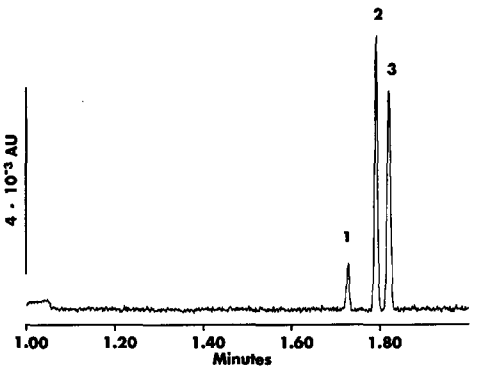

Fig. 10. Low-ppb anions using direct UV detection. Peaks and concentration [ppb] injected: 1 = bromide [4]; 2 = nitrite [4]; 3 = nitrate [4]. The electrolyte is for 25 m*M* chloride, 0.5 m*M* OFM Anion-BT (converted to chloride form), pH 8.0. Applied potential 20 kV (negative polarity), detection at 214 nm, 40 cm (L_t), 32 cm (L_d) and 75 μm I.D. fused-silica capillary with a 5 kV for 45 s electromigration injection. Sample was prepared by spiking 40 μ*M* sodium octanesulfonate standard prior to injection.

after 10 min. A linearity study was performed on hypochlorite from 31 to 77.5 ppm where the standards were prepared immediately prior to injection from a freshly prepared hypochlorite concentrate. The correlation coefficient of the linearity plot was 0.997.

Trace anions

In previous work the authors [5] achieved sub-ppb detection limits for several common anions, Br^-, Cl^-, SO_4^{2-}, NO_2^-, NO_3^-, F^- and HPO_4^{2-} using electromigration to introduce the sample and indirect UV detection. Prior to injection the sample is spiked with 40 μM sodium octanesulfonate. The sample is enriched under the conditions of an isotachophoretic steady state as defined by the Kohlrausch regulation function [26].

Recent work with low-UV absorbing anions Br^-, NO_2^-, and NO_3^- achieves low-ppt detection limits in Fig. 10 by using direct UV detection. The electrolyte contains 25 mM sodium chloride with 0.5 mM OFM Anion-BT converted to the chloride form using chloride form of an anion-exchange resin. After subtracting the contribution of ionic contamination found in a water blank treated with the octanesulfonate additive, the detection limits for nitrite and nitrate at 2× baseline noise are at 125 ppt. To determine the contribution of the impurities found in the water used to make the ppb standard, the concentrate used for sample treatment (5000 ppm octanesulfonate) can be analyzed by the method described in Fig. 6. Impurities found in the sodium octanesulfonate were bromide, sulfate and iodide, with concentrations in the low-ppt range when the additive is at 40 μM (7.73 ppm octanesulfonate) [27]. The ratio of the trace anions to the anionic sample treatment is 618:1 with respect to mass.

CONCLUSIONS

CIE provides a rapid and highly efficient analysis approach in comparison with IC. The simplicity of the method using only fused-silica capillaries and UV detection makes it an attractive alternative to a wide variety of sample matrices. The ability to analyze for trace analytes in fine chemicals with concentration ratios of up to 1 to 50 000, achieving ppt detection limits in high-purity water samples and difficult industrial samples was demonstrated.

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