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Review

Capillary electrophoresis of inorganic anions and its comparison with ion chromatography

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Abstract

Determination of inorganic anions by capillary electrophoresis is critically compared with ion chromatographic determinations on the basis of recent literature in the field. After a very brief summary of the theoretical background, the selection and optimization of the running electrolyte system are discussed, especially in connection with modification of the electroosmotic flow. Preconcentration techniques are surveyed, as are the approaches to the sample introduction and analyte detection. The principal analytical parameters of the determinations are evaluated and illustrated on selected applications described in the literature. © 1997 Elsevier Science B.V.

Keywords: Reviews; Inorganic anions

Contents

1. Introduction

In contrast to determination of organic analytes, where the use of high-performance separations is almost inevitable in complex matrices, inorganic analysis has powerful tools in highly selective and sensitive spectroscopic methods and thus a separation step is often unnecessary. This is especially true for determination of inorganic cations; for this reason, we do not deal with their separations in this review in spite of the fact that the pertinent literature is quite extensive. There has always been a much more limited selection of methods for the determination of inorganic anions. In addition to spectrophotometric procedures, some useful practical determinations are offered by ion-selective electrode

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potentiometry [1,2]; however, all these methods are usually not sufficiently sensitive for trace analyses and are mostly capable of determining only a single analyte. Therefore, high-performance separations now find extensive use in analyses for inorganic anions.

Traditionally, classical ion-exchange chromatography has long been used to preseparate and/or preconcentrate inorganic ions for their subsequent spectroscopic or electrochemical determination. The development of HPLC has made it possible to carry out multianalyte trace analyses for inorganic ions using not only ion-exchange principles but also employing ion-pairing and complexing agents in the most common HPLC mode, i.e. reversed-phase liquid chromatography (RPLC). The ion-exchange technique called ion chromatography was introduced [3] in 1975, has become highly successful commercially and is now widely used in such important fields like the quality control of all kinds of water.

Ion chromatography (IC) is now a well-established method and has been recommended officially for a number of analyses, e.g. by the Environmental Protection Agency (EPA) in the USA for determination of nitrate and nitrite in potable water [4]. The enormous recent development of various techniques of capillary electrophoresis (CE) has also brought about its application to inorganic ions [5] which is rapidly gaining practical importance. The name, capillary ion electrophoresis (CIE), has been coined. Both IC and CE have been treated in monographs and reviews (see, e.g. Refs. [6–15]).

The relative properties of HPLC and CE are now often discussed and are schematically summarized in Table 1. The following conclusions can be drawn from Table 1:

- CE is generally cheaper and faster than HPLC;
- the small samples accepted by CE make analyses of rare materials easy but cause difficulties when the technique is to be used for preparative purposes;
- CE exhibits a better resolution than HPLC but analyte identification is more difficult;
- CE procedures are usually more easily and rapidly developed and optimized than those in HPLC but the range of possibilities and the number of tunable parameters are more limited;
- the peak capacity in CE tends to be smaller than that in HPLC, especially when gradient elution is employed in HPLC;
- CE has problems with long-term stability of the migration times;
- the on-capillary detection in CE has the advantage of simplicity, a small volume and a simple geometry of the detection space, but the detection sensitivity and application possibilities of detection techniques are limited compared to HPLC;
- CE is more environmentally friendly than HPLC, as the use of organic solvents is limited.

Nevertheless, it can be expected that applications of CE to determination of inorganic anions will further grow and will partially replace IC in practical laboratories. Finally, it should be emphasized that chromatographic and electrophoretic techniques have a common basis in the concept of differential migration (see, e.g. recent work in Ref. [16]) and must be considered as complementary approaches rather than as competitors.

Table 1
Typical operational parameters of IC and CE

Parameter	IC	CE
Sample	1–50 μl	<1–5 nl
Volume flow-rate	0.1–2.0 ml/min	0.1–2.0 μl/min
Peak volume	ca. 500 μl	1–10 nl
Peak elution time	ca. 30 s	1–5 s
Time of analysis	10–40 min	5–15 min
Cost of column or capillary	ca. 300 USD	ca. 10–15 USD
Cost of mobile phase or running buffer per a series of analysis	ca. 15–25 USD	ca. 0.5–2.0 USD
No. of theoretical plates	ca. 10^4	ca. 10^5
LOD (UV detection)	ca. 10^{-7} to 10^{-9} mol/l	ca. 10^{-5} to 10^{-7} mol/l
Reproducibility of the retention parameters	<2.0%	<5%
Precision and accuracy for quantitation	ca. 2.0%	ca. 2.0–5%

2. Basic properties of CE in separations of inorganic ions

As follows from the general theory of CE (see, e.g. Refs. [11,13]), the retention behaviour of inorganic ions and its prediction are much simpler than in chromatography. The separation in CE is based on differences in the electrophoretic mobilities of the solutes. Ions migrate at an apparent velocity ν_{app} given by the sum of the electroosmotic flow velocity ν_{eo} and the electrophoretic velocity, ν_{ep}. The electroosmotic flow (EOF) in fused-silica capillaries with the injection side at the anode is directed toward the cathode; hence, anions move to the positive electrode against the electroosmotic flow. The apparent velocity of an ion is related to its apparent electrophoretic mobility, $\mu_{app(ion)}$, by Eq. (1).

$$\mu_{app(ion)} = \nu_{app}/E \quad (1)$$

where E is the electric field intensity.

The electrophoretic mobility of an ion, $\mu_{ep(ion)}$, can be calculated from the migration time of the ion, t_m, the applied voltage, V, the length of the capillary from the injection port to the detector, L_D, the total length of the capillary, L_T, and the mobility corresponding to the EOF, μ_{eo}, calculated from the migration time of an uncharged compound ($t_{m(eo)}$),

$$\mu_{app(ion)} = L_D L_T/Vt_m = \mu_{ep(ion)} + \mu_{eo} \quad (2)$$

The electrophoretic mobilities depend on the ionic strength of the running electrolyte. According to the Kohlrausch law, they are inversely proportional to the square root of the electrolyte concentration and, as the ionic strength decreases, the electrophoretic mobilities approach limiting values that can be predicted from the limiting ionic equivalent conductances, λ°_{equiv},

$$\mu^\circ_{ep(ion)} = \lambda^\circ_{equiv}/F, \quad (3)$$

where F is the Faraday constant (96 487 A s equivalent^{-1}).

The limiting ionic conductances and thus also the limiting electrophoretic mobilities of ions can be calculated from the hydrated ionic radii (the Stokes radii of the hydrated species), r_i (that are tabulated, e.g. in Ref. [17]),

$$\mu^\circ_{ep(ion)} = \mu^\circ_{equiv}/F = (10^7 z_i e)/(6\pi\eta r_i), \quad (4)$$

where z_i is the valence number of the ion, determining the direction of the electrophoretic mobility vector, e is the electron charge (1.60×210^{-19} C), π is the Ludolf number and η is the dynamic viscosity of the electrolyte (poise).

Eqs. (2)–(4) yield the following dependence for the apparent electrophoretic mobility of an ion, $\mu_{app(ion)}$,

$$\mu_{app(ion)} = (10^7 z_i e)/(6\pi\eta r_i) + L_D L_T/Vt_{m(eo)} \quad (5)$$

Eq. (5) has two limitations: first, the mobilities depend on dissociation of weak acids or bases and, second, the effective charges of ions in an electrolyte are different from the nominal charges (except for the case of infinite dilution, i.e., for the limiting electrophoretic mobilities $\mu^\circ_{ep(ion)}$).

Nevertheless, a good agreement has been obtained between the experimentally measured and calculated values $\mu_{ep(ion)}$ for anions using the data given in Table 2 [13]. A value of 8.45×10^{-12} for the coefficient $(10^7 z_i e)/(6\pi\eta r_i)$ corresponds well to the value found by curve fitting (7.78×10^{-12}).

Table 2
Apparent mobilities $\mu_{app(ion)}$ and hydrated ionic radii r_i for selected anions [13]

Anion	μ_{app}	r_i ($\times10^{-8}$ cm)
Bromide	0.0010690	1.0505
Chloride	0.0010569	1.0750
Iodide	0.0010340	1.0679
Nitrite	0.0010250	1.1423
Nitrate	0.0010010	1.1488
Azide	0.0009683	1.1886
Chlorate	0.0009269	1.2656
Fluoride	0.0008888	1.4806
Formate	0.0008710	1.5021
Chlorite	0.0008293	1.5772
Bicarbonate	0.0007669	1.8430
Ethanesulfonate	0.0007252	2.0711
Acetate	0.0007046	2.0054
Propionate	0.0006744	2.2910
Propanesulfonate	0.0006641	2.2110
Butyrate	0.0006396	2.5150
Benzoate	0.0006018	2.5317

Values of $\mu_{app(ion)}$ were calculated from Eq. (2) using migration times of anions, $L_D=52$ cm, $L_T=60$ cm and $V=30$ kV. Hydrated ionic radii were calculated from limiting ionic conductance taken from Ref. [17] using Eq. (4).

3. Optimization of separation

Great attention has been paid to the selection and optimization of the running electrolyte composition. To attain a good peak shape and an optimal separation of anions, the electrolyte anion (carrier anion) should have a mobility similar to the mobilities of the analytes. If possible, the EOF should have the same direction as the migration of the analytes to shorten the analysis. If indirect UV detection is used, the carrier anion should strongly absorb in the UV region. The most common carrier anions for analyses of inorganic anions in combination with indirect UV detection are chromate and pyromellitic acid. Their dissociation and thus their electrophoretic mobilities are influenced by the pH. The separation of anions with lower mobilities can be optimized by decreasing the pH.

As follows from Eq. (4), the electrophoretic mobility of analytes can be changed by changing their charge-to-mass ratio. For weak acids this can be done by changing the pH in the vicinity of the analyte pK_a.

However, most inorganic acids have pK_a values below 2 and thus the change in the pH to modify the selectivity is not practical. At low pH values the EOF is too low in a silica capillary to carry inorganic anions towards the detector (cathode) and the current generated at a pH lower than 2 makes the analysis difficult if not impossible because of a high Joule heat.

The effect of the pH on the separation of weak acids can be demonstrated on an example of phosphate present at a high concentration (more than 800 μg/l) beside a low concentration of fluoride (1 μg/l). At a pH of 7, protonation of hydrogenphosphate results in its slower migration and leads to an improved separation from fluoride [18].

An addition of a solvent, e.g. 1-butanol, results in selectivity changes. This can be explained by changes in the relative hydration of anions and, as a consequence, an improved separation, e.g. of iodide and chloride [19]. Organic solvents added to the running electrolyte decrease the EOF; they increase the viscosity and decrease the pK_a of silanol groups on the capillary walls and make the migration times more reproducible with a less noisy baseline [20]. The temperature also affects the selectivity, as it influences both the mobilities and the EOF through a change in the solution viscosity.

While cations can be analyzed directly in CE, the elution of anions in bare-silica capillaries requires modulation of the electroosmotic flow. The EOF can be modified by cationic additives, by changing the concentration of the running electrolyte, or by a chemical modification of the capillary walls.

Cationic surfactants are mostly added to modify the EOF in analyses of anions. At concentrations below the critical micelle concentration, CMC, hemicelles are formed at the capillary wall that reverse the EOF. If the anions interact with the monomeric surfactant present in the electrolyte, then their electrophoretic mobilities are influenced through ion association. For a monovalent anion, the ion association constant, K_{IA}, is defined by

$$K_{IA} = [AB]/[A^-][B^+] \quad (6)$$

where [AB], [A^-] and [B^+] are the equilibrium concentrations of the associate, the anion and the free cationic surfactant. As the surfactant is present in an excess over the analytes, [B^+] can be replaced by the bulk surfactant concentration, c_{sf}.

An equation derived by Kaneta et al. [21] relates $\mu_{app(ion)}$ to K_{IA} and c_{sf},

$$1/\mu_{app(ion)} = Kc_{sf}/\mu_{ep} + 1/\mu_{ep} \quad (7)$$

If the surfactant concentration exceeds the CMC value, the partitioning into the micelles occurs and Eq. (7) changes into

$$1/\mu_{app(ion)} = (1 + k')/k'\mu_{mc} + \mu_{app(CMC)} \quad (8)$$

where $\mu_{app(CMC)}$ is the anion mobility at the CMC, μ_{mc} is the mobility of the micelles and k' is the capacity factor, $\mu_{app(ion)}/(\mu_{app(ion)} + \mu_{mc})$.

The most common cationic surfactants used are, e.g. tetrabutylammonium (TBA), dodecyltrimethylammonium (DTA), tetradecyltrimethylammonium (TTA), cetyltrimethylammonium (CTA) bromides or hydroxides, hexadimethrine (HDM) and hexamethonium (HM) hydroxide (patented, together with other running electrolyte components, by Waters) (e.g. Ref. [19], or their binary mixtures, e.g. Ref. [22]). They are added to the running electrolyte in concentrations below the CMC and their association

with inorganic anions is small as proved by the elution order of the anions which corresponds to their molar conductivities (with the exception of iodide that is retarded even below the CMC). Although the use of surfactants at concentrations above the CMC, e.g. in micellar electrokinetic chromatography (MEKC), is not very frequent in the analysis of inorganic anions, the different selectivity obtained in MEKC in comparison with CZE can be useful in special applications [21].

Various EOF modifiers were compared [23]. The size of the alkyl ammonium ion affects not only the EOF, but also determines the optimum concentration range of the surfactant which decreases with increasing ion size. When using high-molecular-mass additives, e.g. HDM, a good efficiency can be obtained even at very low surfactant concentrations (0.0001%). This is important for two reasons: first, hydrophobic alkyl ammonium ions have a limited solubility in the presence of chromophores and, second, there is a danger of formation of insoluble pairs between the alkylammonium ions and the components of both the electrolyte and of the sample. A dependence of the EOF on the concentration of EOF modifiers is shown in Fig. 1 [23]. The optimal separation conditions (except for the modifier concentration) and the analytical parameters are similar for all the EOF modifiers tested, indicating that the influence of these conditions is small provided that the EOF is reversed; HM does not reverse the EOF, only decreases it. When combining HM with the fully dissociated chromophore pyromellitic acid, stable complexes are formed that are adsorbed onto the silanol groups at the capillary walls.

Weak acid anions are more strongly affected by

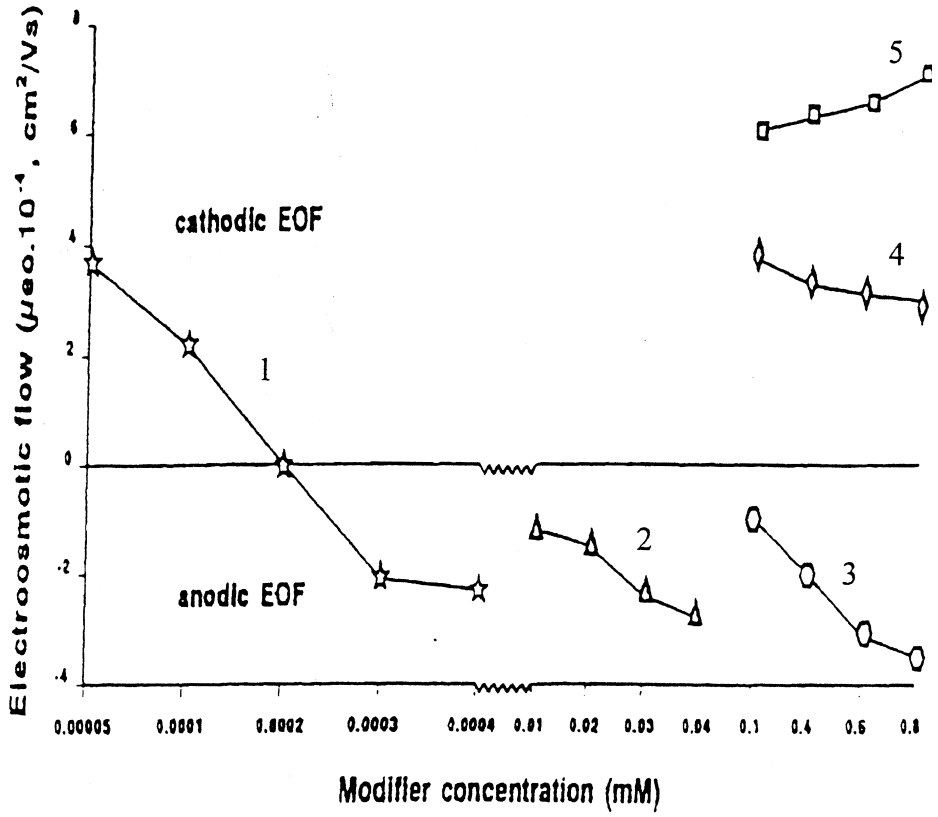

Fig. 1. Dependence of the EOF on the concentration of various modifiers [23]. 1, HDM; 2, CTA; 3, TBA; 4, HM; 5, TTA.

the EOF modifier concentration than strong acid anions. Higher concentrations lead to longer migration times due to the formation of equilibrium ion pairs. This difference in the selectivity allows complex samples to be analyzed by properly selecting the EOF modifier concentration and thus increasing the weak acid anion migration times. An addition of organic solvents increases the solubility of quaternary ions.

Another possibility for EOF modification is the coating of the capillary walls with cationic polymers, e.g. poly(1,1-dimethyl-3,5-dimethylene)piperidinium and -pyrrolidinium chloride [24] or a reactive polyamide with various functional groups [25]. A net positive charge is then formed at the capillary walls. In the former case, the mobility of anions is strongly influenced by organic modifiers (methanol or acetonitrile). The migration of ions is affected by the running electrolyte properties, such as solvation and structural conformation. Ion-exchange is the main interaction, but hydrophobic interactions also play a role. In the latter case, the elution order is the same as in CE with EOF reversal. A good run-to-run, but a poor column-to-column reproducibility is, however, obtained.

The use of EOF modifiers complicates the analysis of those anions that move so slowly that they do not require EOF reversal. Reducing the EOF, e.g. by coating the capillary walls with silane, is sufficient for attaining sufficiently short analysis times for some anions [26]. These capillaries are especially useful with direct UV detection, e.g. of bromide and iodide.

The EOF can also be modified by using capillaries made of materials other than fused silica. For example, an untreated polypropylene hollow fibre was used for the CE analysis of anions [27]. Theoretically these capillaries have no surface charge, but practically there is a small negative charge and thus a small EOF is observed. Fast separations are possible but the efficiency is poorer. Advantages of polypropylene capillaries are their good stability at high pH, a low cost and no hysteresis effect. Fast moving anions can be separated directly without any modification to the electrolyte or the capillary wall. The capillaries are transparent to visible and near UV radiation.

4. Detection modes

Detection in CE must take place directly on the separation column, because the elution profile outside the electric field rapidly changes from plug to parabolic, similar to IC, and the separation efficiency decreases drastically.

Direct UV detection is both selective and sensitive and is often employed in the analysis of cations after their complexation, but its application to the analysis of inorganic anions is limited to a few of them which absorb the UV radiation, e.g. to nitrate, sulfide, nitrite, iodide, bromide and thiocyanate. For example, a detection limit of 10 μg/l was attained for sulfide in waste water using direct UV detection at 229 nm [28]. The running electrolyte contained sodium sulfate and an EOF modifier in the OH form.

Indirect UV detection is most common. It is nearly universal and requires no modification to the instrument. Detection limits in a sub-mg/l region have been obtained with running electrolyte containing chromate, with a time of analysis of 3 min [29]. A disadvantage of chromate lies in its aging that causes changes in the analyte migration times, e.g. for fluoride [30]. *p*-Aminobenzoate was found to be optimal for simultaneous determination of low mobility organic and high mobility inorganic anions. The separation was facilitated by an addition of barium salts [31].

Anionic chromophores (benzoate, anisate) and cationic buffers (Tris, ethanolamine) were tested for simultaneous detection of nonabsorbing anions and cations [32]. An equation was derived for the dependence of the difference in the absorbance, ΔA.

So far the best separation of anions with indirect UV detection has been attained in the IonPhor PMA electrolyte buffer consisting of 2.5 m*M* pyromellitic acid, 6.5 m*M* NaOH, 0.75 m*M* hexamethonium hydroxide and 1.6 m*M* triethanolamine, with a pH of 7.7 (e.g. Ref. [19]).

A CE method with indirect UV detection was validated for eight anions and two electrolyte systems: pyromellitic acid + hexamethonium hydroxide and chromate + TTAB [33]. The detection limits were between 1 and 3 mg/l, the repeatability and reproducibility of the measurement differed for different compounds and were, with the exception of

fluoride and phosphate, 6 and 5–10%, respectively. Linear calibration curves were obtained in a concentration range between 1 and 10 mg/l.

A disadvantage of indirect detection is a high background absorbance and thus a high noise and a limited linear dynamic range. CE with indirect UV detection exhibits a lower concentration sensitivity than IC due to mass loading limitations, despite its superior mass sensitivity.

Direct fluorescence detection is not applicable to inorganic anions as they cannot be suitably derivatized. Indirect fluorescence detection, though possible, has no advantage over indirect UV detection.

Conductivity detection (CD) is a nearly universal bulk property detection mode for small ions and, similar to IC, both non-suppressed and suppressed CD is used. There are more options for the selection of the running electrolyte in combination with CD. The co-ion must have a substantially different conductivity. In non-suppressed CD, low mobility buffers with higher ionic strengths provide an extended linearity and improve preconcentration by sample stacking.

In comparison with indirect UV detection, CD is 10 times more sensitive [34]. The linear dynamic range extends over three concentration decades and the reproducibilities of the migration time, peak area and height are better than 0.15, 1.985 and 1.255%, respectively. A determination of anions in drinking water with CD is shown in Fig. 2 [34].

A borate buffer (2 m*M*, pH 9.2) combined with suppressed conductivity detection provided good peak shapes due to a close match of the borate mobility with those of the separated anions and fulfilled the principal condition of suppressed CD, i.e. could be suppressed to form a weakly conducting species. Additives, such as barium ions, decreased the EOF and the migration velocity of high-mobility anions, so that they could be analyzed simultaneously with organic anions [35]. Detection limits in a range of 1–10 μg/l were reported with suppressed conductivity detection [36]. A similar sensitivity has been attained for inorganic anions in a large-diameter plastic capillary (300 μm) and conductivity detection [37].

Other detection modes can be used, e.g. direct combination of CE with mass spectrometry via an ion spray–sheath flow interface [38] or potentiometry with ion-selective microelectrode [39], but their application has so far been less common.

A combination of various detection modes, e.g. CD-UV on-line, substantially enlarges sample matrix information.

5. Preconcentration techniques for inorganic anions

Sample preconcentration is usually necessary for the analysis of highly dilute solutions of anions, e.g. for the analysis of anions in deionized water or their determination in the presence of a large excess of a matrix component.

Isotachophoretic enrichment by electrostacking at the sample–buffer interface is often used. Isotachophoresis can be carried out off-line, on-line or directly in the analytical CE instrument. The sample matrix can assist the stacking process by functioning as the leading or terminating electrolyte. The co-ion of the running electrolyte has to be chosen so that the analyte mobilities are between those of the ions of the electrolyte and the matrix. Limits of detection lower than 50 nmol/l have been attained in the simultaneous analysis of inorganic and organic anions in rain water when enriching by sample stacking with a dynamic injection (the injection volume was 300 nl, corresponding to a 10% filling of the capillary [31]). This preconcentration method permits determination of inorganic anions in the presence of a fluoride matrix up to an analyte:matrix ratio of $1:6\times10^{6}$ [40]. A mathematical treatment of electrostacking can be found in Ref. [41].

Preconcentration with the electrokinetic injection can be used for non-ionic matrices. With long injection times, the ionic components are preconcentrated at the expense of the interferents. The EOF has the direction opposite to the migration of the analytes. The matrix effects caused by ionic components can be decreased by suppressing their dissociation by a pH change, thus enriching the analytes by up to two orders of magnitude. The choice of the amount injected is influenced by the analyte mobility, the electroosmotic flow and the sample and buffer ionic strengths.

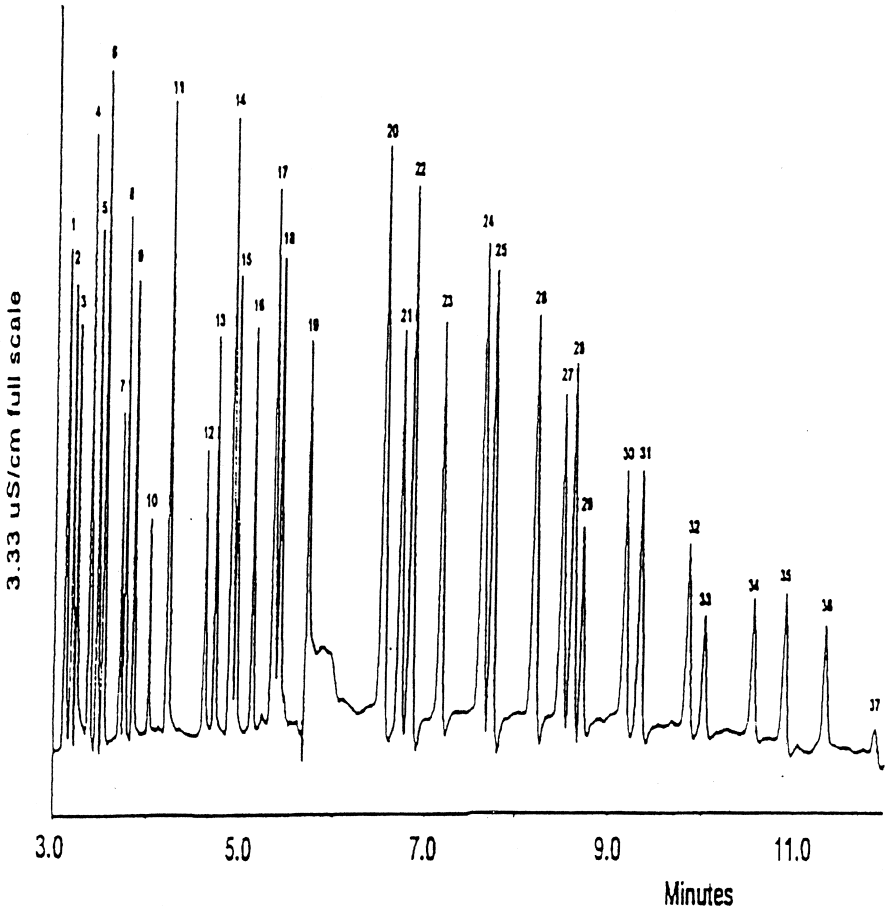

Fig. 2. Determination of inorganic and organic anions by CE with direct conductivity detection [34]. The electrolyte: 50 m*M* CHES (2-N-cyclohexylaminoethane-sulfonate), 20 m*M* LiOH and 0.03% Triton X-100; 60 cm×50 μm I.D. capillary; 25 kV; injection at 25 mbar for 12 s; the EOF was modified by preflushing the capillary with a 1 m*M* CTAB solution. Anions (concentrations in mg/l): 1, bromide (4); 2, chloride (2); 3, hexacyanoferrate (7); 4, nitrite (4); 5, nitrate (4); 6, sulfate (4); 7, azide (2); 8, oxalate (3); 9, molybdate (5); 10, tungstate (6); 11, 1,2,4,5-benzenetetracarboxylic acid (7); 12, fluoride (1); 13, tartrate (5); 14, selenite (10); 15, phosphate (4); 16, citraconate (methylmaleate) (5); 17, glutarate (10); 18, phthalate (10); 19, carbonate (4); 20, acetate (10); 21, chloroacetate (10); 22, ethanesulfonate (20); 23, dichloroacetate (15); 24, propionate (15); 25, propanesulfonate (20); 26, crotonate (15); 27, butanesulfonate (20); 28, butyrate (15); 29, toluenesulfonate (15); 30, pentanesulfonate (20); 31, valerate (15); 32, hexanesulfonate (20); 33, caproate (15); 34, heptanesulfonate (20); 35, morpholineethanesulfonate (35); 36, octanesulfonate (20); 37, *d*-gluconate (40).

The detection limits and the analyte-to-matrix ratios for inorganic and organic anion impurities in boric acid, obtained using hydrostatic or electrokinetic injection and with sample stacking (the capillary is filled with the sample up to the detector, a voltage is applied to preconcentrate the sample anions at the sample–buffer interface, a reversed EOF is used to remove the matrix components and then the CE analysis is carried out), are compared in Table 3 [40].

The effect of the preconcentration time and of the voltage on the sensitivity of a CE determination of trace inorganic and organic anions in matrix-free pure water has been studied [42] and compared with IC: IC yields similar or better detection limits (nl/ml level), but requires trace enrichment times much

Table 3
Comparison of limits of detections (LOD) and analyte-to-matrix ratios (ATMR) for inorganic and organic anion impurities in boric acid obtained using hydrostatic and electrokinetic injection and sample stacking [40]

Anion	Hydrostatic injection		Electrokinetic injection		Sample stacking	
	LOD (μmol/l)	ATMR	LOD (μmol/l)	ATMR	LOD (μmol/l)	ATMR
Bromide	8	$1:1.1\times10^5$	0.3	$1:2.7\times10^6$	0.07	$1:1.2\times10^7$
Chloride	7	$1:1.3\times10^5$	0.5	$1:1.7\times10^6$	0.04	$1:2.2\times10^7$
Sulfate	5	$1:1.8\times10^5$	0.2	$1:3.8\times10^6$	0.02	$1:3.5\times10^7$
Nitrate	7	$1:1.3\times10^5$	0.3	$1:2.8\times10^6$	0.04	$1:2.2\times10^7$
Oxalate	5	$1:1.8\times10^5$	0.4	$1:2.1\times10^6$	0.03	$1:2.8\times10^7$
Chlorate	7	$1:1.3\times10^5$	0.4	$1:2.2\times10^6$	0.05	$1:1.5\times10^7$
Malonate	5	$1:1.8\times10^5$	0.4	$1:2.0\times10^6$	0.05	$1:1.7\times10^7$
Fluoride	10	$1:0.9\times10^5$	0.7	$1:1.2\times10^6$	0.89	$1:9.0\times10^7$

LOD is defined as three times the signal-to-noise ratio.

longer than CE (ca. 5–10 min, compared with 45 s in CE). Using a 45-s electromigration injection, CE detection limits of 0.5 μg/l of anions in deionized water have been obtained (Fig. 3) [42]. The detection of cations is even more sensitive [43].

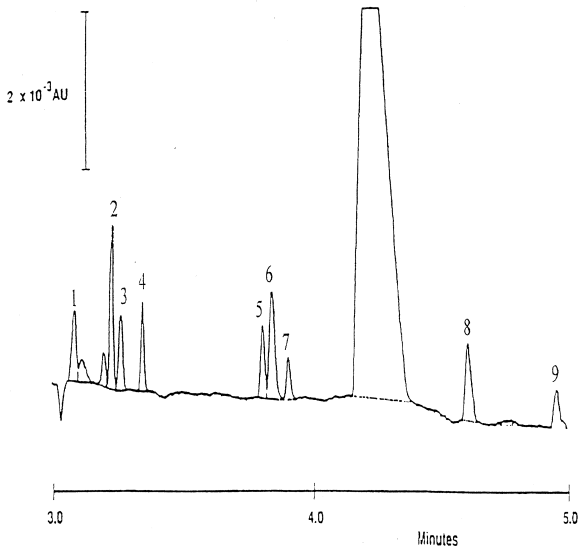

Fig. 3. Trace determination of some inorganic and organic anions in pure water, after an electrophoretic enrichment at 5 kV for 45 s with an addition of 75 μ*M* octanesulfonate to the sample [42]. The electrolyte: 10 m*M* sodium chromate and 0.5 m*M* OFM-BT (a surfactant used as the EOF modifier), adjusted to pH 8 with sulfuric acid; 15 kV; 60 cm×75 μm I.D. capillary, distance to detector, 52 cm; UV photometric detection at 254 nm. Anions (concentrations in mg/l): 1, chloride (3.5); 2, sulfate (4.8); 3, nitrate (6.2); 4, oxalate (5); 5, fluoride (1.9); 6, formate (5); 7, phosphate (3.2); 8, acetate (5); 9, propionate (5).

The reproducibility of the electrokinetic injection is poorer than that of the dynamic pressure injection and strongly depends on the ionic strength. Internal standards are usually added to improve the accuracy and precision [44]. For a stacking injection, a mathematical model has been developed to account for the increase in the migration time with increasing sample injection time; a good agreement with the theory has been found [45].

6. Comparison of CE and IC in selected applications

As pointed out above, IC is a well-established method for the analysis of inorganic anions and has become the method of choice in many application areas. Many techniques are available using single-column [46] or dual-column systems with various detection modes. IC can be used both for analytical and preparative purposes. Large sample volumes, up to 1300 μl, can be injected to determine trace anions and cations and to attain detection limits of 10–400 ng/l. For determinations at a μg/l to mg/l level, a sample size of 10–50 μl is sufficient. Preconcentration is necessary for lower concentrations (an additional column, a sample pump, an extra valve and an extra time are the disadvantages of this approach [47]). With an IEC column and isocratic

elution, it is impossible to separate both inorganic and organic ions.

As pointed out in Section 1, CE and IC are complementary techniques and their use in tandem is advantageous in many cases. For example, CE and IC analyses of anions in residues of explosives were compared (Fig. 4) [48]. The differences in the separation modes of CE and IC help to determine the nature of the sample and the use of the two methods in tandem makes it possible to decrease the interference by other ions and to confirm the peak identity. IC with a greater capacity allows for screening of a variety of explosive residues. Analogously, a combination of CE and IC helps to solve the problems of peak confirmation in complicated matrices, e.g. in atmospheric aerosols (Fig. 5, Ref. [49]). Two IC

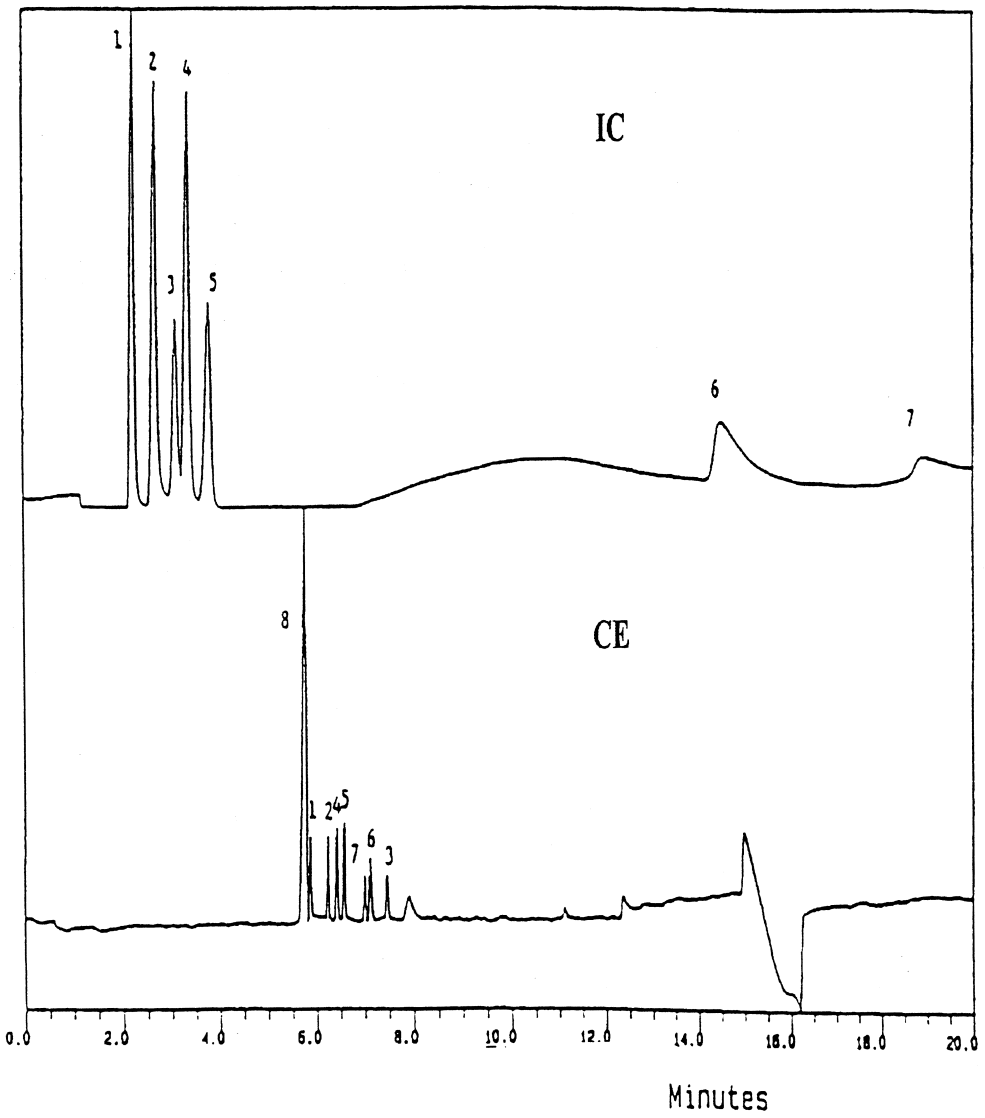

Fig. 4. Analysis of an anion standard solution by IC (a) and CE (b) [48]. IC conditions: a Vydac 302IC4.6 column, a flow-rate of 2.5 ml/min, an injection volume of 25 μl, an isophthalic acid mobile phase, UV detection at 280 nm. CE conditions: an electrolyte of potassium dichromate, sodium tetraborate, boric acid and the DETA (diethylenetriamine) EOF modifier, pH 7.8; 65 cm×75 μm I.D. capillary; 20 kV; indirect UV detection at 280 nm. Anions: 1, chloride; 2, nitrite; 3, chlorate; 4, nitrate; 5, sulfate; 6, thiocyanate; 7, perchlorate; 8, bromide.

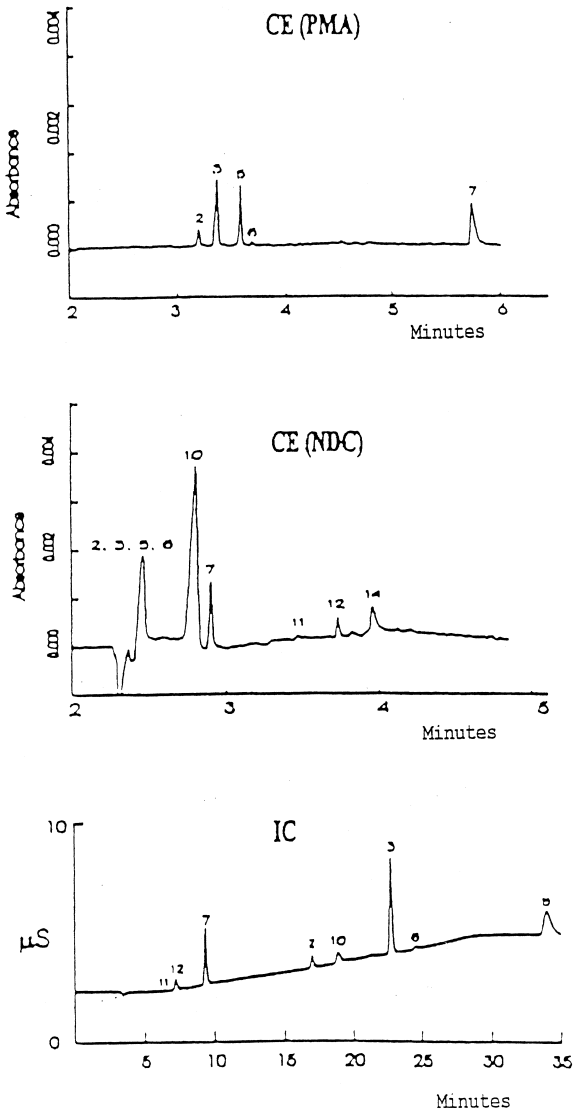

Fig. 5. An analysis of a coarse atmospheric aerosol extract by CE and IC [49]. CE conditions: a 57 cm×75 μm I.D. capillary, distance to detector, 50 cm. Electrolyte: 2.25 m*M* PMA (pyromellitic acid), 0.75 m*M* HMOH (hexamethonium hydroxide), 6.50 m*M* NaOH and 1.60 m*M* TEA (triethanolamine), pH 7.7 or 2.0 m*M* NDC (2,6-naphthalenedicarboxylic acid), 0.5 m*M* TTAB (tetradecyltrimethylammonium bromide) and 5.0 m*M* NaOH, pH 10.9; 30 kV (PMA) or 20 kV (NDC); pressure injection for 10 s; indirect UV detection at 254 nm (PMA) or 280 nm (NDC). IC conditions: an IonPac-AS10 column with an IonPac-AG10 guard precolumn; conductivity detection using an anion self-regenerating suppressor (ASRS-I) in the recycle mode. Analytes: 2, chloride; 3, sulfate; 5, nitrate; 6, oxalate; 7, formate; 10, hydrocarbonate or carbonate; 11, acetate; 12, propionate; 14, benzoate.

columns with automated column switching or CE combined with IC can separate anions in aqueous soil extracts and process solutions [30]. The IC detection limits were found to be lower than in CE (0.2 μg/ml for IC compared with 2 μg/ml for CE), but, due to a higher separation efficiency, the peaks were resolved better in CE than in IC and the quantitation was easier.

A CE determination of fluoride in rain water was compared with IC and ISE potentiometry; the IC response was related to the total concentration, whereas CE and ISE responded to free fluoride [50]. The fluoride concentrations obtained by CE and ISE were systematically lower than those obtained by IC due to the fluoride complexation with aluminium. The detection limits for IC and ISE were similar (0.2 and 0.3 μmol/l) and somewhat lower than those for CE (0.6 μmol/l). CE was evaluated as an alternative method to the EPA ion chromatographic method for the determination of anions in water and a better resolution and a shorter analysis time were found for CE [51].

A strong adsorption of dyes observed in IC columns was not encountered in CE when analyzing chloride, sulfate and phosphate in sulfonated dyes [52]. Proteins need not be removed prior to CE analysis and do not interfere with low-molecular-mass ions as is the case in IC [53].

The IC analysis of polyphosphates and polycarboxylates (builders in detergents) is complicated by strong affinities of these compounds toward ion exchangers [54]. CE can readily be used for this purpose (a LOD of 2×10^{-5}–5×10^{-5} *M*).

The applications of CE analysis to inorganic anions are already numerous and are rapidly growing. The application ranges include, e.g. clinical chemistry [53], the pulp and paper industry [55], environmental samples [49], waste waters from processing plants [56], process control, industrial applications [43,57–59], explosive residue analysis [48], biological samples [60], or drugs and intermediates [61,62].

7. Conclusion

As can be seen from the above examples, the relative advantages and drawbacks of IC and CE in

analyses for inorganic (an)ions basically correspond to the brief general survey given in Section 1. It can be expected that the future development in the field will primarily be based on judicious combinations of chromatography and electrophoresis and in their coupling with more sophisticated detection techniques.

References

[1] J. Koryta, K. Štulík, Ion-Selective Electrodes, Cambridge University Press, Cambridge, 1983.
[2] J. Veselý, D. Weiss, K. Štulík, Analysis with Ion-Selective Electrodes, Ellis. Horwood, Chichester, 1978.
[3] H. Small, T.S. Stevens, W.C. Bauman, Anal. Chem. 47 (1975) 1801.
[4] Manual for the Certification of Laboratories Analyzing Drinking Water, EPA Publication No. 570-9-90-008 EPA, Washington, DC, 1990.
[5] W.R. Jones, P. Jandik, Am. Lab. 22 (1990) 51.
[6] J.D. Lamb (Guest Ed.), J. Chromatogr., vol. 602, 1992.
[7] G.K. Bonn (Guest Ed.), J. Chromatogr., vol. 640, 1993.
[8] R.M. Cassidy (Guest Ed.), J. Chromatogr. A, vol. 671, 1994.
[9] C. Sarzanini (Guest Ed.), J. Chromatogr. A, vol. 706, 1995.
[10] D.J. Pietrzyk (Guest Ed.), J. Chromatogr. A, vol. 739, 1996.
[11] S.F.Y. Li, Capillary Electrophoresis (Journal of Chromatography Library, vol. 52), Elsevier, Amsterdam, 1992.
[12] P.R. Haddad, P.E. Jackson, Ion Chromatography–Principles and Applications (Journal Chromatography Library, vol. 46), Elsevier, Amsterdam, 1990.
[13] P. Jandik, G. Bonn, Capillary Electrophoresis of Small Molecules and Ions, VCH, New York, 1993.
[14] J.C. MacDonald (Ed.), Inorganic Chromatographic Analysis (Chemical Analysis, vol. 78), Wiley, New York, 1985.
[15] G. Schwedt, Chromatographic Methods in Inorganic Analysis, Hüthig, Heidelberg, 1981.
[16] A.S. Rathore, Cs. Horváth, J. Chromatogr. A 743 (1996) 231.
[17] Handbook of Chemistry and Physics, 67th ed., CRC Press, Boca Raton, FL, 1986–1987.
[18] A.H. Harakuwe, P.R. Haddad, J. Chromatogr. A 734 (1996) 416.
[19] M.P. Harrold, M.J. Wojtusik, J. Riviello, P. Henson, J. Chromatogr. 640 (1993) 463.
[20] N.J. Benz, J.S. Fritz, J. Chromatogr. A 671 (1994) 437.
[21] T. Kaneta, S. Tanaka, M. Taga, H. Yoshida, Anal. Chem. 64 (1992) 798.
[22] A.H. Harakuwe, P.R. Haddad, W. Buchberger, J. Chromatogr. A 685 (1994) 161.
[23] M.T. Galceran, L. Puignou, M. Diez, J. Chromatogr. A 732 (1996) 167.
[24] C. Stathakis, R. Cassidy, J. Chromatogr. A 699 (1995) 353.
[25] H. Burth, D.M. Lewis, K.N. Tapley, J. Chromatogr. A 739 (1996) 367.
[26] G.W. Tindall, R.L. Perry, J. Chromatogr. A 696 (1995) 349.
[27] J.D. Lamb, T.L. Huxford, K.B. Czirr, J. Chromatogr. A 739 (1996) 373.
[28] J. Font, J. Gutiérrez, J. Lalueza, X. Pérez, J. Chromatogr. A 740 (1996) 125.
[29] W.R. Jones, P. Jandik, J. Chromatogr. 608 (1992) 385.
[30] R. Stahl, J. Chromatogr. A 686 (1994) 143.
[31] A. Röder, K. Bächmann, J. Chromatogr. A 689 (1995) 305.
[32] J. Collet, P. Gareil, J. Chromatogr. A 716 (1995) 115.
[33] M.M. Rhemrev-Boom, J. Chromatogr. A 680 (1994) 675.
[34] W.R. Jones, J. Soglia, M. McGlynn, C. Haber, 1995, presented at the 1995 Pittsburgh Conference, New Orleans, oral presention No. 1366.
[35] M. Harrold, J. Stillian, L. Bao, R. Rocklin, N. Avdalovic, J. Chromatogr. A 717 (1995) 371.
[36] N. Avdalovic, C.A. Pohl, R.D. Rocklin, J.R. Stillian, Anal. Chem. 65 (1993) 1470.
[37] D. Kanianský, V. Zelenská, D. Baluchová, Electrophoresis 17 (1996) 1890.
[38] T.G. Huggins, J.D. Henion, Electrophoresis 14 (1993) 531.
[39] A. Nann, E. Pretsch, J. Chromatogr. A 676 (1994) 437.
[40] J. Boden, M. Darius, K. Bächmann, J. Chromatogr. A 716 (1995) 311.
[41] R.L. Chien, Anal. Chem. 63 (1991) 2866.
[42] G. Bondoux, P. Jandik, W.R. Jones, J. Chromatogr. 602 (1992) 79.
[43] G. Bondoux, T. Jones, LC·GC Int. 7 (1994) 29.
[44] P.E. Jackson, P.R. Haddad, J. Chromatogr. 640 (1993) 481.
[45] Zhang H.-W-., X.-G- Chen, Z.-D. Hu, J. Chromatogr. A 677 (1994) 159.
[46] V. Pacáková, K. Štulík, Mingjia Wu, J. Chromatogr. 520 (1990) 349.
[47] E. Kaiser, J. Riviello, M. Rey, J. Statler, S. Heberling, J. Chromatogr. A 739 (1996) 71.
[48] K.A. Hargadon, B.R. McCord, J. Chromatogr. 602 (1992) 241.
[49] E. Dabek-Zlotorzynska, J.F. Dlouhy, J. Chromatogr. A 671 (1994) 389.
[50] M.A.G.T. van den Hoop, R.F.M.J. Cleven, J.J. van Staden, J. Neele, J. Chromatogr. A 739 (1996) 241.
[51] J.P. Romano, J. Krol, J. Chromatogr. 602 (1992) 205.
[52] S.A. Oehrle, J. Chromatogr. A 671 (1994) 383.
[53] W. Buchberger, K. Winna, M. Turner, J. Chromatogr. A 671 (1994) 375.
[54] T. Wang, A.F.Y. Li, J. Chromatogr. A 723 (1996) 197.
[55] D.R. Salomon, J. Romano, J. Chromatogr. 602 (1992) 219.
[56] S.A. Oehrle, R.D. Blanchard, C.L. Stumpff, D.L. Wulfeck, J. Chromatogr. A 680 (1994) 645.
[57] S.C. Grocott, L.P. Jefferies, T. Bowser, J. Carnevale, P.E. Jackson, J. Chromatogr. 602 (1992) 257.
[58] A. Oehre, J. Chromatogr. A 745 (1996) 81.
[59] S.A. Oehrle, J. Chromatogr. A 739 (1996) 413.
[60] C. Bjergegaard, P. Moller, H. Sorensen, J. Chromatogr. A 717 (1995) 409.
[61] J.B. Nair, C.G. Izzo, J. Chromatogr. 640 (1993) 445.
[62] M.E. Swartz, J. Chromatogr. 640 (1993) 441.