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1 Introduction

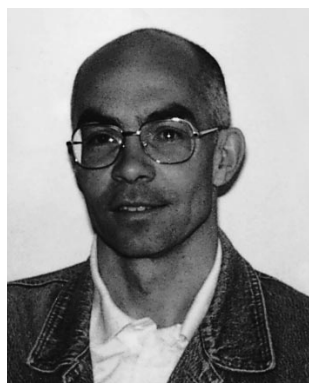
The ever-increasing demand for maintaining a healthy environment requires sophisticated ambient monitoring technologies

for the determination of lower contaminant concentration levels in a diversity of environmental samples. Control of the risks associated with potentially dangerous substances, including inorganic pollutants, achieved through measurement, is now essential to fulfil environmental protection goals. Trace levels of inorganic impurities from both natural sources and anthropogenic emissions have become important, needing determination. Furthermore, environmental protection care-takers attempt to safeguard our surroundings by focusing analysts on using complex multi-elemental methodology and instrumentation that would not have been considered previously. Consequently, the analyst has to learn to use technologies that operate very close to the theoretical limits of performance.

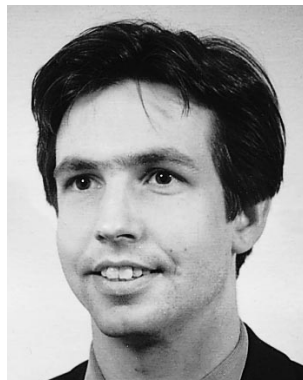
One such technology that received much attention from environmental scientists is capillary electrophoresis (CE). Initially introduced as a technique for the separation of biological macromolecules, CE has since attracted much interest in other application areas, including the environmental field. The prospects for CE in environmental analysis seem to be



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highly promising owing to the technique's merits such as the proven ability to separate complex mixtures of ionic species in a fast and efficient manner, ease of operation, low running costs, and full possibilities of automation. Additionally, the element speciation potential of CE is an important benefit related to the toxicity of inorganic species because the toxicity varies markedly with the particular chemical form. Also, capabilities to conduct analyses in a miniaturised format would interest analysts who analyse routinely samples containing hazardous chemicals. However, in view of the trace levels at which many toxic inorganics occur in environmental matrices, certain problems are encountered as a consequence of sometimes inadequate detection sensitivity. With the evolution of coupled methods combining CE separation with very sensitive detectors (e.g., ICP-MS), these problems appear to be solved in a majority of environmental applications. In this regard, the commercial availability of CE-ICP-MS and different detection systems designed for CE from many experienced, bona fide companies would enhance substantially the utility of CE.

The growing importance of CE in the field of environmental analysis is emphasized by the fact that many organisations involved, including the authors' institutions, are currently evaluating CE as a standard method. For example, CE is currently being considered by the US EPA for inclusion in the methods compendium SW-846 as an anion determination method,¹ which is appropriate for the determination of dissolved inorganic anions in drinking water, groundwater, surface water and waste water.² Also notable is the appearance of first review articles^{3–7} and book chapters^{8–10} dealing almost entirely with different aspects of the environmental applications of CE. So far, however, most published reports have dealt with demonstrating the technique's high resolution potential regarding specific pollutants; the widespread use of CE as a routine quantitative assay for environmental analysis is still limited.

The aim of this review is to give the reader and, primarily, separation scientists working at environmental analytical laboratories a better overview of CE techniques currently available for the determination of inorganic species. Special attention is paid to providing a comprehensive coverage of procedures, which are of real use, and on ways to avoid and overcome problems in practice. The applications addressed in this review cover atmospheric, aqueous and solid environmental samples. In addition, brief background information on fundamentals and basic methodological principles of CE in inorganic analysis is given for a better orientation of those just beginning to work with CE method development. Finally, possible future trends and developments of CE in the area are briefly discussed.

2 General separation and detection approaches for ion determination by capillary electrophoresis

A comprehensive coverage of the fundamental and methodological aspects of inorganic ion determination by CE is available in the recent literature.^{8,11–16} This section will focus on separation and detection facets of this technique that require careful consideration relevant to environmental applications. These ultimately include principles on selecting carrier electrolyte compositions optimised with respect to the direction and magnitude of the electroosmotic flow (EOF) and the separation selectivity, and adequate detection techniques. Included are also means to enhance the detectability of CE based on using various sample injection methods and on-line preconcentration techniques.

2.1 Separation principles and modes

Separations in CE take place as a result of differences in the velocities at which the sample ions migrate along the capillary

filled with a suitable conducting electrolyte. The migration generally occurs under the combined action of electrophoretic and electroosmotic flows generated by an electric field applied across the capillary. Whilst the electrophoretic mobility is an inherent property of an ion, no matter what the nature of the capillary used, its electroosmotic mobility can only be observed in a capillary with a charged wall, because the EOF arises from interactions of capillary electrolyte components with the surface charges, followed by the formation of an electric double layer. It is worth mentioning that the EOF affects all ions equally, acting like a sort of electric pump, and hence no separations result from the EOF.

2.1.1 Cations. With the most common use of untreated fused-silica capillaries, the EOF is directed towards the cathode at most pH values. This means that the EOF will accelerate the migration of cations to the detector when a negative polarity is placed at the detection end of the capillary. Hence both electrophoretic and electroosmotic mobility have the same direction (a co-electroosmotic migration mode), and the manipulation of EOF is not of great importance for the separation of inorganic cations. What is more essential is the fact that the differences in mobility between cations of similar charge and size are often not sufficient for the separation. Special measures to circumvent this problem and to enhance the separation selectivity typically imply selective complexation of the sample cations. This can be basically achieved through addition of a complexing reagent, either to the carrier electrolyte and/or to the sample, that complexes a group of metal ions, partially or completely, and provides them with much larger differences in electrophoretic mobility. In the former case, when the partial complexation is established within the capillary, it is the formation of metal complexes of different composition and thereby an average effective charge that allow for modulation of the resolution in a broad range. As the net charge of the analyte metal ion remains positive, these separations are carried out in the co-electroosmotic mode. Complete conversion of metal ions into charged complexes produces substantially different separation selectivity based on their charge and size differences. Correspondingly, one may apply either the co- or counter-electroosmotic mode by changing the polarity of the separation potential. Strategies for selectivity control in CE of metal ions are discussed in more detail in recently published reviews.^{17,18}

2.1.2 Anions. Co-electroosmotic migration of anionic analytes can only be achieved by reversing the direction of the EOF towards the anode. Conventionally, the anodic EOF is effected by incorporating a cationic surfactant in the carrier electrolyte. In this way, coating of the capillary wall with the surfactant will reverse its net charge from negative to positive, providing the EOF in the desired direction. This migration mode results in rapid separations of the majority of inorganic anions of environmental interest. All other situations are generally less appropriate, as the electrophoretic mobility of anions and the EOF are in different directions. This reduces substantially the number of the sample anions which can reach the detector, regardless of polarity, and enables simultaneous separation. It is important to note that unlike metal cations, inorganic anions are well resolved owing to differences in ionic mobilities. When necessary, the separation selectivity can be further enhanced by variation of the composition of the carrier electrolyte (see the next section).

2.2 Choice of electrolyte systems

The majority of carrier electrolytes used in inorganic ion determinations contain a buffer to ensure constant pH condi-

tions. As can be seen below, the buffer pH and composition depend strongly on the nature of the sample ions to be separated. The electrolyte buffer is also a major source of ions providing an electric current. In addition to these factors, the rational search for optimum electrolyte conditions should take into account the following items specific for cationic and anionic analytes.

2.2.1 Cations. As mentioned above, the use of complexing reagents is the key to resolving selectively metal cations having mobilities similar to one another. With the utilisation of the partial complexation principle, which appears to be the most widely used methodology for environmental cationic analyses, various carboxylic and hydroxycarboxylic acids have been found to be suitable in aiding the separation of different metal groups. Of these, α -hydroxyisobutyric acid (HIBA) is undoubtedly a premier complexing reagent, followed by lactic acid (see Tables 1–4).^{19–24} However, in many cases with alkali and alkaline earth metal cations as the only analytes, crown ethers, *e.g.*, 18-crown-6 ether exhibiting a somewhat different partial complexation mechanism, yield attractive separations.^{19–22,25–31} Other possible electrolyte additives for refining the separation selectivity are organic solvents such as methanol,^{21,24,25,32} poly(vinylalcohol)³³ and polyethylene glycol.²³

The pH of the separation electrolyte has also to be carefully selected, taking due account of (i) its influence on ligand complexing ability; (ii) the inclination of the sample metal ions to undergo hydrolysis; and (iii) the degree of protonation for an electrolyte constituent providing UV absorbance background (see below). For these reasons, CE separations of metal ions are predominately performed at a slightly acidic pH (usually 3–5).

When indirect UV detection is a mode of choice, a UV-active cation is added to the electrolyte. Along with an evident requirement of high molar absorptivity, the ionic mobility of a cationic chromophore must be similar to those of the sample ions. A range of aromatic bases, including imidazole,^{22,24,34} 4-methylbenzylamine,^{19,21} 4-methylaminophenol,^{27,28,31} creatinine^{23,35} and, in earlier applications, Waters' proprietary visualising reagents, meet these requirements well.

For cationic separations based on the pre-capillary derivatisation using polydentate (chelating) reagents such as EDTA or CDTA,^{36–39} simple borate buffers are often appropriate. To prevent the formation of less stable complexes from partial dissociation during electrophoresis, it is advisable to incorporate a certain concentration of the complexing reagent in the carrier electrolyte.

2.2.2 Anions. The combination of anodic EOF and indirect UV detection is the most favourable for the fast and complete CE determination of inorganic anions. EOF modifiers commonly used for dynamic modification of the fused-silica surface are long-chain alkyltrimethylammonium salts, such as cetyltrimethylammonium bromide (CTAB), tetradecyltrimethylammonium bromide (TTAB) and hexyl diquaternary ammonium salts, *e.g.*, hexamethonium hydroxide.

The nature and concentration of the EOF modifier are also challenges to regulating the separation selectivity for anions due to ion-pairing or ion-exchange interactions. If anions of weak (or moderately strong) acids are present in the sample, *e.g.*, carbonate and phosphate, variation of the electrolyte pH, especially in the vicinity of the analyte pK_a , is a useful means of selectivity enhancement. Separation selectivity can also be altered by an organic solvent,^{21,24,25,32,33} a neutral surfactant, *e.g.*, Triton X-100,⁴⁰ or a metal cation, *e.g.*, Ca^{2+} ,⁴¹ added to the carrier electrolyte.

As is the case for cationic analytes, adequate detection of many inorganic anions, exhibiting negligible absorbance, requires the use of indirect UV detection. In view of the high

mobility of anionic species of interest, chromate-based electrolytes work very successfully for this purpose.^{19,42–46} Of other background absorbing ions, ensuring reasonably symmetric peak shapes, multiply charged aromatic carboxylates, in particular pyromellitate,^{47–51} have found application in the detection of common inorganic anions.

2.3 Detection techniques

There are many detection schemes implemented with commercial instruments that can be applied to inorganic ions.⁵² UV detection is very attractive, in contrast to other techniques, because it does not interfere with the electrophoretic separation process. In addition, since most inorganic ions are UV-transparent and UV/VIS absorption detectors are still the most popular owing to their versatility and simplicity and because they are supplied with almost every commercial CE system, most CE applications relating to environmental samples utilise indirect UV detection for the quantification of inorganic ions after CE separation, especially of those having a relatively high abundance in the environment, such as alkali and alkaline earth metal cations and common inorganic anions. The key to this approach is the displacement of a highly absorbing electrolyte co-ion by the sample ions. On the other hand, direct UV (or visible light) absorption detection is generally less applicable. For metal cations, it requires a derivatisation step using a suitable chromophore prior to separation, whereas only a limited number of anions possess a sufficient absorbance at useful wavelengths.

With the same principles of indirect format, fluorescence measurements can be employed for detection when a charged fluorophore is combined with the capillary electrolyte. Cerium³⁺ (ref. 53) and fluorescein⁵⁴ or 2,5-dihydroxybenzoic acid²⁷ have been used as the primary electrolyte components for the highly sensitive determination of cations and anions, respectively. This mode of detection, however, has not yet received wide acceptance, although its gains in sensitivity over photometric detection are significant and it is already available commercially.

Recently, conductivity detection has also become commercially available. Despite a so far limited number of published environmental applications, this detection technique holds great potential, with parts per billion sensitivities for many inorganic ions at relatively low cost. Amongst other possible electrochemical detection principles, amperometric detection shows certain promising features, including prominent performance characteristics, high sensitivity and good selectivity for metal ions, in particular, when used in a pulse mode.⁵⁵

The coupling of CE with mass spectrometric detection provides not only sub $\mu g\ l^{-1}$ detection limits for the analysis of various environmental matrices, but also additional selectivity, taking advantage of multi-analyte monitoring. The latter property makes CE-MS an especially attractive tool for element speciation studies^{32,52,56–62} (see also refs. 7, 52 and 56 for general information). Owing to much effort dedicated to interfacing CE with ICP-MS using a wide range of nebuliser and mass spectrometer designs, several accompanying problems, such as the low flow rate of CE separations and carrier electrolyte incompatibilities with the ionisation process have been basically overcome. However, costs need to be lowered further and the instrumentation simplified in the design of a 'user-friendly' detector.

Whatever the detection method employed, the detectability can be reasonably improved by increasing the loadability of a CE system. For instance, sample introduction by the electrokinetic principle lowers the limits of detection by a factor of at least 10 compared with hydrodynamic injection; in some cases, however, the gain in sensitivity is at the expense of calibration linearity and precision.

2.4 Sample preconcentration

Trace concentration levels, at which many inorganic species exist in environmental samples, are often beyond the detection capability of CE; this necessitates further sensitivity enhancement. The papers reviewed reveal a number of approaches that can be adopted to concentrate the target sample ions prior to separation.

The most frequently applied and simplest technique useful for lowering the detection limits, when analysing low ionic strength samples, such as many diluted aquatic samples, is electrostacking. Stacking (or focusing) of a large volume sample injected into the capillary takes place at the initial stage of electrophoresis due to the electric field gradient between the lower (sample) and higher (carrier electrolyte) conductivity zones. In such a way, up to a 100-fold increase in sensitivity can be achieved as, for example, for transition metals.⁶³ During the injection of very large volumes (up to essentially the entire capillary filled with the sample), attention should be paid to problems originating from the mismatch in EOFs with the sample zone and electrolyte zone. Advantageously, applying a reversed voltage leads to removal of the matrix (water) plug out of the capillary accompanied by focusing of the sample ions at the sample/electrolyte interface. When most of the water plug has been removed, the polarity is switched to initiate separation and detection of the stacked ions. The use of this approach, often called *field amplification sample injection*, results, for example, in over 100-fold enrichment for species such as selenium and arsenic oxoanions⁶⁴ or 800–1500-fold improvements in the detection limits of Pb²⁺, Hg²⁺ and Se^{IV}.⁶⁵

Isotachopheresis (ITP) coupled to CE in either of two different instrumental configurations, *i.e.*, coupled column or single column, has also found use in performing the concentration step—before or virtually simultaneously with—the CE separation. In both cases, the enrichment principle is that the sample components undergo concentration (stacking) between the leading and terminating ions possessing a higher and a lower mobility than all analyte ions, respectively. Coupled columns effect this process in the ITP step, resulting in a sharp initial zone that is subsequently transferred to the CE capillary. The advantages of this combination have been demonstrated by Kaniansky *et al.*⁶⁶ for the determination of various anions in rain and lake water samples. On-column ITP-CE assumes that the terminating or/and leading ion are added to the sample or chosen among the analytes or carrier electrolyte ions. The technique has been employed for the determination of Fe³⁺ converted into an anionic EDTA complex with chloride and morpholinoethanesulfonate (MES)-based electrolytes.³⁷

Alternatively, the sample enrichment can be carried out by use of off-line SPE techniques, some of which show promise in environmental CE analyses.⁶⁷ Recently, a combination of CE with solid-phase extraction on a chelating resin has been shown to be highly effective for on-line preconcentration of metal ions accomplished in an FIA system and combined with sample clean-up.⁶⁸

3 Environmental applications

The analytical steps to be performed between the collection of a sample up to the final separation/determination step are specific both to a sample and an analytical technique. The surveyed literature clearly verifies one of the major benefits of CE in the field of environmental analysis, that is, minimal or facilitated sample preparation as compared with chromatographic-based methods. For this reason, a detailed description of sample handling strategies was considered as beyond the scope of this overview. Instead, examples of typical sampling and pre-treatment facets for environmental samples, which can

be followed to ensure the generation of accurate data, are given in the following sections dealing with specific applications, along with a framework of particular procedures given in the corresponding tables.

3.1 Atmospheric samples

The measurement of the chemical composition of various airborne samples (ambient air, aerosols, dust) and wet deposition (rain and snow) continues to be the subject of many environmental studies using different analytical techniques and collection methods. The sample species may be gases, including NO_x and SO_x that have been emitted from anthropogenic sources. Airborne samples also include non-volatile salts and inorganic ions sorbed on particulates such as fly ash or dust. Collection of airborne samples is usually performed with virtual dichotomous or high-volume filter samplers. In this case, the composition of bulk aerosol samples is determined. Although the individual character of the particles is lost in this way, even their size distribution can be measured by bulk methods by applying sampling devices (*e.g.*, cascade impactors and filters) which collect the particles according to their size. Airborne samples collected on filters must first be dissolved in a solvent before analysis. Frequently, water is used as an appropriate extraction solvent.

Much of the work on atmospheric samples involves the determination of common inorganic anions, *e.g.*, Cl[−], NO₃[−] and SO₄^{2−}, although, as indicated in Table 1, studies conducted on other ions of interest, *e.g.*, alkali and alkaline earth metal and ammonium cations, are also abundant. To date, determination of inorganic anions and cations in such samples is generally performed by ion chromatography (IC). This technique has already reached a stage of maturity, so that its potential and limitations are by now well known. The introduction of CE with its radically different selectivity mechanism, higher resolution and shorter analysis times offers an analytical method which is, in many cases, complementary to IC.⁶⁹

3.1.1 Aerosols. The determination of inorganic ions in atmospheric aerosols using CE has received considerable attention.^{19,20,25,42,47–49,70} The first applications of CE in this field were reported by Dabek-Zlotorzynska and Dlouhy.^{25,47} The CE determination of alkali metal, alkaline-earth metal and ammonium cations in atmospheric aerosol extracts was achieved using various electrolytes and indirect UV detection.^{19,20,25,42} With the electrolyte composition proposed in the former study, it was also possible to determine manganese and cadmium. The results obtained by the CE method agreed well with those of IC. Fig. 1 shows a typical electropherogram and chromatogram of aqueous extract of atmospheric aerosols collected with a high-volume sampler. Optimisation of the composition of the carrier electrolytes for the characteristic matrix composition of atmospheric aerosols was reported by Krivacsy *et al.*⁴² By adding 3.8 mmol l^{−1} 18-crown-6 ether and 13.1 mmol l^{−1} HIBA to the 5 mmol l^{−1} 4-methylbenzylamine electrolyte, ammonium and potassium could be well resolved up to a concentration of 16 mg l^{−1} and calcium, sodium and magnesium up to a concentration of 4 mg l^{−1}. Recently, Fung *et al.*²⁰ reported a new analytical procedure for the determination of leachable and total metal and also ammonium content in fine and coarse air particulate matter using a histidine–18-crown-6 ether–lactic acid electrolyte system. Satisfactory working ranges (μg l^{−1} to mg l^{−1}) and sensitive detection limits (μg l^{−1}) were reported for the cations investigated. In addition, the reliability of the procedure developed was established by parallel method comparison with the ICP-AES method. The results obtained showed a better precision of the CE procedure in comparison with the ICP-AES method with no statistical significant difference between the methods.

Various CE electrolyte compositions were utilised for the determination of anions in atmospheric aerosols.^{19,47} The CE method using a pyromellitate-based electrolyte was evaluated and compared with spectrophotometry and IC.⁴⁸ The comparative evaluation included detection limits, linearity, accuracy, precision, correlation between the results, analysis time and other operational considerations such as cost of consumables and less waste generation and disposal. Statistical analysis of the results indicated that there was no evidence for systematic differences between the three techniques. It has been reported

that CE is less expensive to operate and less waste is generated than by IC. Both IC and CE produce less toxic waste than photometric methods. A drawback of the CE method was that it is less sensitive than IC. However, the sensitivity of CE was acceptable for the determination of inorganic anions in such samples. The results suggested that the CE method could be applied advantageously in the routine determination of sulfate, nitrate and other anions in atmospheric aerosol extracts. The long-term reliability of the CE system in the routine determination of major anions in atmospheric aerosols was next evaluated

Table 1 CE procedures for inorganic analysis of atmospheric samples

Analyte	Sample matrix	Sample pre-treatment	CE conditions ^a	Comments	Ref.
Cs ⁺ , Rb ⁺ , NH ₄ ⁺ , K ⁺ , Ca ²⁺ , Na ⁺ , Mg ²⁺ , Mn ²⁺ , Sr ²⁺ , Cd ²⁺ , Ba ²⁺ , Li ⁺	Aerosols	Aqueous extraction, sonication for 30 min	5 mmol l ⁻¹ DHBP, 6 mmol l ⁻¹ glycine, 2 mmol l ⁻¹ 18-crown-6, 2% methanol, pH 6.5; indirect UV (280 nm)	DL, 9–50 µg l ⁻¹ ; results agree well with IC	25
NH ₄ ⁺ , K ⁺ , Ca ²⁺ , Na ⁺ , Mg ²⁺	Aerosols	Filters leached in water for 1 h, then sonicated for 15 min	5 mmol l ⁻¹ 4-methylbenzylamine, 6.5 mmol l ⁻¹ HIBA, 2 mmol l ⁻¹ 18-crown-6, pH 4.4; indirect UV (185 nm)	DL, 95–240 µg l ⁻¹	19
NH ₄ ⁺ , K ⁺ , Ca ²⁺ , Na ⁺ , Mg ²⁺ , Zn ²⁺	Air particulate matters	(1) Aqueous extraction, sonication for 45 min. (2) Addition of HNO ₃ , reflux for 24 h, evaporation to dryness, sonication for 10 min with water	10 mmol l ⁻¹ histidine, 2 mmol l ⁻¹ 18-crown-6, 8 mmol l ⁻¹ lactic acid, pH 4.0; indirect UV (214 nm)	DL, 80–250 µg l ⁻¹ ; results are comparable in accuracy to ICP-AES	20
NH ₄ ⁺ , K ⁺ , Ca ²⁺ , Na ⁺ , Mg ²⁺ , Zn ²⁺	Single rain- and fogdrops	Freezing in liquid nitrogen during sampling, each droplet stored in a propylene conical vial	4 mmol l ⁻¹ 4-methylamino-phenol, 4 mmol l ⁻¹ 18-crown-6, pH 6.5; indirect UV (220 nm)	DL, 40–80 fmol	27, 28
Br ⁻ , Cl ⁻ , SO ₄ ²⁻ , NO ₂ ⁻ , NO ₃ ⁻	Aerosols	Aqueous extraction, sonication for 30 min	2.25 mmol l ⁻¹ pyromellitic acid, 0.75 mmol l ⁻¹ hexamethonium hydroxide, 6.5 mmol l ⁻¹ NaOH, 1.6 mmol l ⁻¹ triethanolamine, pH 7.7; indirect UV (254 nm)	DL, 200 µg l ⁻¹ , good agreement with photometric and IC determination	47–49
Cl ⁻ , SO ₄ ²⁻ , NO ₃ ⁻	Aerosols	Filters leached in water for 1 h, then sonicated for 15 min	7 mmol l ⁻¹ chromate, 0.25 mmol l ⁻¹ TRIS, 0.25 mmol l ⁻¹ TTAB, 0.13 mmol l ⁻¹ potassium hydrogenphthalate, pH 8; indirect UV (254 nm)	DL, 100–200 µg l ⁻¹	19
SO ₂	Atmospheric gases	Liquid droplet	2 mmol l ⁻¹ Na ₂ B ₄ O ₇ ; suppressed conductivity	DL, 1 µg l ⁻¹ (100 cm ³ air)	70
Br ⁻ , Cl ⁻ , SO ₄ ²⁻ , NO ₂ ⁻ , NO ₃ ⁻ , F ⁻ , PO ₄ ³⁻	Rain water	Filtration	100 mmol l ⁻¹ CHES, 40 mmol l ⁻¹ LiOH, 0.02% m/m Triton X-100; non-suppressed conductivity	DL, low µg l ⁻¹ level; the capillary was conditioned with 1 mmol l ⁻¹ CTAB between runs	40
F ⁻	Rain water	Filtration	1.13 mmol l ⁻¹ pyromellitate, 0.8 mmol l ⁻¹ triethanolamine, 2.13 mmol l ⁻¹ hexane-1,6-bis(trimethyl) ammonium hydroxide, pH 7.7; indirect UV (254 nm)	DL, 0.6 µmol l ⁻¹ ; results comparable to ISE, but lower than IC due to presence of aluminum	50
Cl ⁻ , SO ₄ ²⁻ , NO ₃ ⁻ , F ⁻ , organic acids	Rain water	—	5 mmol l ⁻¹ molybdate, 0.15 mmol l ⁻¹ CTAH, 0.01% poly(vinyl alcohol), 5 mmol l ⁻¹ TRIS, pH 7.9; indirect UV (230 nm)	DL, 2–16 µg l ⁻¹ and 10–80 µg l ⁻¹ (electrokinetic and hydrodynamic injection, respectively)	33
SO ₄ ²⁻ , IO ₃ ⁻ , BrO ₃ ⁻ , ClO ₃ ⁻ , ClO ₄ ⁻ , HPO ₄ ²⁻	Single raindrops	Freezing in liquid nitrogen during sampling, each droplet stored in a propylene conical vial	1.4 mmol l ⁻¹ 2,5-dihydroxybenzoic acid; indirect fluorescence		27
Cl ⁻ , SO ₄ ²⁻ , NO ₃ ⁻ , organic acids	Single raindrops	As above	7.5 mmol l ⁻¹ <i>p</i> -aminobenzoate, 100 mmol l ⁻¹ TTAOH, 750 mmol l ⁻¹ Ba(OH) ₂ , pH 9.4; indirect UV (264 nm)		28
Cl ⁻ , SO ₄ ²⁻ , NO ₃ ⁻	Individual snowflakes	Melting	48 mmol l ⁻¹ Na ₂ B ₄ O ₇ , 1 mmol l ⁻¹ diethylenetriamine, 1.8 mmol l ⁻¹ dichromate, 13 mmol l ⁻¹ H ₂ SO ₄ ; indirect UV (265 nm)	DL, 20 µg l ⁻¹	74

^a CHES = 2-(*N*-cyclohexylamino)ethanesulfonic acid; CTAH = cetyltrimethylammonium hydroxide; DHBP = 1,1'-diheptyl-4,4'-bipyridinium hydroxide; HIBA = α -hydroxyisobutyric acid; TRIS = tris(hydroxymethyl)aminomethane; TTAB = tetradecyltrimethylammonium bromide; TTAC = tetradecyltrimethylammonium chloride; TTAH = tetradecyltrimethylammonium hydroxide.

over an 8 month period during which more than 2900 samples were analysed. In addition, approximately 1100 samples were analysed in parallel by IC.⁴⁹ The agreement between the CE and IC results was generally better than 20% at concentrations $> 1 \text{ mg l}^{-1}$. Mihalyi *et al.*¹⁹ used CE data for assessing the size distribution of the ions in aerosols and the composition of particles in the fine particle size range. A high correlation between the CE results and light scattering coefficients was obtained for sulfate and other ions. Dasgupta and Kar⁷⁰ described an interesting direct measurement of soluble ionogenic atmospheric gases by a suppressed conductimetric CE system. To perform gas sampling, a series of automated operations were carried out with a commercial CE instrument modified in a minor fashion. Under the optimum sampling conditions, $1 \text{ } \mu\text{g l}^{-1}$ of SO_2 could be detected in a 100 cm^3 air sample.

3.1.2 Rain depositions. CE has shown great promise for the determination of ionic species in wet deposition.^{26–28,33,40,50,71–74} A method for the determination of chloride, nitrate and sulfate in rain water using CE with non-suppressed conductivity detection was developed and validated by Valsecchi *et al.*⁴⁰ The analytical parameters measured in the validation procedure showed that the method can be applied to monitoring of wet deposition. The main limitation for the application of this method in routine analysis was that migration times are not reproducible. When compared with the official IC method, CE appears to be less reliable for anion determinations, especially concerning the dynamic range and precision; on the other hand, CE is less expensive and its different selectivity complements IC. In another study,⁵⁰ the determination of fluoride in rain water by CE was compared with IC and ion-

selective electrode (ISE) potentiometry. Statistical analysis indicated that there was no evidence for a systematic difference between CE and potentiometry, whereas the fluoride concentrations obtained by IC were significantly higher. It was concluded that the observed differences are most likely due to the presence of aluminium cations. In a recent study, Fung and Lau³³ developed a procedure for the simultaneous determination of both inorganic and organic anions in rain water using a molybdate-based electrolyte and indirect UV detection. Under optimised conditions, low detection limits (*e.g.*, 2 and $11 \text{ } \mu\text{g l}^{-1}$ for chloride using electrokinetic and hydrodynamic injection, respectively) and satisfactory working ranges were reported. The procedure developed has been successfully applied to field monitoring of rain water, showing repeatability and the capability of detecting trace anions at $\mu\text{g l}^{-1}$ levels.

One of the major merits of CE is a capability to conduct analysis with nanolitre sample sizes (microlitre sample volumes). Because of the small volume requirements, CE is well suited for studying the chemistry of individual hydrometeors. No other analytical technique currently available, including IC, can match this small volume capability. Bächmann and co-workers^{27,28,71–73} utilised CE methods for the analysis of single and size-classified rain- (volume: $10 \text{ } \mu\text{l}$ – 3 nl), cloud- or fog-drops (volume: pl – fl) in order to obtain information about anthropogenic air pollution and drop formation processes in the atmosphere. Individual raindrops and size-classified raindrops were collected using a 'Guttalgor method', consisting of a Dewar vessel filled with liquid nitrogen. Each individual raindrop was thus kept as an individual. The main inorganic cations and anions occurring in rain were quantified using UV and fluorescence detection. It was pointed out that the high resolution and miniaturised sample format make the CE method suitable for the quantitative, multi-component chemical analysis of ultra-small volume samples such as single rain- and fog-drops. CE was also used for the determination of chloride, sulfate and nitrate in individual snow crystals and snowflakes.⁷⁴

3.2 Aquatic samples

Many CE applications to the determination of inorganic ionic species in natural aquatic samples have been published over the past decade. In general, samples such as rain water, ground-water, surface water, tap and drinking water, sea-water and soil solutions do not require any pre-treatment other than filtration and can be then introduced directly into the capillary. Differences in water samples are mainly related to variations in matrix composition, *e.g.*, high salt levels for sea-water, the presence of dissolved organic carbon for groundwater and soil solution, *etc.* Hence, to provide a better understanding of how to deal with these typical water samples, application studies will be discussed below as far as possible according to matrix type, with the minor exception of rain water, which has chiefly been considered in Section 3.1. It is worth noting that a substantial number of papers have dealt with the development of CE conditions applicable for separating a variety of ionic analytes, thus exploiting the high separation potential of CE; however, application to real-world systems usually results in the determination of a limited number of target ions because of detection limitations or the presence of these analytes in the sample at a level that is non-relevant for the desired analyses.

3.2.1 Drinking, mineral and tap water. The most intensively analysed aquatic samples for various inorganic species are drinking, mineral and tap waters.^{26,29,30,34,37,43,64,66,75–82} The separation of alkali and alkaline earth metals and ammonium ion in tap and mineral waters was achieved by on-column complexation using tartrate and 18-crown-6 ether, while benzimidazole served as a UV-

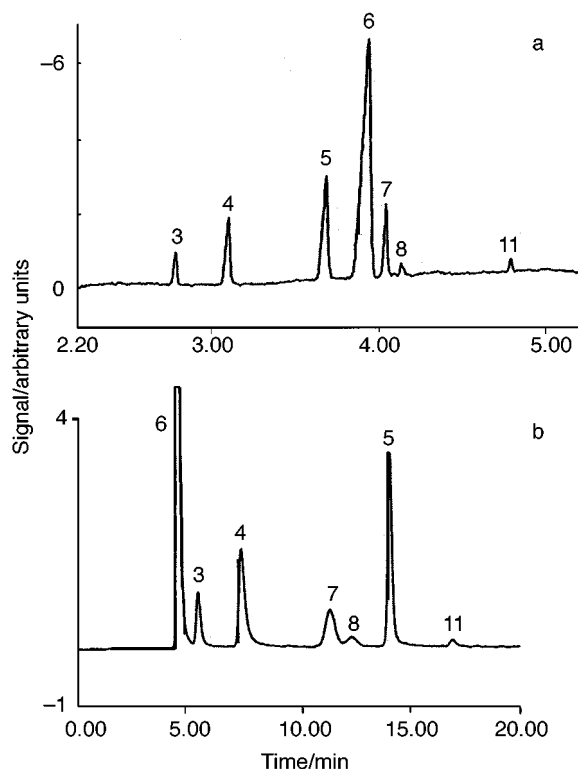


Fig. 1 Cation determination in high-volume sampled atmospheric aerosol extract using (a) CE and (b) IC methods. CE: capillary, fused silica, $75 \text{ cm} \times 50 \text{ } \mu\text{m}$ id; electrolyte, 5 mmol l^{-1} DHBP, 6 mmol l^{-1} glycine, 2 mmol l^{-1} 18-crown-6 ether, 2% methanol, pH 6.5; applied voltage, 25 kV, sample introduction, 10 s at 0.05 psi; detection, indirect UV at 280 nm. IC: columns, Dionex IonPac CS12 ($250 \times 4 \text{ mm}$ id), IonPac CG12 ($50 \times 4 \text{ mm}$ id); eluent, methanesulfonic acid (MSA), gradient elution from 16 mmol l^{-1} MSA to 40 mmol l^{-1} MSA at 8.0 min; flow rate, 1.0 ml min^{-1} ; detection, suppressed conductivity. Peaks: 3 = NH_4^+ ; 4 = K^+ ; 5 = Ca^{2+} ; 6 = Na^+ ; 7 = Mg^{2+} ; 8 = Mn^{2+} ; 11 = Ba^{2+} . Reprinted from ref. 25.

active electrolyte component for indirect UV detection.²⁶ Samples were introduced into the capillary without any pre-treatment using electrokinetic injection. Although the injection conditions were carefully controlled and the injection current was stabilized to within 0.1% of the pre-selected value, the relative standard deviations for the peak areas for both model and practical samples were only seldom better than 7–10%. Mehra and Lucy³⁴ reported the simultaneous determination of alkali and alkaline earth metals and some transition metals by applying a running electrolyte consisting of imidazole and α -alanine at pH 4 and indirect UV detection. Application of this method to tap water resulted in the quantification of 'only' Ca^{2+} , Na^+ and Mg^{2+} cations. Analysis of table water and tap water for alkali and alkaline earth metals using copper sulfate, 18-crown-6 and formic acid as a background electrolyte has been described by Havel *et al.*²⁹ Samples with higher contents of dissolved carbon dioxide were degassed by sonication prior to analysis. Different dilutions were found to be appropriate for the determination of sodium. A different electrolyte system containing Sulfonazo III as a strong complexing ligand was utilised for the determination of barium and strontium in the presence of large excess levels of calcium and magnesium in mineral waters by Macka *et al.*⁷⁵ The results obtained were in good agreement with ICP-MS data. Detection limits of $48 \mu\text{g l}^{-1}$ for barium and $41 \mu\text{g l}^{-1}$ for strontium were possible in the presence of up to a 10^5 -fold excess of Ca^{2+} and Mg^{2+} .

There have been a number of studies concerning the CE determination of iron species.^{37,76–78} Xu and Ma⁷⁶ reported a method for the direct determination of Fe^{2+} in tap water and also in rain water and lake water based on the pre-capillary formation of an Fe^{2+} –1,10-phenanthroline complex that is highly absorbing at 270 nm. It was found that tap water with a high concentration of chlorine needed to be kept for several days before analysis to allow the chlorine to dissipate and the use of a large amount of reducing agent was not required. Under ideal separation and detection conditions, a detection limit as low as $0.28 \mu\text{g l}^{-1}$ was reached, which allowed the authors to claim that no preconcentration procedures are necessary for natural aquatic samples (*e.g.*, the iron concentration in tap water was measured as $21 \mu\text{g l}^{-1}$). The simultaneous determination of Fe^{2+} and Fe^{3+} in tap water and groundwater was reported by Pozdniakova *et al.*⁷⁷ They used a mixture of 1,10-phenanthroline and CDTA in order to complex selectively either type of iron cation. The detection limits reported were 0.06 and 0.1 mg l^{-1} for Fe^{2+} and Fe^{3+} , respectively. Blatny *et al.*³⁷ determined Fe^{3+} , in the form of the negatively charged complex with EDTA, in tap water by on-line coupled ITP and CE. Analyses were performed using $10 \text{ mmol l}^{-1} \text{ HCl}$ – $20 \text{ mmol l}^{-1} \text{ L-histidine}$ – $0.1\% \text{ hydroxypropylmethylcellulose}$ (pH 6.0), $5 \text{ mmol l}^{-1} \text{ MES}$ and $25 \text{ mmol l}^{-1} \text{ MES}$ – $10 \text{ mmol l}^{-1} \text{ bis-tris-propane}$ (pH 6.6), which served as leading, terminating and background electrolyte, respectively. Application to other matrices, *i.e.*, river water and mineral water, was also demonstrated. Seidel and Faubel⁷⁸ developed a method for the determination of Fe^{2+} using laser induced thermal lensing spectroscopy as the detection system. As in the previous studies, 1,10-phenanthroline was used as a chromogenic reagent that forms stable complexes with Fe^{2+} but not with Fe^{3+} . With this complexing–detection system a detection limit of approximately $2 \mu\text{g l}^{-1}$ was achieved and the results obtained for the analysis of tap water agreed well with AAS data.

Kuban and Karlberg³⁰ described an interesting method for determining both cations and anions in aquatic samples such as tap water, rain water and process water. Two portions of the same sample were introduced into the anodic and cathodic ends of a separation capillary filled with a background electrolyte consisting of $6 \text{ mmol l}^{-1} \text{ 4-aminopyridine}$, $2.7 \text{ mmol l}^{-1} \text{ CrO}_4^{2-}$ and $30 \mu\text{mol l}^{-1} \text{ CTAB}$. The detection window was placed approximately at the middle of the capillary. With this approach, as many as 22 small inorganic and organic anions and

alkali and alkaline earth metal cations could be separated within 5 min. In Fig. 2 an application to the analysis of tap water using this new methodology is shown. Another approach for simultaneous cationic and anionic CE analysis of water samples adopted from HPLC involves pre-capillary transformation of metal cations into negatively charged complexes, *e.g.*, with EDTA.⁷⁹

Using the common running electrolyte solution containing sodium chromate and CIA-PAK OFM Anion BT at pH 8, four different chlorine-containing anions, *i.e.*, chloride, chlorite, chlorate and perchlorate, were determined with detection limits ranging from 0.01 to 1.5 mg l^{-1} .⁴³ In tap water, however, only chloride could be detected. Recoveries of the four anions varied from 86 to 97% at a 1 mg l^{-1} level.

The determination of various selenium and arsenic anions in tap and mineral spring water was studied by Li and Li.⁶⁴ The mineral water samples were analysed without pre-treatment, whereas the tap water was filtered through a $0.45 \mu\text{m}$ filter before injection. On-column enrichment by stacking large sample volumes resulted in more than a 100-fold preconcentration, which provided detection limits below $25 \mu\text{g l}^{-1}$. Since none of the target species was detected in both types of samples, the procedure was tested by spiking experiments (see Table 2 for recoveries). In a recent study,⁸⁴ CE with hydride generation (HG) ICP-MS was used to determine four arsenic and two selenium species. Recoveries of Se^{IV} and Se^{VI} in drinking water were measured (see Table 2). Other applications to anion analysis of drinking water were reported by Van Holderbeke *et al.*,⁸⁰ Kaniansky and co-workers,⁶⁶ Choi and Cho⁸¹ and Oehrle⁸² and of mineral water by Françios *et al.*⁸³

3.2.2 Surface water. Surface water is an important source of drinking water. Its ionic composition and ionic strength (matrix) vary widely. The simultaneous separation and photometric detection of Co^{2+} , Fe^{2+} , Cu^{2+} and Zn^{2+} in pond water following derivatisation with 4-(2-pyridylazo)resorcinol was demonstrated by Regan *et al.*⁶³ Both on-column and pre-column complexation were tested. Stacking of the samples provided a decrease in detection limit by a factor of about 100 down to $1 \times 10^{-8} \text{ mol l}^{-1}$ for Co^{2+} , Fe^{2+} and Zn^{2+} and to $4 \times 10^{-7} \text{ mol l}^{-1}$ for Cu^{2+} . Determination of aluminium in surface waters by CE using a fluorescence detector and sample preconcentration by evaporation was described by He *et al.*⁸⁵ The ICP-MS results were slightly higher, which might be ascribed to differences in speciation, *i.e.*, total aluminium concentration determined by ICP-MS against the CE data encompassing Al only in the ionic state (see also ref. 86).

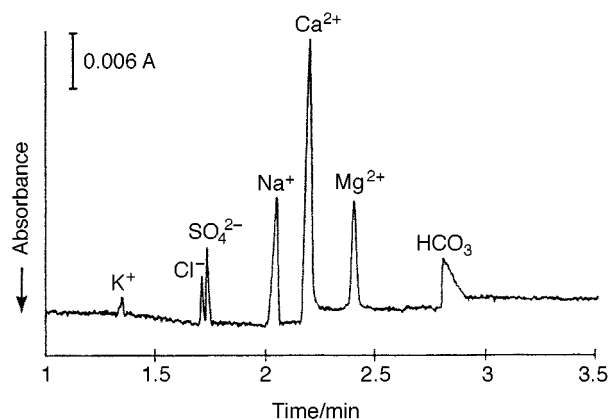


Fig. 2 Simultaneous cation and anion determination in tap water. Capillary, fused silica, $50 \text{ cm} \times 50 \mu\text{m}$ id; electrolyte, $6 \text{ mmol l}^{-1} \text{ 4-aminopyridine}$, $2.7 \text{ mmol l}^{-1} \text{ chromate}$, $30 \mu\text{mol l}^{-1} \text{ CTAB}$, $2 \text{ mmol l}^{-1} \text{ 18-crown-6 ether}$, pH 8.0; applied voltage, 20 kV; sample introduction, 10 s at 10 cm from the cathodic end and 10 s at 5 cm from the anodic end; detection, indirect UV at 262 nm; time between the two injections, 0 s. Reprinted from ref. 30.

Table 2 CE procedures for aquatic samples

Analyte	Sample matrix	Sample pre-treatment	CE conditions ^a	Comments	Ref.
NH ₄ ⁺ , K ⁺ , Li ⁺ , Na ⁺ , Rb ⁺ , Cs ⁺ , Ca ²⁺ , Mg ²⁺ , Ba ²⁺ , Sr ²⁺	Tap water, mineral water	—	5 mmol l ⁻¹ benzimidazole, 5 mmol l ⁻¹ tartrate, 40 mmol l ⁻¹ 18-crown-6, pH 5.2, 0.1% hydroxyethylcellulose, 0.1% hydroxymethylcellulose; indirect UV (254 nm)	RSD for peak areas seldom better than 7–10%	26
K ⁺ , Li ⁺ , Na ⁺ , Ca ²⁺ , Mg ²⁺ , Cu ²⁺ , Cd ²⁺ , Cr ³⁺	Tap water	—	20 mmol l ⁻¹ imidazole, 30 mmol l ⁻¹ α-alanine, pH 4; indirect UV (210 nm)	DL, 5 × 10 ⁻⁵ mol l ⁻¹ ; only Ca ²⁺ , Mg ²⁺ and Na ⁺ were detectable in real samples	34
NH ₄ ⁺ , K ⁺ , Li ⁺ , Na ⁺ , Ca ²⁺ , Mg ²⁺ , Ba ²⁺ , Sr ²⁺	Table water, tap water	De-gassing by sonication	CuSO ₄ , 18-crown-6, formic acid, all 4 mmol l ⁻¹ , pH 3.1; indirect UV (215 nm)	DL, 0.6–13 mg l ⁻¹	29
Ba ²⁺ , Sr ²⁺	Mineral water	—	0.3 mmol l ⁻¹ Sulfonazo III, 20 mmol l ⁻¹ MES, 10 mmol l ⁻¹ TRIS, pH 6.2; light-emitting diode photometry (654 nm)	DL, 48 µg l ⁻¹ Ba ²⁺ , 41 µg l ⁻¹ Sr ²⁺ ; no interference from Ca ²⁺ and Mg ²⁺ up to 10 ⁵ -fold excess	75
Fe ²⁺	Lake water, tap water, rain water	Rain and lake water stand for 30 min, tap water with high chloride concentration for several days; filtration; addition of 0.1 ml of 0.25% thioglycolic acid to reduce all Fe ³⁺ to Fe ²⁺	50 mmol l ⁻¹ acetate buffer, 80 µmol l ⁻¹ 1,10-phenanthroline, pH 5; direct UV (270 nm)	DL, 5 × 10 ⁻⁹ mol l ⁻¹ ; recovery, 90–107%	76
Fe ²⁺ , Fe ³⁺	Tap water, groundwater	Complexation with 0.5 mmol l ⁻¹ CDTA and 0.5 mmol l ⁻¹ 1,10-phenanthroline	100 mmol l ⁻¹ borate buffer, pH 9.0; direct UV (254 nm)	DL, 0.06 mg l ⁻¹ Fe ²⁺ , 0.1 mg l ⁻¹ Fe ³⁺	77
Fe ³⁺	Drinking, table, mineral and lake water	Acidification, sonification, filtration, dilution and addition of 0.1 mmol l ⁻¹ EDTA	10 mmol l ⁻¹ HCl, 20 mmol l ⁻¹ L-histidine, 0.1% hydroxypropylmethylcellulose, pH 6 (leading); 5 mmol l ⁻¹ MES (terminating) and 25 mmol l ⁻¹ MES, 10 mmol l ⁻¹ bis-tris-propane, pH 6.6 (carrier); direct UV (254 nm)	DL, 10 µg l ⁻¹ with on-line coupled ITP-CE system; recovery, 80–115%	37
NH ₄ ⁺ , K ⁺ , Na ⁺ , Ca ²⁺ , Mg ²⁺ , Cl ⁻ , SO ₄ ²⁻ , NO ₃ ⁻ , HCO ₃ ⁻	Tap water, rain water	—	6 mmol l ⁻¹ 4-aminopyridine, 2.7 mmol l ⁻¹ sodium chromate, 30 µmol l ⁻¹ CTAB, 2 mmol l ⁻¹ 18-crown-6, pH 8; indirect UV (262 nm)		30
Ca ²⁺ , Mg ²⁺ , Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻	Tap water, mineral water	Complexation with 10 mmol l ⁻¹ EDTA for 10 min	300 mmol l ⁻¹ borate buffer, 0.5 mmol l ⁻¹ TTAB, 0.5 mmol l ⁻¹ EDTA, pH 9.0; indirect UV (185 nm)	DL, (0.5–2.5) × 10 ⁻⁶ mol l ⁻¹	79
Cl ⁻ , ClO ₂ ⁻ , ClO ₃ ⁻ , ClO ₄ ⁻	Tap water	—	4.6 mmol l ⁻¹ sodium chromate, 0.46 mmol l ⁻¹ CIA-PAK OFM Anion BT, pH 8; indirect UV (254 nm)	DL, 0.01–1.5 mg l ⁻¹ ; recovery, 75–107%	43
AsO ₂ ⁻ , Me ₂ AsO ₂ ⁻ , SeO ₃ ²⁻ , AsO ₄ ³⁻	Tap water, mineral water	Filtration (only for tap water)	Phosphate–borate buffer, pH 7.65; direct UV (180 nm)	Recovery, 88–114% except for AsO ₂ ⁻ (peak overlap with the matrix peak)	64
SeO ₃ ²⁻ , SeO ₄ ²⁻	Drinking water	—	20 mmol l ⁻¹ potassium hydrogenphthalate, 20 mmol l ⁻¹ boric acid, pH 9.03; ICP-MS	Recovery, 86–100%	108
Co ²⁺ , Fe ²⁺ , Cu ²⁺ , Zn ²⁺	Pond water	Complexation with 4-(2-pyridylazo)-resorcinol	10 mmol l ⁻¹ TAPS, pH 8.4; direct photometry (500 nm)	DL, 4 × 10 ⁻⁷ –10 ⁻⁸ mol l ⁻¹ using electrostacking	63
Al ³⁺	Surface water	Filtration, complexation with lumogallion, evaporation	40 mmol l ⁻¹ acetic acid, 10 mmol l ⁻¹ ammonium acetate; pH 4; fluorimetric detection	DL, 20 µg l ⁻¹ ; recovery, 94–104%	85
Br ⁻ , BrO ₃ ⁻ , I ⁻ , IO ₃ ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , SeO ₃ ²⁻ , PO ₄ ³⁻	River water	Filtration	25 mmol l ⁻¹ phosphate buffer, pH 3; direct UV (200 nm)		87
	Lake water	—	10 mmol l ⁻¹ sodium chromate, 1 mmol l ⁻¹ TTAB, pH 8; indirect UV (254 nm)	DL, 10–25 µg l ⁻¹ (depending on sample); results in agreement with photometric method	44

Table continued on next page

Table 2 continued

Analyte	Sample matrix	Sample pre-treatment	CE conditions ^a	Comments	Ref.
PO ₄ ³⁻	Groundwater, surface water; steam flow water	—	1.13 mmol l ⁻¹ pyromellitate, 0.8 mmol l ⁻¹ triethanolamine, 2.13 mmol l ⁻¹ hexane-1,6-bis(trimethyl)ammonium hydroxide, pH 7.7; indirect UV (254 nm)	DL, 0.45 µmol l ⁻¹ ; migration time strongly depends on matrix composition	51
Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺	Sea-water	Filtration, dilution (1:100–1000)	5 mmol l ⁻¹ 4-methylbenzylamine, 6.5 mmol l ⁻¹ HIBA, 6.2 mmol l ⁻¹ 18-crown-6, 25% v/v methanol, pH 4.8; indirect UV (185 nm)	DL, 0.08–0.15 mg l ⁻¹ ; the results agree well with ICP-AES data for K, Mg and Ca but not for Na	21
Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺	Sea-water	Filtration, dilution (1:100)	5 (CC: 10) mmol l ⁻¹ imidazole, 6.5 (CC: 6) mmol l ⁻¹ HIBA 2 (CC: 5) mmol l ⁻¹ 18-crown-6, pH 4.1 (CC: 3.91); indirect UV (220 nm)	Use of both uncoated fused-silica capillary and quaternary amine-coated capillary (CC)	22
Ca ²⁺ , Mg ²⁺	Sea-water	Dilution (1:100), filtration	20 mmol l ⁻¹ sodium tetraborate, 2 mmol l ⁻¹ EDTA; direct UV (200 nm)	DL, 0.13 mg l ⁻¹ Mg ²⁺ , 0.26 mg l ⁻¹ Ca ²⁺ ; recovery, 94–104%	38
Br ⁻	Sea-water	Filtration, dilution (1:10)	10-fold-diluted artificial sea-water; direct UV (200 nm)	DL, 0.46 mg l ⁻¹ ; nitrate can also be determined	92
NH ₄ ⁺ , Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺ , Fe ³⁺ , Al ³⁺	Soil solution	—	5 mmol l ⁻¹ 4-methylamino-phenolsulfate, 1 mmol l ⁻¹ ascorbic acid, 2 mmol l ⁻¹ 18-crown-6; indirect UV (220 nm)	DL, 0.12–3.5 mg l ⁻¹	31
Cl ⁻ , SO ₄ ²⁻ , NO ₃ ⁻	Soil solution	—	3 mmol l ⁻¹ pyromellitic acid adjusted to pH 8.0 with TEMED; direct UV (230 nm); indirect UV (207 nm)	DL, 1.57–3.79 mg l ⁻¹	31
Cl ⁻ , SO ₄ ²⁻ , NO ₃ ⁻	Soil solution	Filtration, addition of 10% v/v 20 mmol l ⁻¹ EDTA at pH 11	3 mmol l ⁻¹ trimellitic acid, 0.02% v/v diethylenetriamine, pH 5.8; indirect UV (254 nm)	DL, 0.28–0.96 µmol l ⁻¹	95
NO ₃ ⁻ , SCN ⁻	High salinity waters	—	100 mmol l ⁻¹ NaCl, 2 mmol l ⁻¹ CTAC; direct UV (214 nm)	Recovery, 91–113%	96
NO ₃ ⁻ , ClO ₄ ⁻	Swimming pool water	—	10 mmol l ⁻¹ chromate, 0.1 mmol l ⁻¹ CTAB; indirect UV (254 nm); 10 mmol l ⁻¹ sulfate, 0.1 mmol l ⁻¹ CTAB; direct UV (214 nm)	DL, 7 mg l ⁻¹ ClO ₄ ; 0.4 and 4 mg l ⁻¹ NO ₃ ⁻ (direct and indirect detection, respectively)	97
SO ₄ ²⁻ , S ₂ O ₄ ²⁻ , S ²⁻ , Cl ⁻	Clayed water	—	1.5 mmol l ⁻¹ pyromellitate, 10 mmol l ⁻¹ TRIS, 0.5 mmol l ⁻¹ diethylenetriamine, pH 8; indirect UV (214 nm)		99

^a CTAB = cetyltrimethylammonium bromide; CTAC = cetyltrimethylammonium chloride; Sulfonazo III = 3,6-bis(2-sulfophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid; TAPS = *N*-tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid; TEMED = *N,N,N',N'*-tetramethylethylenediamine.

Application of CE to the determination of nitrate in river Rhine water has been reported by Amran *et al.*⁸⁷ The method was initially developed for the determination of bromide, bromate, iodide, iodate, nitrite, nitrate and selenite, among which most anions were present in this sample at levels below the limits of direct UV detection. Quantification of nitrate was in accordance with results obtained by IC. It was also found that for the CE method, chloride in the sample adversely affects the peak width for bromide and iodide that can cause interference with the nitrate peak at very high chloride concentrations. In another study,⁴⁴ the phosphate ion was determined in lake water using standard CE operating conditions for anionic analyses (see Table 2). The results were in agreement with spectrophotometric data, and injection carried out in the electromigrative mode ensured detection limits of 10 µg l⁻¹ for standards and clean lake waters and 15–25 µg l⁻¹ for aquatic samples with higher conductivity. In surface water, phosphate was also successfully determined by Van den Hoop and Van Staden.⁵¹ In this study, the responses in terms of both migration time and peak area were found to be highly dependent on the pH of the carrier electrolyte, consisting of pyromellitic acid, triethanolamine and hexane-1,6-bis(trimethyl) ammonium hydroxide. Interference due to the presence of carbonate in some surface samples could be eliminated using an Onguard-H column. In

addition, the migration time for the phosphate peak appeared to differ considerably from sample to sample. The difference in migration time of phosphate between the standard solution and the average migration time in the set of surface samples (Δt) was 0.57 min. This variation could be minimized, down to 0.08 min, by correction for the bromide dip-peak; however, such a Δt value is still not sufficient for direct peak identification and, hence, additional confirmation from, *e.g.*, standard additions is required.

Jackson and Haddad⁸⁸ used electrokinetic injection for the determination of chloride, sulfate, nitrite, nitrate, fluoride and phosphate in estuarine water samples. Decreased detection levels of fluoride and phosphate, by approximately an order of magnitude compared with hydrostatic injection, were reported. The analyte enrichment was found to be strongly dependent on the sample ionic strength, which leads to problems with quantification (for instance, appropriate measures must be taken to account for differences in standard and sample conductance).

3.2.3 Sea-water. An exceptional difference between seawater and the most other natural aquatic solutions is its extremely high ionic strength. This often complicates direct CE analysis. Another serious problem is due to large differences in

concentrations between matrix components, such as sodium or chloride, and minor cationic and anionic constituents.

One way to overcome sea-water matrix effects on separation and detection is dilution of the sample, but this cannot be recognized as a universal approach to be taken at the expense of ions present at lower concentrations, which may be diluted to below the detection limit. In this way, Tangen *et al.*²¹ developed a method for the determination of alkali and alkaline earth metals in mixtures of sea-water and formation water from oil wells in the North Sea diluted by a factor of 100–1000. This resulted in Sr^{2+} and Ba^{2+} concentration levels unattainable by this method. On the other hand, the data for K^+ , Na^+ , Ca^{2+} and Mg^{2+} agreed well with ICP-AES results. For the cationic analysis of sea-water, Schnierle and Hauser²² employed a quaternary amine-coated capillary, which affords increased resolution with respect to sodium and magnesium. As a result, the simultaneous separation of K^+ , Na^+ , Ca^{2+} and Mg^{2+} was achieved following a 100-fold dilution of the samples. The presence of complexing agents, HIBA and 18-crown-6, was also essential for the separation. Fukushi and Hiroy³⁸ reported the determination of Ca^{2+} and Mg^{2+} in sea-water using on-column complexation with EDTA to prevent high sodium interference. Both cations were determined without any sample pre-treatment by injecting 100-fold diluted samples.

For anions, a straightforward on-line approach for eliminating matrix effects is to perform separations in electrolytes containing high salt concentrations. In four published reports known to the authors, chloride ion was added to the electrolyte solution in the range 100–1500 mmol l^{-1} ,^{89–91} or a 10-fold diluted artificial sea-water was adopted as the carrier electrolyte.⁹² In combination with direct UV detection, such an approach looks promising for a range of trace-level sea-water anions having sufficient absorbance in the UV region (bromide,^{90,92} nitrate^{89,92}, nitrite⁸⁹ and possibly iodide and iodate). However, even with a high ionic electrolyte concentration the separation selectivity continues to be a challenge for the adjacent anions, in particular for the fast migrating bromide and iodide. In a recent study by Timerbaev *et al.*,⁹¹ a certain gain in resolution was achieved as based on ion-association interactions with tetrabutylammonium ion and, especially, 18-crown-6 incorporated in the carrier electrolyte, 100 mmol l^{-1} KCl (pH 4.0). The latter additive is capable of forming a positively charged ion-inclusion complex with the electrolyte counter-ion.

3.2.4 Waste water. As soon as it is discharged, waste water becomes no longer an industrial sample but a part of the environment. The determination of inorganic species by CE has tended to grow to significance not only because of the toxicity and the vast amounts of hazardous waste produced every year but also because the main method of its disposal remains landfill (in the European Union, 70% of municipal waste is disposed of by this method). That is why, from an environmental point of view, analysis of waste waters is of great importance in order to characterise their potential danger and, in case of emission to the environment, to detect their spread and/or their origin. As for sea-water, the matrix of waste water is complex and usually requires pre-treatment of the sample prior to analysis.

Oehrle *et al.*⁹³ used CE for the quantification of common cations and anions in an environmental study concerning the dilution of waste water as it mixes with stream water. The waste water originating from a meat processing plant was sampled both above, at the point of discharge and at various locations downstream. Samples of lake water and water from where the lake and creek mix were also collected. These monitoring activities were carried out during summer, autumn and winter to investigate seasonal concentration loading and dilution rates. Measurements of cations and anions were performed without analytical complications with reasonable RSD values. As expected, the concentrations of ionic species decreased with

increasing distance from the point of discharge. Finally, it was concluded that CE offers a reliable means of monitoring with little sample preparation and fast analysis times. The determination of nitrate and nitrite in waste waters with chloride concentrations varying from 15 to 23 g l^{-1} was described by Marti *et al.*⁹⁴ Chloride at levels >200 mg l^{-1} hampered the determination. This problem was solved by precipitation of chloride with lead, mercuric or silver acetate to clean up the sample. The best results were obtained by adding silver acetate at 1.5 times over the stoichiometric amount, for AgCl formation.

3.2.5 Soil solutions. Quantification of cations and anions in soil solutions is of interest for a range of scientific disciplines, including plant nutrition, ecology, soil chemistry and environmental pollution. For the sake of clarity, it is useful to note that we use the term *soil solution* for the natural aquatic part of soil material and not for aqueous extracts of solid soil material, which are the subject of the following section. In the case of sediments, the term *pore water* is commonly used.

Göttlein and Blasek³¹ characterised the cationic and anionic composition of soil solutions by CE using methol- and pyromellitic acid-based electrolytes for the separation of cations and anions, respectively. This work manifested the technique's benefits of minimal sample consumption, that permits new approaches for soil solution collection and analysis on a microscale level. In a later study,⁸⁶ CE was applied to determining the free Al^{3+} in soil solutions (see Fig. 3). Experimentally obtained data showed good agreement with calculated values using a chemical equilibrium model, whereas photometric and ion-exchange methods seriously overestimated the free aluminium concentration.

Westergaard *et al.*⁹⁵ developed a method for the direct quantification of inorganic anions in soil solutions after addition of EDTA at pH 11 for elimination of the aluminium complex formation effect. No matrix interference was observed for major anions such as chloride, sulfate and nitrate.

3.2.6 Miscellaneous. Another type of high-salinity aqueous sample is underground waters. Song *et al.*⁹⁶ elaborated a method for the determination of the petroleum tracers nitrate and thiocyanate in subterranean waters using direct UV detection. By incorporating 100 mmol l^{-1} NaCl in the carrier electrolyte solution, determination of both components was

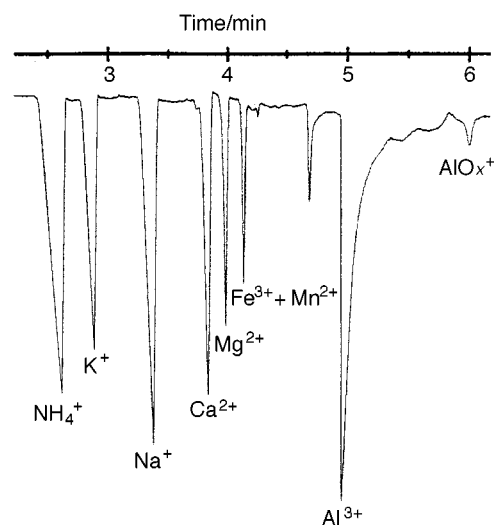


Fig. 3 Electropherogram of a rhizosphere soil solution from the A horizon of the Waldstein experimental plot. Capillary, fused silica, 44 cm \times 75 μm id; electrolyte, 5 mmol l^{-1} 4-methylaminophenolsulfate, 1 mmol l^{-1} ascorbic acid, 2 mmol l^{-1} 18-crown-6 ether; applied voltage, 15 kV; sample introduction, 4 s using vacuum; detection, indirect UV at 220 nm. Reprinted from ref. 86.

accomplished at chloride concentrations in the sample up to 200 mmol l⁻¹. Standard addition recoveries of 10 mg l⁻¹ of nitrate and thiocyanate in four subterranean water samples were between 91 and 113%. Difficult to categorize but nonetheless interesting to mention is a paper by Wang *et al.*⁹⁷ dealing with the measurement of nitrate and chlorate in swimming pool water. Because of interference of high chloride concentrations with nitrate detection, a direct UV detection method was applied.

Van den Broeck and Vandecasteele⁹⁸ applied CE with direct UV detection for the determination of various oxidation states of arsenic in percolate waters and in the leachate of solidified arsenic-containing waste. The lowest detectable concentration was about 100 µg l⁻¹. From a comparison with results obtained with HG-ICP-MS, it was concluded that both sets of results are in good agreement, although HG-ICP-MS is more sensitive.

Motellier *et al.*⁹⁹ found that pyromellitate and naphthalene-trisulfonate ensured the best sensitivity for the determination of a number of sulfur anionic species. The method was applied to natural clayey water sampled from a drill hole. Excellent separation and determination of thiosulfate, chloride, sulfate and sulfide were achieved.

3.3 Soil, sediment and particulate matter

The determination of inorganic ions in these ecological samples with CE has received relatively little attention compared to the wealth of data concerning water analysis. This is probably related to the complexity of the sample matrices and analytical difficulties involved in bringing the analytes into solution. On the other hand, owing to transfer processes between different environmental compartments and the natural ability of soils and sediments to accumulate elements, their concentrations are generally more magnified than those present in adjacent water and air phases. This makes promising the potential of CE to determine trace element contaminants associated with soil, to study the mechanisms related to adsorption and interactions with particulate matter and to provide relevant information regarding pollution, bioavailability and exchange with surrounding water. For the same reason, the requirements on sampling and handling procedures for soil samples are less rigorous from the contamination point of view.

Table 3 provides a survey of pertinent applications of CE to the analysis of various solid environmental samples and gives details of the analytical performance, whenever available. A few specific examples of the most advanced sample handling and detection approaches are cited below.

On-line dialysis in a flow injection analysis (FIA) arrangement, as proposed by Kuban and Karlberg,⁴⁵ was effective for the pre-treatment of samples with a complicated matrix composition before introduction into a CE system. Using the resulting FIA-CE interface, road snow and mud samples containing dust particles and gravel were analysed without any need for clean-up. Multiple sample injections are possible in one uninterrupted electrophoretic run (see Fig. 4), and the entire analytical procedure can easily be automated for continuous on-line monitoring. In a subsequent study,³⁰ the authors developed a CE system for the simultaneous determination of inorganic cations and anions (for more details see Section 3.2), applicable to the analysis of mud samples after dialysis pre-treatment.

An on-line combination of CE with ICP-MS has been utilised for determining chloroplatinates in aqueous extracts from Pt-treated soil.^{62,100} To exclude undesired time-dependent species transformations (*e.g.*, hydrolysis), which may occur before analysis, the extract, containing soluble Pt, was frozen and then analysed immediately after thawing. Specific CE patterns corresponding to the formation of various platinum species due to rapid (within days) interaction with the soil were evident on examining the soil extracts, all the species being apparently

recognised as bioavailable Pt forms. Aqueous extracts of a clay-like humic soil, treated with a Pt-contaminated tunnel dust, showed a different pattern of soil-generated species compared with artificial Pt species.¹⁰⁰ The CE-ICP-MS coupling was demonstrated to fulfil the requirements for low detection limits and a short analysis time. Additionally, this combination was demonstrated to be well suited to monitoring the dynamic changes in the Pt species-soil system.

Organometallic compounds often require special techniques in order to be released from soil and sediment matrices. Subcritical fluid extraction of organoleads and organotins with chlorodifluoromethane as the solvent was used by Li and Li¹⁰¹ for subsequent micellar electrokinetic chromatographic (MEKC) separation and determination. To improve recoveries of less hydrophobic and more volatile trimethylmetallic species, sodium diethyldithiocarbamate was added as a chelating agent to the soil sample before extraction. The advantages of high speed and high efficiency compared with the conventional solvent extraction, and also ease to automation and reduced problems with disposal of toxic solvents, were outlined. In a study by Lai *et al.*,³⁵ the applicability of CE with amperometric detection for the monitoring of methylmercury in contaminated sediments was assessed. The samples were processed by a steam distillation technique to isolate CH₃Hg⁺ from the solid matrix. The acidic distillate was then passed through an OH-cartridge that reduced greatly the conductivity of the injected sample and facilitated the efficiency of electrokinetic injection.

Wen and Cassidy⁵⁵ demonstrated the potential of amperometric detection, in a pulse mode, for the determination of metal ions in another kind of solid matrix, dirty snow samples collected beside busy streets and in parking lots. The CE results indicated the presence of only Zn²⁺ and showed good agreement with AAS.

3.4 Biological material

In this section, CE procedures relevant to the analysis of environmental samples of plant and biotic origin are considered. Information on the determination of inorganic elements, in a variety of forms, serves as a valuable quality indicator of corresponding environmental surroundings such as soils in which plants are growing or the aquatic environment giving life and home to marine organisms. As can be seen from Table 4, although the number of published reports remains small, a representative range of cationic and anionic analytes in various biomatrices are already suitable for determination by CE. Mobility, availability and binding to plants and living organisms, transfer processes, nutrient value, re-sorption, accumulation and toxicological properties are indicated.

The elements of interest can often be released from solid matrices, such as plant material, by water extraction, occasionally at an elevated temperature, or by homogenization in water, followed by centrifugation and filtration of the supernatant (see Table 4); both procedures guarantee a high yield without denaturation. In some cases, however, complete sample dissolution is required. The work by Morawski *et al.*¹⁰² and Massart and co-workers¹⁰³ showed that preference should be given to closed-vessel microwave-assisted acid digestion systems as this type of procedure has a much lower risk of contamination and enhances the rate of decomposition. A mixture of concentrated nitric acid and hydrogen peroxide is appropriate in this context, although the high ionic strength of the sample, caused by the excess of acid, remains a certain limitation.

For the separation and determination of inorganic cations, a carrier electrolyte system composed of HIBA and imidazole as the complexing agent and visualising co-ion, respectively, appears to be most suitable. 18-Crown-6 ether is a useful additive when co-migration of potassium and ammonium ions occurs. Analyses for common anions can be carried out with a

simple chromate electrolyte containing CTAB, whereas a salicylate electrolyte with calcium as a complexation additive provides better resolution of inorganic anions in the presence of carboxylic acids co-existing in plant matrices. When the concentration levels of sample anions are different, as for high level nitrate and low level nitrite in vegetables, the same CE system can be applied with different (hydrodynamic or electrokinetic) injection modes.

Medina *et al.*¹⁰⁴ have developed a CE method for the rapid and simple determination of methylmercury, in the form of the cysteine complex, in various samples of marine environment. The use of CE rectifies the drawbacks associated with conventional GC procedures. Later, this method was refined for

routine analysis by Carro-Díaz *et al.*¹⁰⁵ The application of validation and quality control approaches revealed that the CE procedure, including a two-stage extraction, exhibits high selectivity, excellent linearity, ruggedness and stability. The detection limits achieved using the analytical methodology described (see Table 4) are sufficiently low to monitor the contamination levels of this highly toxic species resulting from industrial emissions and abiotic and biotic methylation (trans-methylation) processes. When necessary, the detection limit can be lowered by a factor of 10, down to 12 ng g⁻¹, exploiting sample stacking.¹⁰⁶ Dithizone sulfonate, used by Hardy and Jones¹⁰⁷ in place of cysteine to separate and detect methylmercury, provides even better detectability, *i.e.*, 2 ng g⁻¹, that

Table 3 Analytical details of CE procedures related to soil analysis

Analyte	Sample matrix	Sample pre-treatment ^a	CE conditions ^a	Comments	Ref.
K ⁺ , Na ⁺ , Ca ²⁺ , Mg ²⁺	Soil	Aqueous extraction, dilution (1 : 25)	10 mmol l ⁻¹ creatinine, 7.5% PEG200, pH 4.27; indirect UV (214 nm)	RSD, 0.2–9%	109
Zn ²⁺	Road snow	Melting, filtration	35 mmol l ⁻¹ creatinine, 8 mmol l ⁻¹ HIBA, pH 4.8; pulse amperometric detection	RSD, 2.4–9.3%; results agreed well with the AAS data	55
(CH ₃) ₃ Pb ⁺ , (C ₂ H ₅) ₃ Pb ⁺ , (CH ₃) ₃ Sn ⁺ , (C ₄ H ₉) ₃ Sn ⁺	Spiked soil	Addition of sodium diethyldithiocarbamate, dynamic subcritical fluid extraction	30 mmol l ⁻¹ phosphate, 15 mmol l ⁻¹ borate buffer, pH 7.65, 50 mmol l ⁻¹ SDS; direct UV (200 nm)	Recovery, 89–96%; RSD, 9%; additional preconcentration via evaporation/dissolution was used for low level spikes	101
(C ₄ H ₉) ₂ Sn ²⁺ , (C ₄ H ₉) ₃ Sn ⁺	Spiked marine sediments	Leaching with 6 M HCl solution in methanol, addition of NaCl, triple extraction with benzene, evaporation to dryness, dissolution of the residue in methanol	3 mmol l ⁻¹ 4-aminopyridine, 15 mmol l ⁻¹ α-CD, pH 3.0; indirect UV (261 nm)	Recovery, 53–60%	23
CH ₃ Hg ⁺	Sediment	Addition of H ₂ SO ₄ and KCl, steam distillation, passing of the distillate through an OH-cartridge	100 mmol l ⁻¹ creatinine, pH 4.8; amperometric detection	DL, 3 µg l ⁻¹	35
Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻	Soil	Aqueous extraction, filtration	5 mmol l ⁻¹ sodium chromate, 0.2 mmol l ⁻¹ TTAB, pH 8.2; indirect UV (275 nm)	DL, 1.0–4.3 mg l ⁻¹ ; results are comparable in accuracy and precision with IC	46
HAsO ₄ ²⁻	Coal fly ash	Extraction with an alkaline solution (pH 10), filtration	6 mmol l ⁻¹ sodium chromate, NICE-Pak OFM Anion-BT (1 : 40 v/v), pH 10; indirect UV (274 nm)	DL, 0.66 mg l ⁻¹	110
HAsO ₄ ²⁻ , HAsO ₃ S ²⁻	Soil	Extraction with NaOH, centrifugation, filtration	10 mmol l ⁻¹ phosphate buffer, pH 10; direct UV (195–300 nm)	Repeatability better than that of IC	103
[PtCl ₄] ²⁻ , [PtCl ₆] ²⁻ , Pt (metallic)	Soil spiked with the Pt compound or a Pt-contaminated tunnel dust	Centrifugation of suspension, filtration	50 mmol l ⁻¹ phosphate buffer, pH 6.0; ICP-MS	DL, 1 µg l ⁻¹ ; resolution exceeds that of HPLC	62
Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻	Mud, road snow	Dispersion in water, mixing (mud); melting (snow)	6 mmol l ⁻¹ sodium chromate, 3.2 × 10 ⁻⁵ mol l ⁻¹ CTAB, 3 mmol l ⁻¹ boric acid, pH 8.0; indirect UV (372 nm)	On-line dialysis in a FIA system	45
Cl ⁻ , NO ₂ ⁻ , SO ₄ ²⁻ , NO ₃ ⁻ , F ⁻	Soil (sand, clay, sediment), sludge	Extraction with a 0.05% solution of DTPA by sonication for 1 h, filtration	4 mmol l ⁻¹ sodium chromate, 3 mmol l ⁻¹ TTAH, 1 mmol l ⁻¹ CHES, pH 9; indirect UV (254 nm)	DL, 20–84 µg l ⁻¹ ; precision and accuracy data are presented; substantial interference with the phosphate determination due to carbonate and organic anions	111
Cl ⁻ , SO ₄ ²⁻ , NO ₃ ⁻ , HPO ₄ ²⁻ , HCO ₃ ⁻ , K ⁺ , Na ⁺ , Ca ²⁺ , Mg ²⁺	Mud	On-line dialysis	6 mmol l ⁻¹ 4-aminopyridine, 2.7 mmol l ⁻¹ H ₂ CrO ₄ , 30 mmol l ⁻¹ CTAB, 2 mmol l ⁻¹ 18-crown-6 ether, pH 8; indirect UV (262 nm)	Total analysis time < 4.5 min	30

^a α-CD = α-cyclodextrin; CHES = 2-(N-cyclohexylamino)ethanesulfonic acid; CTAB = cetyltrimethylammonium bromide; DTPA = diethylenetriaminepentaacetic acid; HIBA = α-hydroxyisobutyric acid; PEG = polyethylene glycol; SDS = sodium dodecylsulfate; TTAH = tetradecyltrimethylammonium hydroxide; TTAB = tetradecyltrimethylammonium bromide.

extends the quantitative performance of CE to less contaminated salmon and crab samples.

In recent work by Schlegel *et al.*,³² the coupling of CE with an ICP-MS detection system was optimised for the highly sensitive determination of arsenic inorganic and organic species. Fig. 5 depicts an electropherogram of a plant extract demonstrating that three of seven arsenic forms studied can be determined simultaneously.

3.5 Speciation studies

A great deal of research has been carried out to evaluate the potential and practical usefulness of CE techniques for chemical speciation purposes. A recently published overview⁷ provides a comprehensive survey of the literature for the period 1989–97 and addresses, among other items, the ability of CE to render reliable speciation information for environmental matrices. Therefore, only a brief examination of the utilisation of CE for environmental speciation analysis will be presented in this section, with emphasis on major publications of the last 2 years.

Supplementing well GC and HPLC methods as the dominant means of speciation, CE shows promise by exerting only a minor disturbance on the pre-existing equilibrium between different species of one element. Since separation in CE is mainly governed by differences in charge-to-size ratio of separands, the technique is extremely powerful in discriminating the speciation pattern of redox-sensitive elements and organometallics. This has been proved for various environmentally important elements such as mercury,^{35,104–107} arsenic,^{32,84,108} selenium,¹⁰⁸ lead,⁶⁴ iron,⁷⁷ chlorine,⁴³ sulfur⁹⁹ and nitrogen.⁴¹

To date, however, most published papers on this subject have dealt with demonstrating high-resolution speciation performance of CE using spikes in 'negative' samples. The fact that relatively little use has been made of CE in speciation measurements of real samples is not surprising given that most commercial instruments are equipped only with photometric detectors. The latter are not ideal for trace element detection. Thus, one of the major efforts of research on the applicability of CE for element speciation analysis is focused on the improvements in the technique's detectability. The introduction of more sensitive detectors, particularly ICP-MS or ICP-AES,^{32,52,56–60,62} and the application of various preconcentration techniques^{65,105,108} are the most promising options.

Several application examples can be found in Sections 3.2–3.4. Two recent accounts, demonstrating considerable increases in sensitivity and a shift towards applications to real-world samples, are worth mentioning. An interesting paper by Magnuson *et al.*⁸⁴ described the novel use of two methodo-

logical approaches for improved detectability of arsenic species by CE-ICP-MS. First, post-capillary HG was adopted to convert the species into their hydrides which, after passing through a gas-liquid membrane separator, can be nearly 100% introduced into the plasma (without the dissolved salts associated with CE buffers). Second, the EOF was hydrodynamically balanced by applying a small pressure in the direction opposite to EOF. This allowed the capability of increasing the amount of analyte injected electrokinetically and of eliminating the accompanying peak broadening effects. As a result, the detection limits were lowered to 6–50 ng l⁻¹ and the analysis of two drinking water samples was amenable by using a CE-HG-ICP-MS system. In another important study, Liu and Lee⁶⁵ employed field-amplified sample injection (see Section 2.4) for the determination of various lead, mercury and selenium forms complexed pre-capillary with a polyaminocarboxylic acid. Up to a 1500-fold on-line enrichment and sub-μg l⁻¹ detection limits were obtained under optimum stacking conditions. This ensured the method's applicability to direct sea-water analysis. From an electropherogram generated from a typical sea-water sample and presented in Fig. 6, Pb²⁺ and Se^{IV} were quantified (the concentrations of respective organometallic species were still below their detection limits).

4 Conclusions

A successful decade of development in the field of ion determination, with advances more revolutionary than evolutionary taking place, has brought CE the status of the method of choice for numerous inorganic analytes. The continuing efforts by many research groups have led to vast improvements in analytical figures of merit, expansions of the application areas and, in particular, to a better understanding of what the possible impact of CE in environmental analysis is. The method's growing acceptance by practising analytical chemists, working in environmental control and regulatory laboratories, has underscored the need for a comprehensive treatise on the methodology and practices of this rapidly expanding area. This overview concludes with more than 100 references to applications which are mostly of real world use and which can keep the reader on top of the field. To assist the reader in deciding the potential relevance of a specific article, most cited references are included in the tables.

The future looks bright for analysts involved in developing CE methods in environmental chemistry, even though there is still plenty of room for further advances, mostly in detection and sample preconcentration technologies. It is these facets that require the next stage of innovation. In this respect, it is important to remember that contaminants rather than components of natural origin tend to receive most attention in the environmental analyst's work. Trace levels at which inorganic pollutants occur in environmental matrices are often beyond the current detection capability of CE. On the other hand, even a range of commercially available, unsophisticated detectors adequately serve the needs of quantification of inorganic analytes, such as alkali and alkaline earth metals or common anions, which customarily attract acute interest in the local or global environment. The same is true about the separation methodology, that appears to be well refined for a large proportion of inorganic analytes in essentially all major environmental samples and hence needs only small advances in terms of customising the separation procedures. Hence it is time to formulate what standard separation conditions for specific analytes and specific samples are.

One of the major steps forward is likely to be made in the expansion of more sensitive detection systems, primarily ICP-MS, which holds the most prominent position in the field of trace inorganic analysis. The clear trend will be towards ICP-

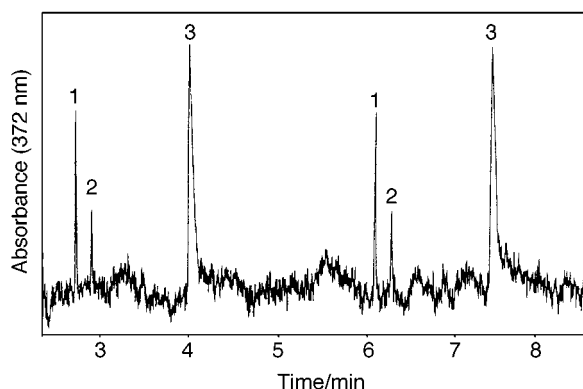


Fig. 4 FIA-CE analysis of a mud sample. Capillary, fused silica, 80 cm × 50 μm id; electrolyte, 6 mmol l⁻¹ sodium chromate, 3.2 × 10⁻⁵ mol l⁻¹ CTAB, 3 mmol l⁻¹ boric acid, pH 8.0; applied voltage, 25 kV, detection, indirect UV at 372 nm; time interval between the two injections, 3.5 min. Peaks: 1 = Cl⁻; 2 = NO₃⁻; 3 = HCO₃⁻. Reprinted from ref. 45.

MS detectors that are cheaper to purchase and maintain. As more manufacturers begin to produce commercial CE-ICP-MS instruments, they should become cheaper. However, the potential savings from reduced material consumption, simpler instrumentation, fast separations and element-specific information could offset the cost of available ICP-MS detectors. For easier use by the operator, who is not formally trained as a mass spectrometrists, simplified instrumentation is also highly welcome. Along with this and other sophisticated detection techniques, sample enrichment methodology will be increasingly used in environmental work to yield significant sensitivity enhancements of existing CE systems at a more affordable cost.

Whereas it is commonplace that the sample pre-treatment step is of minor importance for many CE applications, one can envision that considerable research emphasis will be placed on a better understanding and control of matrix interferences (especially from non-aquatic matrices) and on developing more reliable, automated sample preparation systems, in an ideal case interfaced to CE instruments. Environmental analysts should also expect from a new generation of capillary electropherographs combined detection techniques (*e.g.*, photodiode array and mass spectrometry), bench-top architecture, improved capability of recognizing and avoiding operational difficulties, extended data-processing assays for computer-aided interpretation of analysis results, ease of taking into the field as early

Table 4 Analytical schemes for environmental biosamples

Analyte	Sample matrix	Sample pre-treatment ^a	CE conditions ^a	Comments	Ref.
K ⁺ , Na ⁺ , Ca ²⁺ , Mg ²⁺	Parsley	Successive addition of HNO ₃ and H ₂ O ₂ ; closed-vessel microwave digestion, dilution, filtration	1.2 mmol l ⁻¹ UV-Cat 2, 3 mmol l ⁻¹ tropolone; indirect UV (185 nm)	Elevated results were observed owing to comigration of K ⁺ and NH ₄ ⁺ ; results were compared with IC and AAS; separation time was four times shorter than that of IC	102
K ⁺ , Na ⁺ , Ca ²⁺ , Mg ²⁺ , Mn ²⁺	Fish and oyster tissue; pine needles, citrus leaves	Addition of HNO ₃ and H ₂ O ₂ ; closed-vessel microwave digestion, dilution (1 : 50 or more)	5 mmol l ⁻¹ imidazole, 6.5 mmol l ⁻¹ HIBA, 20% methanol, 0.55 mmol l ⁻¹ 18-crown-6, pH 4.5; indirect UV (214 nm)	DL, 50–400 µg l ⁻¹ ; repeatability, < 6%; reproducibility, < 9%; results agreed well with the certified values; the effect of nitric acid in the sample on analytical performance was investigated	24
Ca ²⁺	Vegetables	Extraction with boiled water, filtration	20 mmol l ⁻¹ sodium tetraborate, 2 mmol l ⁻¹ EDTA, pH 9.2; indirect UV (200 nm)	DL, 0.26 mg l ⁻¹ , recovery, 96–111%; no interferences from sample proteins were observed	39
CH ₃ Hg ⁺	Marine samples (dogfish, tuna, mussels)	Addition of HCl, double extraction with toluene, back-extraction with cysteine solution	100 mmol l ⁻¹ borate buffer, pH 8.35, 10% methanol; direct UV (200 nm)	DL, 0.13 mg l ⁻¹ ; recovery was 65% that required correction for losses; results are compared with certified reference material and GC	104
CH ₃ Hg ⁺	Dog fish, tuna	Clean-up by shaking/centrifugation with a water–acetone mixture (three times) and then toluene, the clean residue is treated as described in ref. 104	200 mmol l ⁻¹ borate buffer, pH 8.24; direct UV (200–400 nm)	DL, 12 ng g ⁻¹ using electrostacking	105
CH ₃ Hg ⁺	Tuna	See ref. 104	200 mmol l ⁻¹ borate buffer, pH 8.11; direct UV (200–400 nm)	Repeatability, 3–4%; reproducibility, 3–8%, recovery, 96–101%; data on the quality control were presented	105
CH ₃ Hg ⁺	Fish and crab meat	Addition of HCl, extraction with toluene, back-extraction with a DzS solution, centrifugation	10 mmol l ⁻¹ acetate buffer, 5 µg ml ⁻¹ DzS, pH 4.5 (coated capillary); direct photometry (480 nm)	DL, 2 ng g ⁻¹ ; recovery, 99–105%; RSD, 1.0–5.5%; no interferences from matrix components	107
As ^{III} , As ^V , dimethylarsenic acid species	Lettuce	Extraction with HClO ₄ , neutralisation with carbonate	5.2 mmol l ⁻¹ borate, 1.2 mmol l ⁻¹ tetraborate, 0.7 mmol l ⁻¹ KBr (pH 10.5), 2.5% methanol; ICP-MS	DL, 8.3–9.4 µg l ⁻¹ ; speciation of other arsenic species is possible	32
NO ₂ ⁻ , NO ₃ ⁻ , Cl ⁻ , Br ⁻ , SO ₄ ²⁻ , HPO ₄ ²⁻	Vegetables (15 kinds)	Aqueous extraction at 50 °C, filtration, dilution (for nitrate)	10 mmol l ⁻¹ sodium chromate, 2.3 mmol l ⁻¹ CTAB, pH 11.5; indirect UV (254 nm)	DL, 34 and 37 µg l ⁻¹ for nitrite and nitrate, respectively; precision and accuracy comparable to those of a reference photometric method	112
Cl ⁻ , NO ₃ ⁻ , HPO ₄ ²⁻ , HCO ₃ ⁻	Plant tissue sap and exudate	Incision of vascular bundle or root exudation, dilution	7.5 mmol l ⁻¹ salicylic acid, 15 mmol l ⁻¹ TRIS, 0.5 mmol l ⁻¹ DDTAHOH, 0.18 mmol l ⁻¹ calcium hydroxide, pH 8.3; indirect UV (232 nm)	DL, 0.5–2 µmol l ⁻¹	41

^a CTAB = cetyltrimethylammonium bromide; DDTAHOH = dodecyltrimethylammonium hydroxide; DzS = dithizone sulfonate. HIBA = α-hydroxyisobutyric acid; TRIS = tris(hydroxymethyl)aminomethane.

warning environmental monitors, using the full potential of chip technology, etc.

Following the advances outlined, a move out of the domain of research and becoming a routine tool for environmental

analytical laboratories is anticipated for the CE method within the first few years of the coming millennium.

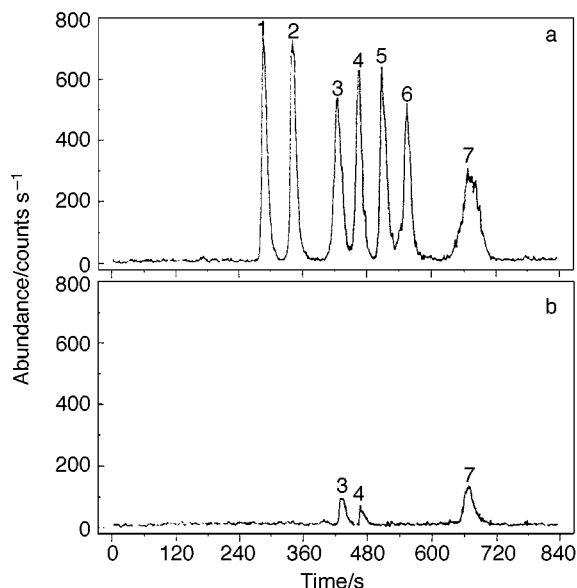


Fig. 5 Arsenic speciation in a plant material (garden lettuce) by CE-ICP-MS. Capillary, fused silica, 100 cm \times 75 μ m id; electrolyte, 5.2 mmol l⁻¹ sodium borate, 1.2 mmol l⁻¹ sodium tetraborate (pH 10.5), 0.7 mmol l⁻¹ KBr, 2.5% methanol; sample introduction, 15 s at 50 mbar; applied voltage, 25 kV, detection: ICP-MS, m/z 75; temperature, 22 °C. Sample: (a) standard; (b) plant extract. Peaks: 1 = arsenocholine; 2 = arsenobetaine; 3 = dimethylarsinic acid; 4 = As^{III}; 5 = monomethylarsonic acid; 6 = monophenylarsonic acid; 7 = As^V. Electropherograms courtesy of Dr. Mattusch.

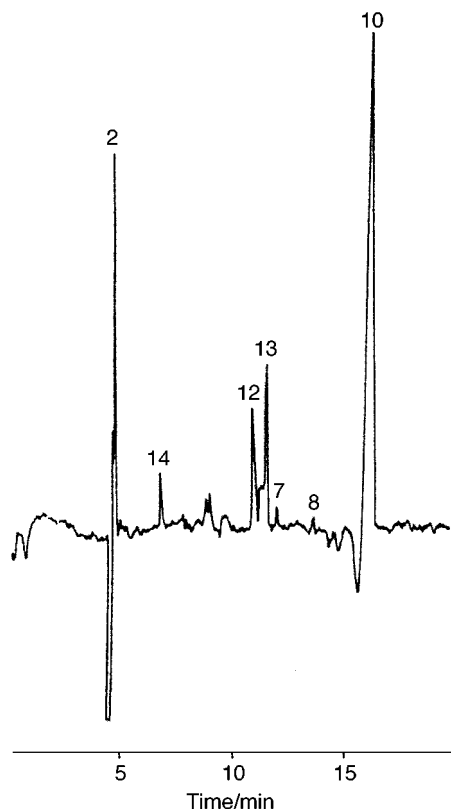


Fig. 6 Electropherogram of a sea-water sample. Capillary, fused silica, 64.5 cm \times 50 μ m id; electrolyte, 40 mmol l⁻¹ phosphate-borate buffer, 2.5 mmol l⁻¹ triethylenetetraminehexaacetic acid (TTHA), 2 mmol l⁻¹ SDS, pH 7.5; applied voltage, 20 kV; sample introduction, 6 s at 50 mbar. Peaks: 2 = MeOH; 7 = Pb²⁺; 8 = Se^{IV}; 10 = TTHA; 12 = Mg²⁺; 13 = Ca²⁺; 14 = Na⁺. Reprinted from ref. 65.

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