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## Review

# Analysis of inorganic species in environmental samples by capillary electrophoresis

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### Abstract

The use of capillary electrophoresis for the determination of inorganic species in environmental samples is reviewed. Topics covered include the separation of inorganic anions, inorganic cations, transition metal cations and organometals in different environmental matrices, such as atmospheric deposition, atmospheric aerosols, gases, natural waters, waste waters, soil, sediment and marine biological samples. Cited literature is gathered according to the type of matrix, so that the focus is on the discussion of matrix effects rather than on the method development for a single class of compounds. For each matrix, surveyed methods are tabulated in order to assist the method selection. Innovative applications of capillary electrophoresis to advanced environmental research are also emphasised. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Reviews; Environmental analysis; Water analysis; Soil; Sediments; Inorganic anions; Inorganic cations; Metals

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## 1. Introduction

Since 1989 [1,2] capillary electrophoresis (CE)

has been shown to be a powerful tool for inorganic ion analysis. This methodology appeared to be a viable alternative to ion chromatography (IC) for the determination of inorganic ions and other low-molecular-mass ionic solutes [3–5]. CE offers a number of advantages over IC, including simplicity, greater

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separation efficiency, unique selectivity and a high degree of matrix independence, all of which make it ideal for the analysis of ionic solutes in very complex matrices, such as environmental samples. The most common CE detection method is indirect ultraviolet spectroscopy (UV) detection, where the migrating analyte causes a vacancy in the absorbance of a chromophore (usually chromate) which is added to the background electrolyte [1–5]. 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.

A certain number of reviews dealing with the application of CE to environmental analysis have been published [6–10], one of which was specifically devoted to the CE analysis of inorganic pollutants [11]. The potential of CE in the field of metal speciation has also been reviewed [12–15], with particular emphasis on the characterisation of metal interactions with large molecules like humic substances and proteins [15].

The high resolving power, as well as the ease of operation and the low operating costs, should have made CE well suited for routine environmental analysis [16], but, despite these expectations, it has not found wide application in real-world problems. Our survey of the literature from 1993 shows that the use of CE analysis in monitoring campaigns is still limited. Very few works, which used CE as an analytical method, have been published in applied journals. This fact can be explained by the suspicion of analysts for new techniques and by the wide diffusion of a very reliable technique for inorganic analysis such as IC. Despite this, CE has been demonstrated to have very unique features which can solve specific problems in the environmental sciences. The aim of this review is to investigate the potential and the limits of CE when it is applied to real environmental samples. Cited literature is gathered according to the matrix type, so that the focus will be pointed on the discussion of matrix effects rather than on the method development for a single class of compounds. For each matrix, surveyed methods are tabulated in order to assist the method selection. For a more comprehensive ap-

proach to method development very exhaustive and up-to-date reviews are available [11,15] which give an overview of the state-of-the-art of the analysis of environmental relevant inorganic compounds.

## 2. Atmospheric samples

CE is a well suited technique for the analysis of atmospheric deposition samples, which are characterised by a very low ionic strength (Table 1). The natural composition of the samples allowed very low detection limits under stacking or electrostacking conditions [17–20]; the preferred detection method was indirect UV, but conductivity detection was also applied to capillary zone electrophoresis (CZE) anion analysis [17,21] and to isotachopheresis (ITP) cation analysis [22] in rain waters. The good agreement between CE data and IC determination showed that CE methods were sufficiently accurate [17,18,23], but sometimes less reproducible. The lack of reproducibility was corrected by using an internal standard [20]. Another unique feature of CE methods is the possibility of simultaneous determination both of organic and inorganic anions in the same run [19,24,25], the simultaneous determination of organic and inorganic anions and inorganic cations was also demonstrated in a rain water sample [26].

Although CE technique provides a quick, sensitive (beyond the IC working range), economic and reliable method to meet the need for the acid rain monitoring programme, relatively few laboratories use this technique in field campaigns. International intercomparison exercises on rain water samples, performed in the framework of the European Union (EU) AQUACON project [27], showed that only three laboratories (over 115 participating in the exercise) used CE for ion determination, and moreover some results lacked accuracy. CE was used for the determination of fluoride concentrations in Dutch rain water [28], and the results were compared with those obtained by IC and ion selective potentiometry. Statistical analysis performed on 42 samples indicated that there was no evidence of systematic differences between CE and ion selective electrode (ISE), whereas the fluoride concentrations obtained by IC were significantly higher. The observed differ-

Table 1  
Atmospheric samples

Compound	Sample matrix	Injection method	Electrolyte buffer, separation voltage	Detection mode	Detection limits	Ref.
Chloride, nitrate, sulphate	Rain water	Hydrodynamic (500 mbar for 15 s)	1 mM CTAB, 100 mM CHES, 40 mM LiOH, 0.02% (w/w) Triton X-100 (pH 9.3); 25 kV	Conductivity	2–3 µg/l	[17]
Organic and inorganic anions	Rain water	Electrokinetic	5 mM molybdate, 0.15 mM CTAOH, 0.01% PVA, 5 mM Tris buffer (pH 7.9)	Indirect UV	2 µg/l (Cl <sup>-</sup> )	[18]
Fluoride	Rain water	10 <sup>-4</sup> M Tiron, hydrostatic (10 cm for 240 s)	1.13 mM PMA, 0.8 mM TEA, 2.13 mM HMOH (pH 7.7); 30 kV	Indirect UV 254 nm	0.6 µM	[28]
Organic and inorganic anions	Rain water	Vacuum (1.5 p.s.i. for 30 s)	7.5 mM p-AB, 0.76 mM Ba(OH) <sub>2</sub> , 55 µM TTAOH (pH 9.4); 30 kV	Indirect UV 264 nm	0.6 µM	[19]
Organic and inorganic anions	Single cloud, fog and rain drop	Hydrostatic (10 cm for 45 s)	20 mM salicylic acid, 32 mM Tris-(hydroxymethyl)- aminomethane, 0.001% HDB (pH 8.1); 25 kV	Indirect UV 220–232 nm	40–70 fmol	[33,35]
Inorganic cations	Single cloud, fog and rain drop	Hydrodynamic (9.9 s)	4 mM 4- <i>N</i> -methylaminophenol, 4 mM 18-crown-6 (pH 4.5–6.5); 25 kV	Indirect UV 220 nm	40–50 fmol	[30,31,35]
Chloride, nitrate, sulphate	Snowflake, individual snow crystal	Hydrodynamic (9.9 s)	13 µM sulphuric acid, 1 mM DETA, 48 mM borate, 1.8 mM dichromate; 28 kV	Indirect UV 265 nm	17–28 µg/l	[36]
Ag(I), Cd(II), Co(II), Cu(II), Hg(II), Ni(II), Pb(II), Ti(II), Zn(II)	Snow	Electrokinetic (5 kV for 10 s)	8–10 mM HIBA, 30–50 mM creatinine, HAc (pH 4.8); 20 kV	Anodic and cathodic pulse amperometry	2–20 µM	[38]
Sodium, potassium, magnesium, calcium, ammonium, zinc	Air particulate matter	Hydrodynamic (0.5 p.s.i. for 10 s)	10 mM histidine, 2 mM 18-crown-6, 8 mM lactic acid (pH 4.0)	µg/l		[45]
Inorganic anions, oxalate	Atmospheric aerosol	Hydrodynamic (0.5 p.s.i. for 10 s)	2.25 mM PMA, 6.5 mM NaOH, 0.75 mM HMOH, 1.6 mM TEA (pH 7.9); 30 kV	Indirect UV 254 nm	0.07–0.15 mg/l	[39,40,43]
Alkali metals, alkaline-earth metals, ammonium, Mn(II)	Atmospheric aerosol	Hydrodynamic (0.5 p.s.i. for 10 s)	5 mM DHBP, 6 mM glycine, 2 mM 18-crown-6, 2% MeOH (pH 6.5); 25 kV	Indirect UV 280 nm	9–57 µg/l	[44]
Organic and inorganic anions	Atmospheric aerosol	Hydrostatic (10 cm for 30 s)	6 mM chromate, Anion BT (pH 8.0); 20 kV	Indirect UV 254 nm	33–119 µg/l	[41]
Inorganic cations	Atmospheric aerosol	Hydrostatic (10 cm for 30 s)	3.78 mM 18-crown-6, 13.06 mM HIBA, 5 mM 4-methylbenzylamine (pH 3.5); 20 kV	Indirect UV 185–214 nm	30–78 µg/l	[41]
Soluble ionogenic atmospheric gases	Air	Electrokinetic, hydrodynamic, hydrostatic	2 mM sodium tetraborate; 15 kV	Suppressed conductivity	1 ppbv	[46]

1 p.s.i.=6894.76 Pa.

ence was explained with the presence of aluminum in the natural samples. The applied decomplexing agents in the CE and ISE methods were not able to totally decomplex all fluoride anions bound by aluminum. Here, the response was more related to the free fluoride concentration than to the total concentration.

A major advantage of CE over IC is that CE analyses nanolitre size samples. Because of this small volume requirement CE is well suited for studying the chemistry of individual hydrometeors, and a new interesting field in atmospheric sciences can be opened. The analysis of the chemical constituents of rain, cloud and fog water has been always carried out on the assumption that individual drops and the bulk phase have the same concentration of trace compounds. A dependence of the concentration of trace compounds on the radius of drops was found by analysing size-classified raindrops. More detailed information about the above mentioned processes is available by the analysis of single raindrops (volume 10  $\mu\text{l}$ –3 nl) and single fog drops (volume pl–fl). The determination of analytes in volumes in the nanolitre and subnanolitre range affords the development of sampling procedures, handling techniques and methods for the analysis in the ultra trace level. Sampling of single and size-classified rain-, fog- and cloud drops was performed using the so-called "Guttalgor" method developed in Bächmann's laboratory [29–35]. Raindrops falling in liquid nitrogen froze out and were separated by polyethylene sieves of varying mesh widths. After sampling, the single raindrops were kept under water extracted paraffin oil in petri dishes of polystyrol in order to avoid evaporation. Analysis was carried out with a modified CE apparatus. The capillary [74 cm (60 cm to detector)  $\times$  50  $\mu\text{m}$  I.D.] was arranged at a 30° angle to allow the observation of the injection of a single raindrop into the separation capillary by a microscope which was also used to measure the drop diameter. Applying a vacuum at the opposite end of the capillary connected to the petri dish, the drop was injected into the capillary.

Single cloud and fog drops were sampled with an electrostatic precipitator based on a corona discharge. A copper electrode serving as a discharge electrode was positioned at a distance of 10 cm above a precipitation electrode consisting of alu-

minium. The corona electrode was fixed at a sufficiently high voltage (25–30 kV) to produce a spray of electrons. The strong field around the copper electrode generated further charges by ionising the surrounding gas molecules. The charged droplets moved to the precipitation electrode and were collected in a petri dish and handled like raindrops. As diameters of fog drops were in the range of 1–50  $\mu\text{m}$ , the capillary injection end had to be modified by etching in 40% HF under an uniform nitrogen flow. The injection and the analysis of the fog drops were similar to those of single raindrops. Calibration curves for constant concentration and varying drop size, and calibration graphs for constant drop size and varying concentration were generated from simulated raindrops produced by a sprayer system. Analyses of cations [30–32,35], inorganic [32,33,35] and organic anions [29,32,33] were carried out using indirect UV detection. The absolute limits of detection (LODs, in the fmol range) allowed the study of the dependence of the solute concentration (ammonium, magnesium and zinc cations, and sulphate and nitrate anions) on the size of single cloud and fog drops [35]. In all cases a decrease in the concentration of solutes with increasing drop size was found. Laser induced fluorescence (LIF) detection of carbonyl compounds and amperometric detection of sulphite and nitrite were used as means of improving sensitivity and selectivity for specific classes of compounds [32].

A technique for collecting snowflakes and crystals of various habits and subsequent anion analysis by CE was also described [36]. Individual crystals or clusters of crystals were collected on flat frozen surface and immediately transferred into a conical vessel using a stainless steel syringe needle. The melted samples were transferred under a Class 100 hood to dry CE vials using a syringe. Prior to snowmelt transfer, the syringe was rinsed with a 2  $\text{mg l}^{-1}$  bromide solution in order to correct for any dilution that may occur from residual liquid in the syringe. This handling procedure allowed analyses of sample volumes as small as 0.3  $\mu\text{l}$ . Preliminary findings suggested that the anion composition of snowflakes varies both temporally and with crystal habit.

CE was also employed for the analysis of atmospheric samples containing difficult or dirty matrices.

Anions in road snow were analysed by a flow injection analysis–CE (FIA–CE) dialysis system in order to automate the filtration and the analysis [37]; the metal ion content in urban snow was determined by anodic and cathodic pulse amperometric detection [38]. The samples were directly injected after filtration, but a standard addition calibration had to be used, due to appreciable matrix effects in these dirty samples. CE was found to be a suitable technique for the routine analysis of inorganic [39–42] and organic anions [41,43], alkali and alkaline-earth cations [41,42,44,45], and metal cations [45] in atmospheric aerosol collected on filters by a high volume sampler. A complete validation of CE methods for anions and cations in aerosol extracts was carried out by Dabek-Zlotorzynska and co-workers [39,40,43,44]. The comparison with IC and standard photometric methods, performed on 1100 samples, showed that comparable results can be obtained using CE and IC at ppm concentrations [40]; below  $1 \text{ mg l}^{-1}$  a poorer agreement was observed due to the poorer sensitivity of the CE method. Furthermore, in the CE methods analyte migration times were more strongly affected by the sample matrix and the use of an internal standard was strongly recommended. On the contrary CE was less expensive to operate and generated less waste than IC; the number of analytes determined per day by both IC and CE was comparable and larger than that of the photometric automated wet chemistry system [39].

An improved method for the simultaneous separation of inorganic and organic anions in atmospheric aerosol was discussed by Krivácsy et al. [41]. By using chromate as the UV absorbing ion in the running buffer, both inorganic and organic anions were well resolved. The overall matrix effect of the inorganic anions on the separation of organic acids was not found to be significant. In order to reduce the significant shift of migration times with the changing conductivity of the sample, a constant current separation ( $30 \mu\text{A}$  for 4 min) followed by a constant voltage separation (20 kV for 1 min) was used. The optimised method was applied to the determination of the total concentration and size distribution of the species in urban atmospheric aerosol collected by a Berner-type cascade impactor [42].

A very innovative application of CE techniques in

atmospheric science is the direct measurement of soluble ionogenic atmospheric gases [46]. The sampling was performed by a small wire loop deployed at the tip of the capillary (Fig. 1). When the loop was dipped into a solution and withdrawn, a liquid film, which could be used as an absorber for gases collected in a sample chamber, was formed on it. The film was in fluid communication with the capillary and acted as a microreservoir. The injection was performed by lifting the film end [46] or by electromigration [47]. Under hydrostatic injection conditions 1 ppb  $\text{SO}_2$  could be detected by suppressed conductimetric detection [46]. The determination of soluble gases and organic vapours (phenolic compounds, acetic and formic acids) in air by UV detection was also demonstrated [48–50].

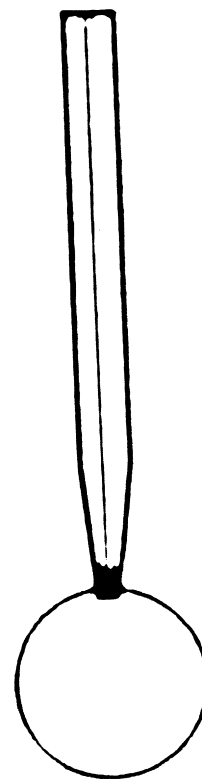


Fig. 1. Design of the loop-bearing capillary used to sample gases; the support wire and the capillary are held by a Jig not shown in this figure (capillary:  $56 \text{ cm} \times 75 \mu\text{m}$  I.D.  $\times 375 \mu\text{m}$  O.D.,  $140 \mu\text{m}$  O.D. at the tip; loop:  $0.5\text{--}2 \text{ mm}$  I.D. formed from  $50 \mu\text{m}$  Ni wire or  $100 \mu\text{m}$  diameter Pt wire). Reprinted from Ref. [47].

Table 2  
Fresh water and sea water samples

Compound	Sample matrix	Injection	Electrolyte buffer, separation voltage	Detection mode	Detection limits	Ref.
Fluoride, chloride, bromide, sulphate, nitrate, nitrite, thiosulfate, phosphate	Tap water	Hydrodynamic (50 mbar for 6 s)	2.25 mM PMA, 6.5 mM NaOH, 0.75 mM HMOH, 1.6 mM TEA (pH 7.7); 20 kV	Indirect UV 250 nm	1–3 mg/l	[51]
Perchlorate, bromide, fluoride, nitrate, thiocyanate	Tap water	Electrokinetic (10 kV for 10 s)	20 mM sodium sulphate, (pH 2.5); 30 kV	Ion selective microelectrode	5 µg/l	[52]
Nitrate, thiocyanate, iodide	Subterranean water	Hydrostatic (10 cm for 30 s)	100 mM sodium chloride, 2.0 mM CTAC, 10 kV	Direct UV 214 nm	0.3 mg/l (NO <sub>3</sub> <sup>-</sup> ) 5–6 mg/l (SCN <sup>-</sup> )	[60]
Bromide	Sea water	Vacuum (2 s)	Ten-fold diluted artificial seawater (pH 7.0); 11 kV	Direct UV 200 nm	0.46 mg/l	[62]
Inorganic anions	Drinking water	Direct	5 mM chromate, 20 mM TTAB (pH 8.0), 25 kV	Indirect UV 254 nm	50–300 µg/l	[53]
Phosphate	Lake water	Electrokinetic (5 kV for 25 s)	10 mM chromate, 1 mM TTAB; 20 kV	Indirect UV 254 nm	10–25 µg/l	[58]
10 organic and inorganic anions	Tap and rain waters	FIA	6 mM chromate, 3.2·10 <sup>-5</sup> M CTAB, 3 mM boric acid (pH 8.0), 25 kV	Indirect UV 372 nm	0.05–0.3 mg/l	[24]
Thiosulphate, tetrathionate, sulphate, sulphide	Natural clayey water	Hydrostatic (10 cm for 30 s)	1.5 mM PMA, 10 mM Tris, 0.5 mM DETA (pH 8.0) 20 kV	Indirect UV 214 nm	3–20·10 <sup>-6</sup> M	[61]
12 organic and inorganic anions	Mineral, tap and rain waters	Direct	8.2 mM chromate, 4.8·10 <sup>-5</sup> M CTAB (pH 7.5–10); 25–30 kV	Indirect UV 254 nm	0.12–0.84 mg/l	[25]
Inorganic anions	Drinking water	Hydrostatic (9.8 cm for 30 s)	4.5 mM chromate, 0.4 mM CIA-Pak OFM Anion, 15 kV	Indirect UV 254 nm		[54]
Chlorite, chlorate, perchlorate, chloride	Tap and swimming pool waters	Hydrostatic (10 cm for 30 s)	4.6 mM chromate, 0.46 mM CIA-Pak OFM Anion (pH 8.0), 20 kV	Indirect UV 254 nm	0.1–0.6 mg/l	[55]
Nitrite, nitrate, bromide	Tap and river waters	Electrokinetic (7.5 kV for 5 s)	1.1 mM CTAC, 20 mM tetraborate (pH 8.94); 10 kV	Direct UV 200 nm	1 µg/l	[56]
Inorganic anions	Drinking, ground- and waste-waters	Hydrostatic (10 cm for 30 s)	4 mM chromate, 0.3 mM CIA-Pak OFM Anion (pH 8.1), 20 kV	Indirect UV 254 nm		[57]
Inorganic anions	Drinking, river and rain water	490 nl sample injection loop	7 mM succinate, β-alanine, 0.2% methylhydroxyethylcellulose (pH 3.55); 30 µA	Conductivity	3–10 µg/l	[21]
Bromide, bromate, iodide, iodate, nitrate, nitrite, selenite	River water	Vacuum	Phosphate buffer (pH 2.9), 40°C; 20 kV	Direct UV 200 nm		[59]
Fluoride, phosphate	Estuarine water	Electrokinetic (3 kV for 30 s)	5 mM chromate, 0.5 mM CIA-Pak OFM Anion-BT (pH 8); 20 kV	Indirect UV 254 nm	6–7 µmg/l	[63]
Nitrite, nitrate	Estuarine water	Electrokinetic (3 kV for 30 s)	1 mM sulphate, 0.5 mM CIA-Pak OFM Anion-BT (pH 8); 14 kV	Direct UV 214 nm	2 µg/l	[63]

Chromate	Water	Direct	100 mM Tris-HCl, 2 mM 1,6-hexanediamine	Direct UV	1.0 mg/l	[90]
Arsenical species	Drinking water	Vacuum ( $\Delta p = 1.7 \cdot 10^4$ Pa)	0.025 mM phosphate buffer (pH 6.8); 40°C; 25 kV	Direct UV 190 nm	<2 mg/l	[91]
Selenium and arsenical species	Drinking water	Electrokinetic	20 mM KHP, 20 mM boric acid (pH 9.03); hydrodynamically modified EOF; 22 kV	Hydride generation-ICP-MS	6–58 ng/l	[87,88]
Selenium and arsenical species	Tap and spring water	Stacking by field-amplified injection (10 kV)	75 mM dihydrogenphosphate, 25 mM tetraborate (pH 7.65); 20 kV	Direct UV 195 nm	12–25 µg/l	[83]
Selenium species	Thermal water	Electrokinetic (10 kV for 20 s)	Chromate, 0.5 mM TTAOH (pH 10.5); 20 kV	Indirect UV 254 nm	10 µg/l (inorganics); 300 µg/l (amino acids)	[82]
Magnesium	River water	Hydrostatic (4.0 cm for 15 s)	10 mM pyridine, 0.8 mM EDTA (pH 5); 7.5 kV	Indirect UV 254 nm	0.15 mg/l	[69]
Magnesium, calcium	Sea water	Dilution 1:100 vacuum injection (3 s)	20 mM tetraborate, 2.0 mM EDTA; 20 kV	Direct UV 200 nm	0.13–0.26 mg/l	[89]
Sodium, potassium, magnesium, calcium	Well water	Hydrostatic (10 cm for 15 s)	5 mM imidazole, 6.5 mM HIBA, 2 mM 18-crown-6 (pH 4.1); 20 kV	Indirect UV 214 nm		[70]
Sodium, potassium, magnesium, calcium	Sea water and formation water	Hydrostatic (9.8 cm for 20 s)	5.0 mM 4-methylbenzylamine, 6.5 mM HIBA, 6.2 mM 18-crown-6, 25% MeOH (pH 4.8); 20 kV	Indirect UV 185 nm	0.08–0.14 mg/l	[71]
Alkali and alkaline-earth cations	Tap and mineral water	Hydrodynamic (0.5 s)	$10^{-2}$ M imidazole (pH 4.5); 30 kV	Indirect UV 214 nm	0.05 mg/l	[72]
Alkali and alkaline-earth cations and ammonium	Drinking water	Hydrostatic (10 cm for 30 s)	4.0 mM cupric sulphate, 4.0 mM formic acid, 4.0 mM 18-crown-6 (pH 3.0); 20 kV	Indirect UV 215 nm	0.06–0.16 mg/l	[73]
Simultaneous cation and anion analysis	Process and tap water, rainwater	Hydrostatic (cathode end: 10 cm for 10 s; anode end: 5 cm for 10 s)	6 mM 4-aminopyridine, 2.7 mM chromate, 30 µM CTAB, 2.0 mM 18-crown-6 (pH 8); 20 kV	Indirect UV 262 nm		[26]
Fe(III)	Tap and river water	$10^{-4}$ M EDTA addition, ITP	10 mM HCl, 20 mM L-histidine, 0.1% hydroxypropylmethyl cellulosa; 5 mM MES; 25 mM MES + 10 mM bis-Tris-propane (pH 6.6), leading, terminating and background electrolyte	Direct UV 254 nm	10 µg/l	[78]
Fe(II)	Lake and tap water, rainwater	Pre-column complexation with 1,10-phenantroline electrokinetic (5 kV for 20 s)	50 mM $\text{NH}_4\text{Ac-HAc}$ (pH 5); 12.5 kV	Direct UV 270 nm	0.3 µg/l	[74]
Fe(II)	Tap water, rainwater seawater	Pre-column complexation with 1,10-phenantroline hydrodynamic (0.3 s)	50 mM $\text{NH}_4\text{Ac-HAc}$ (pH 4.5); 15 kV	Laser induced thermal lens spectroscopy (514 nm)	2 µg/l	[75]
Uranyl cation ( $\text{UO}_2^{2+}$ )	River water	Pre-column complexation with arsenazo III; hydrostatic; field amplified injection	10 mM perchloric acid, 1 mM phosphate, 0.6 mM borate, 0.01–0.1 mM arsenazo III, 50–150 mM NaCl, 10% MeOH; 375 V/cm	Direct UV-Vis 650 nm	10 µg/l	[80]
Zn <sup>2+</sup> and transition metal cations	Tap water	Pre-column complexation with HQS; hydrostatic (10 cm for 5 s)	10 mM borate buffer, 0.1 mM HQS (pH 9.2); 15 kV	Direct UV 254 nm	3–225 µg/l	[79]
Al(III)	River, reservoir and spring water	Pre-column complexation with 50 mg/l lumogallion; hydrostatic (15 cm for 10s)	40 mM HAc, 10 mM $\text{NH}_4\text{Ac}$ (pH 4.0); 15 kV	Fluorescence ex. 491 and em. 576 nm	19 µg/l	[81]

### 3. Natural water samples

#### 3.1. Freshwater

Water samples are particularly suitable for direct injection in CE, and this technique was used to analyse inorganic anions in drinking waters [21,24,25,51–57], surface waters [21,58,56,59], ground waters [57,60,61] and sea water [62,63] (Table 2). Nevertheless most papers cited in Table 2 are specifically devoted to the development and discussion of new methods and the real sample analyses are showed only as examples of applications. The method of choice is the use of electroosmotic flow (EOF) modifier and indirect UV detection which achieves detection limits of hundreds of ppbs by using hydrostatic or hydrodynamic injection mode. These LODs are comparable with the concentrations of main anionic compounds (chloride, nitrate and sulphate) in natural waters but they are insufficient for the determination of minor components which can be more interesting for environmental or toxicological purpose. Amran et al. [59] demonstrated the feasibility of the separation of seven anions (bromide, bromate, iodide, iodate, nitrite, nitrate and selenite), although only nitrate was detected in fact in Rhine river water. A method for the analysis of chlorine containing anions in tap and swimming pool waters was presented [55], but it lacked sufficient sensitivity when real samples were analysed. To achieve the low ppb range useful for perchlorate analysis in tap water electrokinetic injection with ion selective microelectrode detection was applied [52]. This work shows that anion selective microelectrodes can be used as powerful detectors in CE. Considering the detection limits and the possibility of miniaturising the separation systems, even better results are achievable than with conventional detection methods.

Electromigration and indirect UV detection were used to determine phosphate in lake waters at low ppb concentrations [58]. Phosphate is found to be the most restrictive nutrient for productivity in inner lakes and values in the upper  $10 \mu\text{g l}^{-1}$  have been considered an index of mesotrophic condition [64]. The CE method offered short run times per sample and sufficient sensitivity for natural waters. The problem of discrimination in electrokinetic injection,

due to the different ionic strengths of standards and samples, was overcome by using the method of standard addition for quantitation. Comparison with the classical colorimetric method (measure of the absorbance of the molybdate complex at 880 nm) showed that the CE method had a comparable accuracy but a worse repeatability. It had however the advantage, that it could be applied to samples of very small volume (1 ml), and therefore some very important types of environmental samples, like interstitial water, could be analysed. CE was also employed for the separation of smaller polyphosphates [65,66] and longer chain polyphosphates with chain length  $>5$  carbon atoms [67] in food and commercial samples. This topic, which is potentially of environmental interest, was recently reviewed by Rosset et al. [68].

The CE separation of alkali and alkaline-earth cations was generally performed by modulating cation mobility by a complexing agent [ $\alpha$ -hydroxyisobutyric acid (HIBA), crown ethers, ethylenediaminetetraacetic acid (EDTA)]. The use of absorbing organic electrolytes, such as pyridine, imidazole and benzylamine [69–72,26], or inorganic electrolytes, such as cupric ion [73], achieved detection limits of tens of ppbs which are adequate for most applications.

An interesting improvement of the CE technique was the simultaneous determination of 22 small inorganic and organic anions, alkali and alkaline-earth cations within 5 min in a single electrophoretic run, using one capillary and one detector placed in the middle of the capillary [26]. The sample was injected into the first end of the separation capillary and subsequently into the second end. When the high voltage was applied the cations and the anions in the two injected sample portions started to migrate against each other toward the centre of the capillary where the detection window was placed. The method was applied to the analysis of real samples such as tap water, rain water, waste water and even mud sample after off-line dialysis pre-treatment (Fig. 2). Samples were injected directly in the capillary and no interferences, neither adsorption nor blocking effect were observed.

The application of CE to the separation and determination of metal ions after pre-column formation of negatively charged chelates has been de-



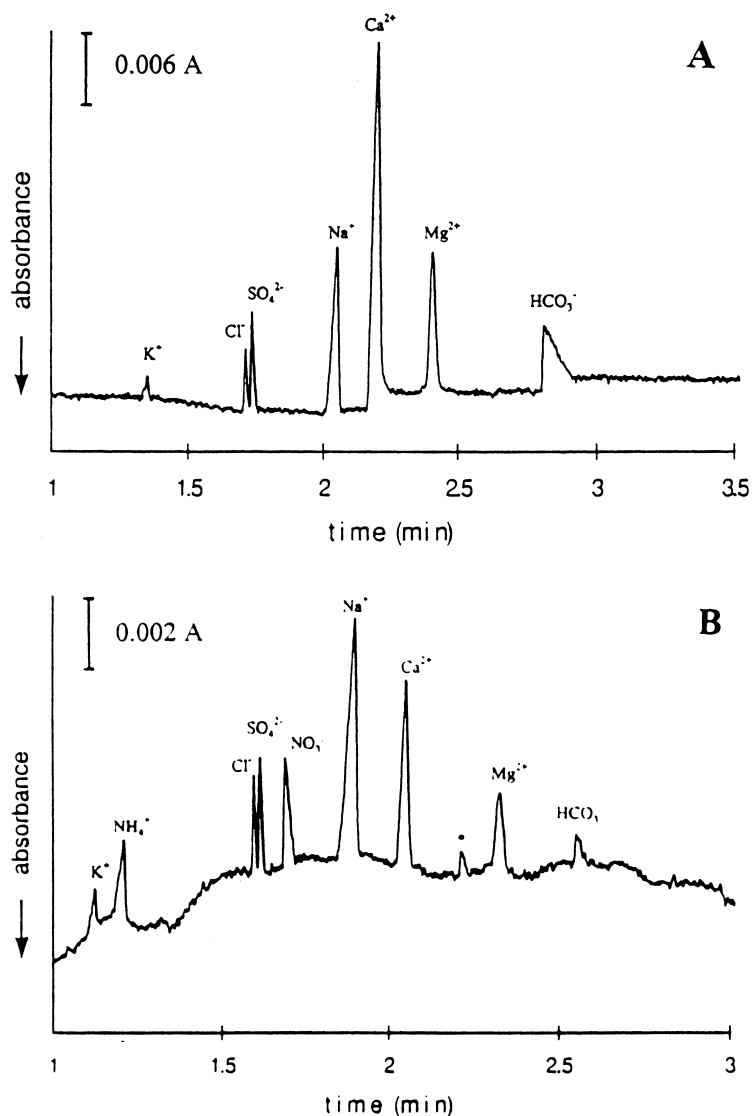


Fig. 2. Simultaneous determination of inorganic cations and anions in tap water (A) and rainwater (B) samples. Conditions as in Table 2. Reprinted from Ref. [26].

scribed [11,15]. This kind of approach was applied to the determination of ferrous ions in natural waters [74,75] by using 1,10-phenantroline which forms a red coloured Fe(II) complex. The corresponding colorimetric method is highly sensitive but not specific for iron and a combination with the CE separation technique is required. Electrokinetic injection achieved low ppb concentrations, which are the typical concentration range of Fe(II) in natural

waters [76]. This method was applied to the direct determination of Fe(II) levels in rain water, lake water and tap water [74], measuring the absorbance at 270 nm. To avoid the problems of electromigrative techniques [77], the same method was applied to natural water samples with a more sensitive laser-based detection technique, using hydrodynamic injection [75]. The detector unit, which had the typical configuration of a double laser pump and probe

equipment, was based on the thermal lens spectroscopy principle, and was designed to detect probe volumes within the pl range.

Ferric ion was determined in tap and river water as a negatively charged complex with EDTA which is highly UV absorbing [78]. The determination of Fe(III) at trace levels could be performed by on-line coupling of ITP and CE: the low concentration sensitivity of CE is overcome by the high sample load of ITP. On the other hand, the resolution power of CE allows the separation of ITP zones of UV-active compounds without the use of spacers. In the electropherograms of real samples, no other peak than that of the Fe complex was detected and the authors concluded that interferences from other sample components were not to be expected. The acidification of the samples prior to the addition of EDTA and the ITP–CE analysis allowed better recoveries avoiding the presence of  $\text{Fe}(\text{OH})_3$  colloids.

The pre-column formation of negatively charged chelates allowed the separation and the determination of metal ions which form stable complexes. Incorporating the chelating reagent in the electrophoretic buffer markedly improves the detectability of unstable chelates. This approach was developed by Timerbaev et al. [79], who, having added 8-hydroxyquinoline-5-sulphonic acid (HQS) both to the sample and the running buffer, were able to sensitively detect relatively unstable chelates, such as those of Co(II), Zn(II) and Cd(II), and separate metal ions that form unstable chelates, such as Mn(II) and alkaline-earth metals. This method allowed the determination of zinc at less than 10 ppb concentration in tap water, and can be used for environmental samples without any pre-concentration steps.

A similar approach was used to determine uranyl cation in river water at 10 ppb concentration by pre-column addition of arsenazo III [80]. The same complexing reagent and sodium chloride were added

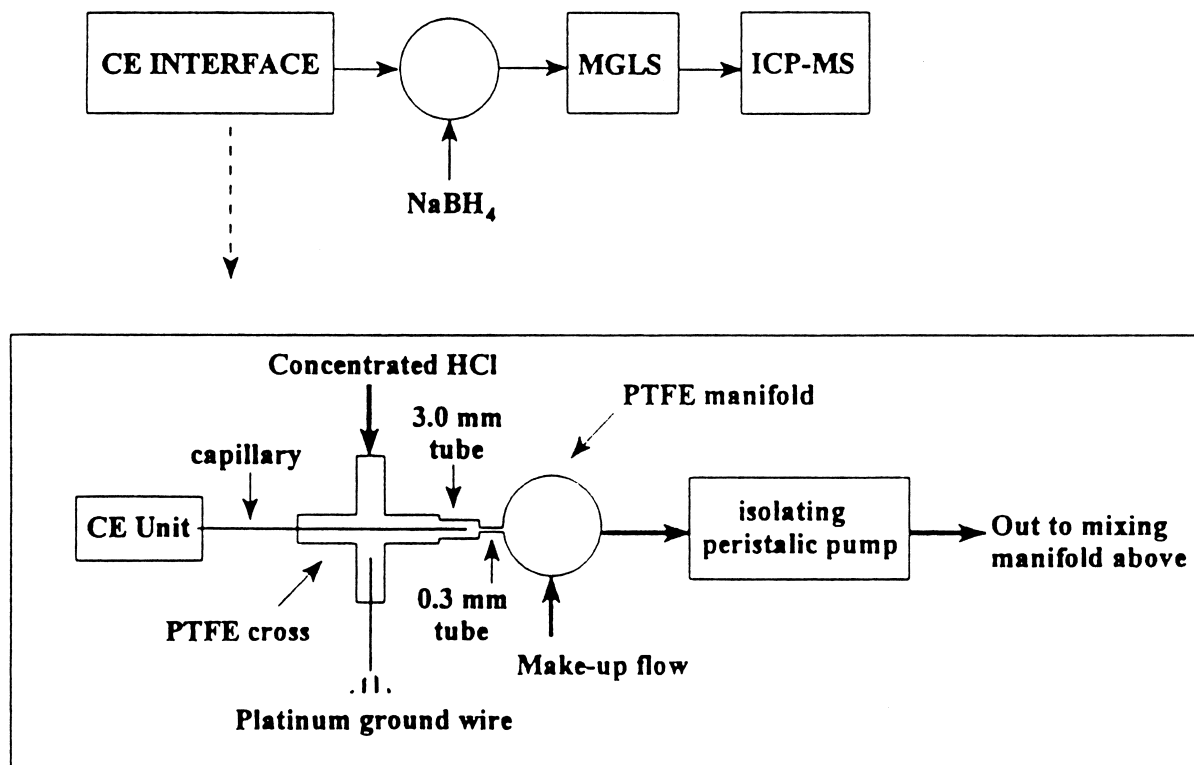


Fig. 3. Schematic diagram of CE–hydride generation–ICP-MS unit. MGLS represents the membrane gas–liquid separator. Reprinted from Ref. [88].

to the running buffer to prevent complex dissociation and to improve stacking. The complex formed between the uranyl ion and arsenazo III was negatively charged, while most other complexes were neutral or positively charged. This method proved to be extremely selective and free from interferences caused by the metals expected to be present in real samples (i.e., Hg, Pb, or Ca), and by the river water matrix.

Detection limits in metal analysis could be improved by forming a fluorescent metal complex. Aluminium was detected in spring and river water at low ppb concentrations by pre-column complexation with Luminogallion and fluorescence detection [81]. This method proved to be very selective because no interferences were observed in the presence of Fe, Ca, Mg, Cu and Zn at ppm concentrations.

CE was shown to be very suitable for metal speciation analysis: this technique found promising applications in the speciation of selenium and arsenic compounds in natural waters. Detection limits in the order of tens of ppbs have been achieved in natural water samples by using electrokinetic injection [82] or on-column pre-concentration achieved by stacking large volumes of sample by means of the field amplified injection technique [83]. Using a chromate buffer with tetradecyltrimethylammonium hydroxide (TTAOH) as EOF modifier, the separation of selenite, selenate, selenocystine and selenomethionine was achieved in a single run [82], but the indirect UV detection did not show sufficient sensitivity for organometallic compounds. The application of CE to the study of arsenic and selenium speciation in environmental matrices depends on the development of more selective and sensitive detectors. One possibility may be the coupling of CE with inductively coupled plasma mass spectrometry (ICP-MS) for speciation investigation [84–86]. Magnuson et al. [87,88] coupled CE with hydride generation ICP-MS (Fig. 3) to determine four arsenicals and two selenium species. Selenate was reduced on line to selenite by mixing the CE effluent with concentrated HCl. The direction of the EOF during CE run was reversed with hydrodynamic pressure, which allowed an increased freedom of the buffer choice. Recoveries from spiked drinking water were quite good, with detection limits in the ppt range. The use of Ge as a surrogate to correct for electrokinetic

sampling bias, allowed the direct determination of As(III) with high accuracy, but was not appropriate for As(V), possibly because of electrophoretic mobility differences [87].

### 3.2. Seawater

A few works have been devoted to the study of the matrix effect in high saline matrices (Table 2). In order to determine the petroleum tracers nitrate and thiocyanate in saline subterranean waters, the effect of high concentrations of salts in samples was examined [60]. High concentration of salts caused differences in peak heights and widths (i.e., in efficiencies) because of electrostacking and its inverse process, but apparently did not influence peak areas. By using 100 mM NaCl with 2 mM cetyltrimethylammonium bromide (CTAB) as carrier electrolyte solution, the determination of nitrate and thiocyanate in samples with NaCl concentration from 0 to 200 mM was achieved using an external standard calibration procedure. A similar result was obtained by Fukushi et al. [62] for the determination of bromide in sea water. A ten-fold diluted artificial sea water sample was adopted as the buffer solution, to prevent interference from high concentrations of chloride in sea water. It was found that the analyte peak height decreased linearly with an increase in salinity, while the peak area and migration time were almost constant, despite differences in the salinity of sample solutions. The analytical results obtained by the external calibration agreed with those obtained by the standard addition method.

The CE analysis of alkali and alkaline-earth cations seems to be less affected by coexisting components in sample solutions than the anion determination: moreover, detection limits are lower and a major dilution factor can be applied before the analysis. Fukushi and Hiroyoshi [89] showed that magnesium and calcium could be determined without any pre-treatment by injecting 100-fold diluted sea water samples. Despite these promising features, CE has been little used for cation analysis in sea water samples. An interesting application was reported by Tangen et al. [71] who needed a simple and rugged method for off-shore analysis of mixtures of sea water and formation water from oil wells in the North Sea. They used a CE method with indirect UV

Table 3  
Waste water and industrial process water samples

Compound	Sample matrix	Injection	Electrolyte buffer, separation voltage	Detection mode	Detection limits	Ref.
Sulfide	Waste water from tanneries	Hydrostatic (10 cm for 30 s)	10 mM sulphate, 0.5 mM CIA Pak OFM-OH (pH 10.5); 20 kV	Direct UV 229 nm	10 µg/l	[93]
Anions	Car wash sewage	Hydrostatic (10 cm for 30 s)	2.25 mM PMA, 6.5 mM NaOH, 0.75 mM HMOH, 1.6 mM TEA; 30 kV	Indirect UV 250 nm	50–200 µg/l	[92]
Organic and inorganic anions	Waste water from a dumping area	Hydrostatic (10 cm for 30 s)	9 mM PDCA, 0.05 mM TTAB (pH 7.8); 20 kV	Indirect UV 254 nm		[95]
Chromate	Waste water from tanneries		0.02 mM phosphate buffer (pH 7)	Direct UV		[94]
Anions	Liquors from pulp and paper industry; tap water	On-line dialysis-FIA	6 mM chromate, 0.032 mM CTAB, 3 mM boric acid (pH 8.0); 25 kV	Indirect UV 372 nm		[37]
Sulfur containing anions, inorganic and organic anions	Kraft pulping liquors	Hydrostatic (10 cm for 15 s)	5 mM chromate, 0.001% HMB, 20–32% acetonitrile (pH 11); 15–30 kV	Direct and indirect UV 185, 214 and 254 nm		[97,98]
Organic and inorganic anions	Bayer liquor	Hydrostatic (10 cm for 45 s)	3 mM TTAB, 3 mM DTAB, 7.5 mM chromate (pH 9); 20 kV	Indirect UV 254 nm	0.09–0.34 mg/l	[99]
Chloride, sulfate, oxalate	Bayer liquor	Hydrostatic (10 cm for 20 s)	5 mM chromate, 0.5 mM CIA Pak OFM Anion-BT (pH 8.0); 20 kV	Indirect UV 254 nm		[100]
Organic and inorganic anions	Water from power plant	Electrokinetic (5 kV for 45 s; 75 µM octanesulfonate)	7 mM chromate, 0.7 mM NICE Pak OFM Anion-OH form; 15 kV	Indirect UV 254 nm	0.3–0.8 µg/l	[104,105]
Sodium, potassium, magnesium, calcium	Waste water from meat processing plant, lake	Hydrostatic (10 cm for 30 s)	1.2 mM UV Car-2, 3.0 mM tropolone; 20 kV	Indirect UV 185		[121]
Chloride, nitrite, nitrate, sulphate, phosphate	Water purification plant	Pre-concentration by Chelex-100; FIA	2 mM chromate, 2 mM DETA (pH 7.5); 30 kV	Indirect UV 265 nm	0.24–0.34 mg/l	[106]
ammonium, alkali, alkaline-earth, metal cations	Water purification plant	Pre-concentration by Chelex-100; FIA	4 mM CuSO <sub>4</sub> , 4 mM formic acid, 3 mM 18-crown-6 (pH 4.5); 20 kV	Indirect UV 265 nm	0.04–0.52 mg/l	[106]
Anions	Kraft pulping liquors	Hydrostatic (10 cm for 30 s)	5 mM chromate, 0.5 mM NICE Pak OFM Anion-BT (pH 10.6); 20 kV	Indirect UV 254 nm; direct UV 214 nm		[96]
Sodium, potassium	Kraft pulping liquors	Hydrostatic (10 cm for 30 s)	5 mM Waters UV Car-1, 6.5 mM HIBA (pH 4.4); 20 kV	Indirect UV 214 nm		[96]

Cr(VI)	Rinse water from chromium plating bath	Vacuum	0.01 M carbonate buffer, 5 mM TTAB (pH 10); 20 kV	Direct UV 273 nm	1.2 mg/l	[109]
Cr(VI)	Rinse water from chromium plating bath	Stacking; vacuum (3.4 kPa for 100 s)	0.1 M carbonate buffer, 0.2 mM TTAB (pH 10.14); 20 kV	Direct UV 265 nm	11 µg/l	[110]
Cr(III), Cr(VI)	Rinse water from chromium plating bath	Hydrostatic (10 cm for 10 s)	1 mM CDTA, 10 mM formate buffer (pH 3.8); 20 kV	Direct UV 214 and 254 nm	10–50 µg/l	[111,112]
Fe(II), Cu(I), Ni(II), Pt(II), Pt(II)-cyano complexes	Leaching solutions of automobile catalytic converters	Vacuum (3.4 kPa for 50–100 s)	20 mM phosphate buffer, 100 mM NaCl, 3 mM NaCN, 1.2 mM TBAB, 40 µM TTAB (pH 11); 15 kV	Direct UV 208 nm	40–200 µg/l	[114]
Metal-cyanide complexes, sulphide, thiocyanate	Gold processing solutions	Vacuum (3.4 kPa for 30 s)	20 mM phosphate buffer, 36 mM NaCl, 1 mM NaCN, 30 µM TTAB (pH 11); 12 kV	Direct UV 204 nm	10–200 µg/l	[115]
Metal-cyanide complexes	Gold leaching process solution	Off-line pre-concentration on liquid membranes; hydrostatic injection (10 cm for 10 s)	5 mM hydrogenphosphate, 5 mM TEA, 0.8 mM HMB; 0.1 mM NaCN, 15 mM perchlorate; 25 kV	Direct UV 214	6.6–200·10 <sup>-9</sup> M	[116]
Free and labile cyanide	Surface water, gold leaching process solution	Off-line pre-concentration on liquid membranes; addition of 1 mM nickel sulfate; hydrostatic injection (10 cm for 10 s)	5 mM hydrogenphosphate, 5 mM TEA, 0.8 mM HMB; 25 kV	Direct UV 254 nm	5·10 <sup>-7</sup> M (CN <sup>-</sup> )	[116]
Transition metal ions	Waste water from electroplating plant	Hydrodynamic (0.5 p.s.i. for 12 s)	20 mM hydrogenphosphate, 0.5 mM TTAOH, 5 mM DTPA (pH 8.5); 25 kV	Direct UV 214 nm	2–8·10 <sup>-6</sup> M	[113]
Transition metal ions	Nuclear fuel waste	ITP	Leading: 10 mM HIBA, 20 mM ammonia, HAc buffer (pH 4.8)	Off-line PIXE		[107,108]
Arsenic species	Coal fly ash extract	Manual	6 mM chromate, 1:40 NICE Pak OFM Anion-BT (pH 10); 28 kV	Indirect UV 274 nm	0.65–1.95 mg/l	[117]
Arsenic and selenium species	Water from a tin mining process	Hydrodynamic (25 mbar for 0.13 min)	15 mM phosphate buffer 1 mM CTAB, 50 mM CHES, 0.03% Triton X-100, 20 mM LiOH (pH 9.4); 25 kV	Conductivity	0.04–0.08 mg/l	[118]
Organolead, organoselenium	Waste water from a car park	Hydrostatic (2 cm for 4 s)	50 mM SDS, 5 mM β-cyclodextrin, 25 mM phosphate buffer (pH 6.0); 15 kV	Direct UV 210 nm	10–20 pg	[119]

detection to monitor the composition of the water introduced to pressurise the oil reservoir, in order to prevent precipitation in the pipelines.

#### 4. Waste water and industrial process water

CE with cheap fused-silica capillaries, which can be easily cleaned with sodium hydroxide solution, can also be the method of choice for the analysis of highly contaminated samples. A direct measurement can be done without any further sample pre-treatment. Camman et al. [92] examined an authentic sample with a high surfactant content from a car wash sewage plant in order to compare IC, CE and electrochemical sensors for the anion determination in waste water. These sensors showed to be extremely selective, but the long term stability was very poor, especially when used in environmental samples with complex matrices. IC needed some pre-treatment of the samples, but the preparation of the sample was reduced to filtering and sometimes diluting it. These operations can be done automatically by modern autosamplers, offering the possibility for quasi-continuous monitoring of inorganic anions. However, direct measurements of water samples with a high content of organic substances, e.g., humic acids and surfactants as in the sample from a car wash, was possible for a short time only, because the column was damaged after some injections. CE allowed the direct injection of the samples and needed a cleaning step with NaOH after each analysis. The drawback of CE separation was that the organic substances, like surfactant, present in the sample altered the microenvironment of the capillary walls and influenced the migration and resolution of the components. Therefore, the identification of the analytes according to their migration times, determined with standard solutions, is rather difficult especially in routine analyses because of these shifts in real samples. The reproducibility can be improved by using an internal standard or a dedicated software.

Numerous examples of the application of CE techniques to different typologies of waste waters are reported in the current literature (Table 3). CE was applied to samples from the leather industry for the determination of sulphide [93] and chromate [94]. These samples are alkaline (pH values up to 12.5)

and have an antioxidant matrix that contains thiosulphate, sulphite, and organic compounds such as aldehydes, carbohydrates and amino acids, obtained from collagen and keratin degradation. CE with direct detection at 229 nm provided a rapid and sensitive method for determining sulphide in this kind of sample [93]. The sample preparation was as simple as filtration, dilution and addition of molybdate as internal standard. No interference from matrix components or other anions present in the samples (thiosulphate, nitrite and nitrate) was found. This method appears to be an excellent alternative to classical procedures for samples containing interfering substances that may give inaccurate or false results by iodometric and colorimetric methods.

CE allowed the simultaneous determination of organic and inorganic anions in dumping sites [95]. The determination of organic acids is of great interest for monitoring the ill-smelling effects of waste waters; the only pre-treatment was filtration and for some samples dilution was also necessary, since excessive levels of carbonate caused large peak overlapping with some organic anion peaks.

CE found a good number of applications in the pulp and paper industry [96], both in monitoring processes and in controlling waste waters. In the kraft pulping process lignin is removed by cooking wood chips in an aqueous solution of NaOH and Na<sub>2</sub>S (white liquor). The white liquor contains small amounts of carbonate, sulphate, thiosulphate and sulphite. The spent liquor (black liquor) is concentrated and burned in a furnace to obtain a smelt of sodium carbonate and sulphide (green liquor), which is used to regenerate white liquor by reaction with Ca(OH)<sub>2</sub>. Salomon and Romano [96] applied CE for the first time on kraft process streams using an EOF modifier and indirect UV detection to monitor inorganic and organic anions; alkali cations were also determined. The results were used to evaluate important process variables as sulphidity (white liquor), reduction efficiency (recovery furnace performance) and causticisation efficiency (slaker performance). This work showed that CE could monitor these complex process streams with little sample manipulation, low operating costs and high speed compared with existing analytical methodologies. In order to shorten analytical times for process control purpose, a new technique for coupling on-line dialysis in a FIA system to a CE system was described [37]: the

FIA–CE interface allowed consecutive injections in one uninterrupted electrophoretic run and the samples were introduced without any pre-treatment.

The former separation method was improved employing a cationic polymer (1,5-dimethyl-1,5-diazaundecamethylene polymethobromide) to reverse EOF at alkaline electrolyte pH values [97,98]. The main advantage of cationic polymer over hemimicellar based EOF modifier like CTAB is the relative sensitivity of the latter class of EOF modifiers against changes in pH and the presence of organic solvents in the electrolyte. The use of high alkaline conditions, both in the sample and in the electrolyte (pH 11), reduced interfering redox reaction among the matrix components (quinoid lignin degradation compounds), the analytes (particularly sulphide present in high concentration) and chromate used as background electrolyte. By using acetonitrile as the organic solvent in the electrolyte, a baseline resolution between sulphate and sulphide was achieved. The anion analysis was performed on-site directly after sampling by simple dilution with freshly prepared NaOH solution adjusted to pH 11.

CE found interesting applications for the anion determination in Bayer liquor, an industrial process solution used in the extraction and precipitation of alumina from bauxite [99–102]. Liquors from these processes are typically of high pH and ionic strength and contain numerous anions, such as chloride, sulphate, phosphate, fluoride, oxalate, silicate, succinate, malonate and formate. The Bayer liquor is extremely difficult to separate by IC without clean-up or pre-treatment, like dialysis [100,103]. In the first study about the application of CE to Bayer liquors [102], a single cationic surfactant was used to reverse the EOF. The main impediment appeared to be the inadequate resolution of a closely migrating cluster of anions comprising tartrate, succinate, fluoride, phosphate and formate. The simultaneous separation of inorganic and organic anions in Bayer liquors was achieved by using a binary mixture of surfactants, tetradecyltrimethylammonium bromide (TTAB) and dodecyltrimethylammonium bromide (DTAB) [99]. The separation selectivities of these electrolytes differ and the choice between them rests on consideration of the relative concentrations of the ionic composition of the samples.

In the previous industrial examples selectivity takes priority over detectability since the latter can

be easily enhanced by using a lower sample dilution. The main problem was to handle a very complex and often not homogeneous sample matrix. Nevertheless CE was also used in the control of relatively pure waste waters, such as the water from power plants [104,105] or from water purification plants [106], which needed determination at trace concentrations. In the former works [104,105] electromigration was used as the injection mode for low level anion analysis. Sodium octanesulphonate was added as an electromigrative additive to improve the trace enrichment process. EOF modifier was added to the chromate electrolyte in the hydroxide form to make the pH of the working electrolyte more alkaline. Alternatively anions and cations (alkali and alkaline-earth cations, iron, heavy metals) were analysed at trace concentrations in a water purification plant by an automated interface for coupling flow injection and CE [106]. The coupling was achieved by a laboratory-made programmable arm, which automatically filled the CE sample vials. The same system allowed the automated pre-concentration of heavy metal cations (manganese, aluminium, lead and cadmium) on a Chelex 100 minicolumn (Fig. 4). The proposed system fulfilled the legislative requirements of Organization for Economic Co-operation and Development (OECD) countries for the analysis of ions in drinking water.

ITP was used as an efficient fractionating method to separate more than 20 alkali, alkaline-earth, transition and lanthanide metal cations in a non-radioactive model solution of a nuclear fuel waste using a continuous free-flow ITP analyser [107,108]. The fractions were analysed off-line by means of proton induced X-ray emission (PIXE) spectroscopy.

Another important field of application of CE is the analysis of transition metals in rinse water and waste water from metal processing plants. Chromate was determined in a chromium plating bath using a micellar solution of TTAB [109], but the achieved detection limit (in the ppm range) was not adequate for measurements of trace concentrations. The sensitivity of the Cr(VI) detection was increased by injecting large volumes of samples under stacking conditions [110]. The speciation of chromium in samples from the galvanic industry was discussed by Timerbaev and co-workers [111,112]. The opposite charge on the two chromium ions,  $\text{Cr}^{3+}$  and  $\text{CrO}_4^{2-}$ , presents an evident problem for their determination

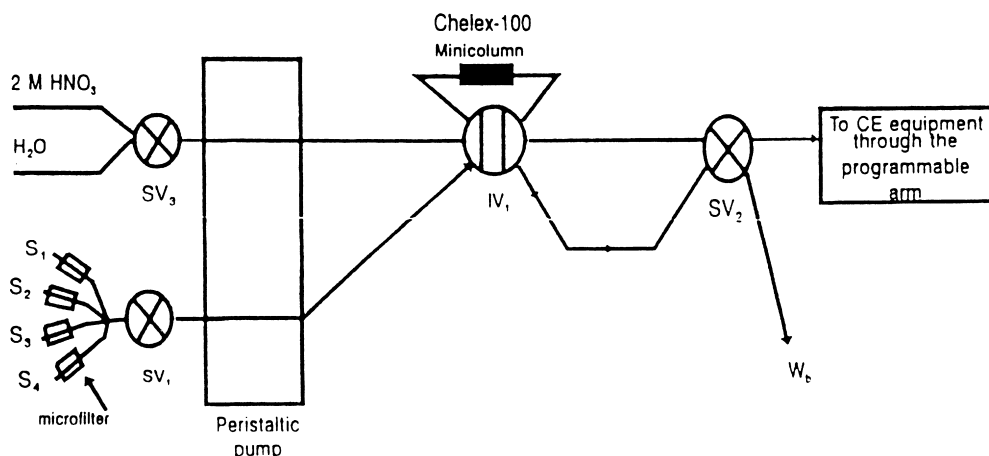


Fig. 4. Single flow injection system for sample preparation/introduction in the CE system. IV: Injection valve; SV: selecting valve; w: waste. Reprinted from Ref. [106].

in a single run by CE. The problem could be solved by converting Cr(III) into a negatively charged complex with 1,2-cyclohexanediaminetetraacetic acid (CDTA) and carrying out the separation in an acidic buffer to reduce EOF. Samples were injected after appropriate dilution (the only sample pre-treatment); transition metal ions commonly associated with chromium were found as impurities and could be quantified at lower dilution factors. CDTA was incorporated in the running buffer to prevent the in-capillary dissociation of kinetically labile transition metal complexes. The CDTA concentration was optimised to achieve the best compromise between completeness of the complexation and background signal.

The multi-elemental separation of metal chelates with aminopolycarboxylic acids [EDTA, CDTA and diethylenetriaminepentaacetic acid (DTPA)] was extensively investigated by Padaruskas and Schewdt [113]. Chromate, Cr(III), Fe(III) and Ni(II) as DTPA chelates, and simple anions such as nitrate, nitrite and molybdate, were simultaneously determined in electroplating waste waters by direct UV detection at 214 nm under coelectroosmotic separation mode. Many other metal ions such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> also form stable chelates with DTPA, but their absorbance is so low that the direct detection at the selected wavelength is not feasible.

Many different industrial processes based on cyanidation have been developed to recover pure

metal from mineral or exhausted industrial products: the process involves the leaching of the starting material with an alkaline solution of sodium or potassium cyanide. An analytical control is needed to study the dissolution and the recovery of metals and to control wastes. A new approach is to use CE that has proven to be effective in the separation and detection of some metal cyanide complexes [11,114–116]. The methods (Table 3) were generally based on the use of an EOF modifier and cyanide in the running buffer. The sensitivity was improved by using the stacking effect [114,115] or by pre-concentration on supported liquid membranes [116]. The term “supported liquid membrane” refers to an organic liquid phase that is held in the pores of a thin porous support [usually a polytetrafluoroethylene (PTFE) membrane]. This organic layer is interposed between two aqueous solutions, one of them being the sample solution and the other the acceptor solution. The enrichment process is based on a diffusive transport of the analytes across the liquid membrane from a relatively large volume of sample into a much smaller volume of acceptor solution. The same pre-concentration and separation procedure was applied to the determination of free cyanide and weakly bound cyanide (e.g., metallo-cyanides with a low stability constant), converting free and labile cyanide into the Ni(II) complex [116]. By this method cyanide species can be detected well below the limits stated for drinking water.



CE was employed for the speciation of arsenic and selenium compounds in various matrices [117–120]. The separation methods were based on the use of EOF modifier to simultaneously separate inorganic and metallorganic species. The use of conductivity detection [118] showed a slight sensitivity improvement with respect to the photometric mode, but it has a high potential for further developments. This method was applied to a contaminated water sample from a tailing of tin ore processing. The relatively low ionic strength of this water matrix and the absence of charged organic contaminants like humic acids are advantageous for conductivity detection, simplifying the signal evaluation. Limitations of the unspecific detection mode appeared in other experiments covering plant extracts, where, in spite of the high sensitivity of conductivity monitoring, extended interferences by charged organic compounds may occur.

The determination of organometallic compounds such as organolead and organoselenium was demonstrated in a waste water from a car park by using  $\beta$ -cyclodextrin-modified micellar electrokinetic capillary chromatography (MEKC) after chloroform extraction [119].

## 5. Soil and sediment samples

The application of CE to anion and cation analysis in soil was recently reviewed [122,123] (Table 4). With regard to the intents of pedologists and the usually large number of soil analyses, the advantage of this analytical technique is the minimal time and sample consumption (5 to 10 nl) per analytical run.

Arce et al. [124] developed an integrated continuous flow-capillary electrophoresis system for the real/routine analyses of soluble anions in soil samples. A hydrodynamic injection probe was used to clean-up the soil sample previously suspended in an aqueous solution. Sample extracts were then passed to the CE equipment by a programmable arm, allowing the anions to be determined in a single experiment. A wide group of inorganic anions in real soil samples was obtained in water extracts, and no interference was found. The procedure was up to four-times faster than the competitive manual methods.

Sulphate analysis in soil extracts, widely used as an indication of soil fertility, was carried out using electromigration as a pre-concentration tool [63]. Citrate was added as the internal standard since analyte enrichment rate, achieved using electromigration injection, was strongly dependent upon sample ionic strength.

CE separation of lithium, potassium, magnesium, barium, zinc, lead, lanthanum, samarium, europium and dysprosium cations was examined in the presence of polyethylene glycol (PEG) additives (0.01–10%) having relative molecular masses between 200 and 20 000 000 g mol<sup>-1</sup> [125]. These polymers, used for selectivity control in CE metal ion separation, should minimise Joule heating and solubility problems because of the absence of ionizable functional groups. Separated metal species were monitored by indirect detection using a creatinine electrolyte which does not form strong complexes with the PEGs or the metal ions. Calibration was briefly examined for sodium and magnesium in an aqueous soil extract sample and the application on real soil extract samples was limited to the separation of four metals (sodium, potassium, magnesium and calcium).

CE with ICP-MS detection was used for the separation of platinum species in soil extracts [126,127]. Many platinum compounds are potent sensitizers, even in very small doses. Estimation of the bioavailability of Pt is important since platinum is used as a catalyst material for the refinement of automobile exhaust gases. After its emission from the automobile, platinum is mainly deposited onto the road-near soil. The interaction of the respective soil with platinum is therefore decisive for further migration steps, i.e., immobilisation or formation of bioavailable species and their translocation into the foodchain. Aqueous extracts of a clay-like humic soil treated with a Pt contaminated tunnel dust were examined by CE-ICP-MS and HPLC-ICP-MS in parallel to elucidate transformation processes of Pt species in soil. High-performance liquid chromatography (HPLC) showed better detection limits than CE (25 ppt and 1 ppb, respectively), but a worse resolution power. By using the HPLC method very similar chemical species could not be distinguished, but only a fractionation based on polarity was achieved. On the contrary, electropherograms were very difficult to interpret because of the great number

Table 4  
Soil, sediment and biological samples

Compound	Sample matrix	Injection	Electrolyte buffer, separation voltage	Detection mode	Detection limits	Ref.
Organic and inorganic anions	Soil extract	Electrokinetic (3 kV for 10 s)	5 mM chromate, 0.5 mM CIA-Pack OFM Anion-BT (pH 8); 20 kV	Indirect UV 254 nm		[63]
Organic and inorganic anions	Soil extract	Hydrodynamic (25 mbar for 6 s)	5 mM chromate, 0.2 mM TTAB (pH 8.2); 30 kV	Indirect UV 275 nm	1.0–4.3 mg/l	[138]
Inorganic anions	Soil extract	FIA	2 mM chromate, 2 mM DETA (pH 7.5); 20 kV	Indirect UV 265 nm	0.1 mg/l	[124]
Metal cations	Soil extract	Electrokinetic (10 kV for 5 s), hydrodynamic	pyridine–imidazole, glycolitic acid (pH 4); 25 kV	Indirect UV 210–254 nm	0.02–208 µg/l	[139]
Metal cations	Soil extract	Electrokinetic (30 kV for 3 s)	0.01 M creatinine, 5% (v/v) PEG200 (pH 4.27); 30 kV	Indirect UV 214 nm		[125]
Platinum species	Soil extract	Stacking injection (100 mM phosphate buffer)	50 mM phosphate buffer (pH 6.0)	ICP-MS	1 µg/l (Pt)	[127]
Alkyllead, alkyltin	Soil extract	Hydrostatic (12 cm for 10 s)	SDS, phosphate buffer (pH 7.65); 15 kV	Direct UV 200 nm		[128]
Dj- and triorganotin cations	Marine sediment	Hydrostatic (15 cm for 20 s)	5 mM acetate, 3 mM 4-aminopyridine, α-cyclodextrin (pH 4.5); 300–330 V/cm	Indirect UV 261 nm	2–20 µM (Sn)	[129]
Organomercurials	Fish muscle, CRM, mussel tissue	Hydrodynamic (8.6 s)	0.1 M borate buffer (pH 8.35); 15–20 kV	Direct UV 200 nm	10 pg	[132]
Methylmercury	Fish muscle, CRM	Stacking, hydrodynamic injection (40–50 mbar for 12 s)	0.2 M borate buffer (pH 8.11); 15–30 kV	Drode array 200–400 nm	2 pg	[134,135]
Methylmercury	Fish, crab, CRM	Hydrostatic (10 cm for 30 s)	100 mM acetate, 5 mg/l dithizone sulphamate (pH 5); 25 kV	Direct UV-Vis 480 nm	2 µg/kg	[137]

of resolved species, particularly platinum–humic acid complexes. Very useful structural information would be obtained if CE were coupled with another mass spectrometry (MS) technique such as electro-spray mass spectrometry (ESI-MS).

Alkyllead and alkyltin compounds are widely used in industry and are known to be potential causes of environmental pollution. Li and Li [128] investigated the application of MEKC to the analysis of these compounds after supercritical and subcritical fluid extraction of soil samples. This method exhibited higher efficiencies than HPLC and also avoided the derivatization step necessary in gas chromatography (GC) separations. Therefore the combined subcritical fluid extraction–MEKC method is a promising technique for the extraction, separation and determination of alkyllead and alkyltin compounds in solid samples because of its simplicity, high efficiency and rapidity.

The determination of organotin compounds in sediment by CE was also investigated [129]. The five triorganotin cations were efficiently separated by CE in 10 min using 4-aminopyridine as the UV-absorbing co-ion for the indirect detection. The simultaneous separation of di- and triorganotin was achieved with the addition of  $\alpha$ -cyclodextrin as a modifier in the electrophoresis buffer. However the method was not compatible with the extraction procedure for marine sediments because the complexing agent, added during the leaching stage, degraded the background stability of the CE separation and had a negative effect on the indirect detection.

The speciation and simultaneous determination of inorganic and organic mercury in contaminated sediments from the Great Lakes were achieved when the high resolution power of CE was coupled with a very selective amperometric detection system [130,131].

## 6. Biological samples

In recent years CE demonstrated powerful capabilities for resolution and analysis of organomercurials in biological samples (Table 4). Organic mercury forms, especially the methylated forms, are considerably more toxic than the inorganic forms. Methylmercury is considered to be one of the most

dangerous chemical species in the environment because of its intrinsic toxicity and availability to living organisms. Therefore, the analytical measurement and speciation of organomercurials in environmental samples require high selectivity and very low detection limits. Medina et al. [132] developed a CE procedure for the speciation of organomercurials and the quantitative determination of methylmercury in marine samples. Cysteine was used to complex organomercurials according to the classic Westoo extraction procedure [133], a 0.1% solution of cysteine chlorhydrate allowing the complexation of all the organomercurials in the samples without impairing the peak separation. The recovery of methylmercury in real samples was about 65%, because of the matrix effects in the extraction procedure. Analytical results of real marine samples and certified reference materials, corrected for the losses in the extraction stage, were in good agreement with those obtained by GC, the commonly accepted procedure, as well as with certified reference material (CRM) values.

The complete validation of the aforementioned method for routine analysis of methylmercury in biological materials of marine origin, was carried out by Carro Diaz et al. [134]. The same authors investigated the feasibility of the stacking pre-concentration technique to improve sensitivity of this method [135]. The detection limit was lowered by a factor of 10 as compared with conventional CE injection techniques.

Jones and Hardy [136,137] used dithizone sulpho-nate in place of cysteine to separate methylmercury in the final stage of a simplified Westoo extraction procedure. The intensely absorbing methylmercury–dithizone sulpho-nate complex was then separated by CE using a coated capillary and determined by direct absorption measurement at 480 nm. Good quality performance was demonstrated by spiking experiments and analysis of DORM-1 CRM. The very stable baseline and lack of interfering peaks achieved a LOD of  $2 \mu\text{g kg}^{-1}$  for a 10 g sample.

## 7. Conclusions

The review of current literature shows that CE offers superior resolution, greater flexibility with

regard to the choice of separation conditions, and better matrix tolerance compared to HPLC, a generally accepted analytical method for inorganic ions analysis; CE can be considered a valuable alternative in determining inorganic species in relatively concentrated, complex matrices [11]. CE has also the advantage in the field of metal speciation in that there are no interactions between the analytes and the stationary phases, shifting the equilibrium between different complexing forms. The introduction of the MEKC technique widens the potential of CE to the analysis of neutral metal derivatives such as organometals [13,119,128]. The simultaneous determination of positive and negative charged species has also been demonstrated [26]. Despite all these advantages, CE application in routine analysis is hindered by the limited sensitivity for real samples and by the need for a better performance stability. For example, concerning reproducibility, the migration time dependence on the sample conductivity gives problems to the laboratories which must validate their data according to international standardised procedures. This is one of the reasons why CE has never been accepted in official methods of environmental analysis, and this fact limits its use in routine laboratories.

Advanced research in environmental sciences has not yet widely recognised the unique feature of CE techniques, i.e., the possibility to analyse very small volumes of sample, which can open new interesting research fields and can reduce the need for large volume collection. For example the development of CE methods for the analysis of individual hydro-meteors has been particularly useful in the study of atmospheric microprocesses influencing the chemistry of precipitation [35,36]. Nevertheless, according to Timerbaev [11], a real breakthrough in the environmental application is only possible after substantial gain in detection sensitivity, which can be achieved both with the introduction of more powerful detection systems and with the development of pre-concentration steps prior to CE, such as ITP, field amplification injections and in-capillary solid-phase extraction (SPE) [140].

## 8. List of abbreviations

p-AB *p*-Amminobenzoate

CDTA	1,2-Cyclohexanediaminetetraacetic acid
CE	Capillary electrophoresis
CHES	2-( <i>N</i> -Cyclohexylamino)ethanesulphonic acid
CRM	Certified reference material
CTAB	Cetyltrimethylammonium bromide
CTAOH	Cetyltrimethylammonium hydroxide
CZE	Capillary zone electrophoresis
DETA	Diethylene triamine
DHBP	1,1'-Di- <i>n</i> -heptyl-4,4'-bipyridinium
DTAB	Dodecyltrimethylammonium bromide
DTPA	Diethylenetriaminepentaacetic acid
EDTA	Ethylenediaminetetraacetic acid
EOF	Electroosmotic flow
ESI-MS	Electrospray mass spectrometry
FIA	Flow injection analysis
GC	Gas chromatography
HAc	Acetic acid
HIBA	$\alpha$ -Hydroxyisobutyric acid
HMB	Hexamethonium bromide
HMOH	Hexamethonium hydroxide
HPLC	High-performance liquid chromatography
HQS	8-Hydroxyquinoline-5-sulphonic acid
IC	Ion chromatography
ICP-MS	Inductively coupled plasma mass spectrometry
ISE	Ion selective electrode
ITP	Isotachophoresis
KHP	Potassium hydrogenphthalate
LIF	Laser induced fluorescence
LOD	Limit of detection
MEKC	Micellar electrokinetic capillary chromatography
MeOH	Methanol
MES	Morpholinoethanesulphonic acid
MS	Mass spectrometry
NH <sub>4</sub> Ac	Ammonium acetate
OECD	Organization for Economic Co-operation and Development
PDCA	Pyridin-2,6-dicarboxylic acid
PEG	Polyethylene glycol
PIXE	Proton induced X-ray emission
PMA	Pyromellitic acid
PTFE	Polytetrafluoroethylene
PVA	Poly(vinyl alcohol)
SDS	Sodium dodecyl sulphate
SPE	Solid-phase extraction
TBAB	Tetrabutylammonium bromide

TEA	Triethanolamine
TTAB	Tetradecyltrimethylammonium bromide
TTAOH	Tetradecyltrimethylammonium hydroxide
UV	Ultraviolet spectroscopy
UV-Vis	Ultraviolet-visible spectroscopy

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