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Review

Application of capillary electrophoresis to the analysis of inorganic ions in environmental samples

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Abstract

A comprehensive review is presented of the state-of-the-art of capillary electrophoresis for application to the analysis of inorganic species, mainly ions, in environmental samples. This brief review covers the developments principally in sensitivity and matrix interference for the determination of inorganic ions in the following samples: drinking, mineral, surface, and ground waters, rainwater, snow, seawater, brine and waste waters, aerosol, and others. References published mainly from 1995 to 1997 were summarized in this review. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Reviews; Environmental analysis; Water analysis; Inorganic cations; Inorganic anions

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1. Introduction

Capillary electrophoresis (CE) has several advantages over high-performance liquid chromatography (HPLC): simplicity, high efficiency, possibility of

simultaneous determination of positive, neutral, and negatively charged species, small samples, small volume of eluent, and short analysis time etc. Consequently, it is becoming more and more popular in modern analytical chemistry after the 1980s. Since the fully automatic analyzers have been commercially available from several companies around 1990,

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the range of analytes were spread out over inorganic ions, organic acids, synthetic organic compounds, and medicines as well as vital macromolecular substances [1]. Currently, CE is growing rapidly in the region of inorganic ions and often compared to ion chromatography (IC).

Several reviews on CE have already been published. Physicochemical principles, separation mechanisms, and methodological problems of CE were described, and examples of CE of inorganic cations and anions, chlorophenols, explosives, and pesticides were given by Belen'kii et al. [2]. McLaughlin et al. [3] focused on CE method development and sensitivity enhancement strategies for the separation of industrial and environmental analytes including chlorinated phenols, phenoxy acid herbicides, aromatic acids, isomerized α - and β -hop acids, nitroaromatic and nitramine compounds, acidic dyes, linear benzene alkylsulfonates, inorganic anions, and charged polymers. Method development and optimization procedures in CE were also discussed for small, mainly inorganic, ions and examples of applications were provided, e.g., anions in drinking, ground and waste waters, vegetables, urine, and pharmaceuticals, and cations in beverages, food-stuffs, and pharmaceuticals by Jimidar et al. [4]. Dietrich et al. [5] summarized various analytical techniques (including electrophoretic methods with several applications) for the determination of chemical species in natural waters, waste, and drinking waters. Timerbaev [6] named CE methodologies and underlying chemistries providing separations of potentially harmful pollutants including metal ions, metal oxoanions, metal complexes, organometallic compounds, and anionic species. The techniques of CE and IC were compared as analytical methods for the determination of inorganic anions and cations by Haddad [7]. It was shown that the two techniques were complementary rather than competitive. CE and IC were also compared for the determination of inorganic anions by Pacáková and Štulík [8]. Song et al. [9] surveyed separation strategies of capillary zone electrophoresis (CZE) and its variants with pseudostationary phases and micellar electrokinetic chromatography (MEKC) with various micelles, and other kinds of electrokinetic chromatography. Manipulating the sensitivity was also introduced in the paper. Finally, separation and analysis of environ-

mental pollutants were described: polynuclear aromatic hydrocarbons, polychlorinated biphenyls and polychlorodibenzo-*p*-dioxins, herbicides, phenols, nitroaromatic and other chemical warfare-related compounds, amines, aromatic sulfonic acids and carboxylic acids, organometallic compounds, phthalate esters, carbonyls, and dyes. The use of MEKC for the separation of metal ions, and metal-containing species such as organometallic species and stable metal complexes was reviewed by Haddad et al. [10]. Sutton et al. [11] reviewed the coupling of CE to inductively coupled plasma-mass spectrometry (ICP-MS) as the detection technique as well as other hyphenated techniques of various modes of chromatography with the ICP-MS. However, there are not very many reviews on the environmental applications of CE, especially for inorganic ions. The analysis of real samples seems to receive little attention compared to separation and detection.

This brief review covers the developments mainly concerning sensitivity and matrix interference for the determination of inorganic species, primarily ions, in the following environmental samples: drinking, mineral, surface, and ground waters, rainwater, snow, seawater, brine, and waste waters, aerosol, and others in the references published mainly from 1995 to 1997. The aim of this review is to classify the applications according to kind of environmental sample and thereby contributing further developments of CE in environmental analysis. The classification depends on the kind of main sample that is treated in each application. However, some papers also involve the applications for kinds of samples other than the main sample.

2. Drinking and mineral waters

It is important to monitor anionic and cationic species during water treatment in a purification plant [12]. CE is an attractive method for the purpose due to its advantages mentioned in Section 1. Havel et al. [13] performed the indirect determination of alkali and alkaline-earth metal ions in mineral and tap water samples using a background electrolyte containing cupric sulfate, 18-crown-6, and formic acid. They also offered a CE method for the determination of sulfate stability constant. Macka et al. [14] applied

CZE to the separation and detection of strontium(II) and barium(II) in the presence of excess levels of magnesium and calcium using an electrolyte containing sulfonazo III. The analytes were separated and detected as their anionic chelates, using direct spectrophotometric detection at 654 nm. The method was applied to the determination of strontium(II) and barium(II) in a mineral sample. A method for the separation and determination of selenium and arsenic compounds by CZE was developed by Li and Li [15]. These species should be at ultratrace levels in tap and drinking waters. Online column enrichment of selenium and arsenic was performed by stacking large volumes of sample injected on to the column with field-amplified injection techniques. Over a 100-fold preconcentration for selenium and arsenic compounds without solvent extraction and cartridge extraction has been achieved. The authors demonstrated that the CZE method eliminated the complexing or derivatization steps often required in conventional separation techniques, such as HPLC, gas chromatography, and supercritical fluid chromatography. Arce et al. [12] determined both inorganic cations and anions in drinking and mineral waters. The authors performed the determination by coupling a flow injection (FI) system with CE. The FI system was used to preconcentrate these ions. The applicability of this arrangement has been demonstrated by providing continuous control of the quality of samples in a water purification plant.

The applications for the analysis of anions in drinking and mineral waters are as follows. Kaniansky et al. [16] established a carrier electrolyte system for CE with a current conductivity detector resolving fluoride, chloride, bromide, iodide, sulfate, nitrite, and phosphate in a hydrodynamically closed separation compartment. The application potentials for various samples such as tap and drinking waters were described. The direct determination of nitrite and nitrate in tap water by CE with a buffer solution containing tetraborate and cetyltrimethylammonium chloride (CTAC) was described by Guan et al. [17]. Most researchers investigated indirect UV detection methods. Choi and Cho [18] compared the CE performance with the IC performance, and showed the quantitation of inorganic anions such as bromide, chloride, sulfate, and nitrate in various drinking waters using CE analysis with a chromate electrolyte

and indirect UV detection at 254 nm. Cationic surfactants (quaternary ammonium, phosphonium and methonium) were tested as electroosmotic flow (EOF) modifiers in a chromate-based buffer for indirect UV detection at 260 nm by François et al. [19]. They demonstrated that optimization of the electrolyte chemical composition and of some physical parameters (temperature and negative applied voltage) avoided the comigration of several anions. Oehrle [20] used CIA-Pak OFM anion BT as the EOF modifier added to the chromate electrolyte for indirect UV detection at 254 nm, and gave a negative power supply for the analysis of fluoride, chloride, sulfate, and nitrate in drinking waters. A good correlation between the results obtained by CE and IC was demonstrated. Separation and quantitation of chlorine containing anions were performed by Biesaga et al. [21]. Chloride, chlorite, chlorate and perchlorate in tap and swimming pool waters were determined by CE using a potassium phthalate eluent which has high background absorption and indirect UV detection at 254 nm. The performance of CE showed the results to be superior to the IC results.

Table 1 summarizes validation data such as limit of detection (LOD) and relative standard deviation (R.S.D.) of peak areas and migration time on the determination of inorganic ions in drinking and mineral water samples.

3. Surface and ground waters

As river and ground waters are sources of the drinking and mineral waters, it is possible to apply the methods described in Section 2 for the analysis of surface and ground waters. Papers which described the determination of cations are as follows. Wang and Li [22] developed a CE method for the separation of alkali and alkaline-earth metal ions using ethylenediaminetetraacetic acid (EDTA) as the complexing agent and pyridine as a UV chromophore for indirect detection at pH 5.0. The migration behavior of metal–EDTA complexes was investigated. This method was applied to river water samples. Sodium, potassium, magnesium, and calcium in well water were analyzed with the indirect method using an electrolyte solution containing imidazole, α -hydroxyisobutyric acid (HIBA), and

Table 1
Validation data of drinking and mineral water samples

Sample	Ion	LOD ($\mu\text{g/l}$)	R.S.D. of PA ^a (%)	R.S.D. of t_m^b (%)	Ref.
Drinking, mineral waters	Na^+ , K^+ , NH_4^+	90, 100, 150			[12]
	Mg^{2+} , Ca^{2+} , Al^{3+}	30, 80, 20			
	Mn^{2+} , Fe^{3+} , Cd^{2+}	50, 100, 10			
	Pb^{2+}	20			
	Cl^- , SO_4^{2-} , NO_2^-	70, 70, 90			
Table, tap waters	NO_3^- , HPO_4^{2-}	150, 100			[13]
	Li^+ , Na^+	0.59, 1.58 mg/l			
	K^+ , NH_4^+	1.48, 3.34 mg/l			
	Mg^{2+} , Ca^{2+}	0.96, 2.01 mg/l			
Mineral water	Sr^{2+} , Ba^{2+}	4.47, 12.92 mg/l			[14]
	Sr^{2+}	41	2.9	2.9	
Mineral water	Ba^{2+}	48	1.2	1.2	[15]
	SeO_3^{2-} , SeO_4^{2-}	12 $\mu\text{g/l}$, 202 mg/l			
Tap, drinking waters	AsO_2^- , AsO_4^{3-}	800, 25			[16]
	F^- , Cl^- , Br^- , I^-	8, 3, 6, 9			
	SO_4^{2-} , NO_2^-	4, 5			
Tap water	NO_3^- , PO_4^{3-}	3, 10			[17]
	NO_2^-	400		<0.6	
Drinking water	NO_3^-	400		<0.6	[18]
	Cl^-	300–500	18.02	0.010	
Mineral water	Br^-		24.74	0.010	[19]
	SO_4^{2-}		13.71	0.030	
	NO_3^-		6.00	0.020	
	F^- , Cl^- , ClO_3^- , SO_4^{2-} , NO_2^- , NO_3^- , PO_4^{3-} , CO_3^{2-}	2.5–50 mg/l			
Tap, pool waters	Cl^-	100	2		[21]
	ClO_2^-	200	0.6		
	ClO_3^-	200	0.4		
	ClO_4^-	600	1		

^a PA: peak area; ^b t_m : migration time.

18-crown-6 by Pantsar-Kallio and Manninen [23]. The repeatabilities of the method, linearities, and LODs were compared with those obtained by IC. Pozdniakova et al. [24] applied CZE to the simultaneous determination of iron(II) and iron(III) selectively complexed with 1,10-phenanthroline and 1,2-cyclohexanediaminetetraacetic acid (CDTA). Both dissolved iron species in ground water were determined. The method for iron(III) in river water by online coupled capillary isotachopheresis and CZE with a commercial column coupling device was proposed by Blatný et al. [25]. Iron was determined as the negatively charged complex with EDTA that was detectable directly at 254 nm. Colburn et al. [26] used CE as a screening protocol for the determination of uranyl ion complexed with arsenazo III.

They showed that the long sample plugs were injected and stacked to narrow zones, which made possible the sensitive determination of uranyl ion.

Papers which report the analysis of anions are as follows. Phosphate which was one of nutrients in lake water was analyzed by Pantsar-Kallio and Manninen [27]. The results obtained by CE with the indirect method using the chromate electrolyte was compared with a conventional colorimetric method by forming blue molybdate complex. van den Hoop and van Staden [28] also developed the CE method for phosphate in ground water, surface water, and stemflow samples. A carrier solution containing 1,2,4,5-benzenetetracarboxylic acid (pyromellitic acid, PMA) for the indirect UV detection and the EOF modifier solution containing hexane-1,6-bis-

Table 2
Validation data of surface and ground water samples

Sample	Ion	LOD ($\mu\text{g}/\text{l}$)	R.S.D. of PA ^a (%)	R.S.D. of t_m^b (%)	Ref.
River water	Mg^{2+}	75	5–9		[22]
Well water	Na^+ , K^+	200, 400			[23]
	Mg^{2+} , Ca^{2+}	100, 200			
Ground water	Fe^{2+}	60	0.8		[24]
	Fe^{3+}	100	5		
River water	Fe^{3+}	10	3		[25]
River water	UO_2^{2+}	10			[26]
Lake, river waters	PO_4^{3-}	10	3		[27]
Ground, surface, stemflow waters	PO_4^{3-}	0.45 μM			[28]
Subterranean water	NO_3^-	0.182		2.1	[29]
	SCN^-	4.785 mg/l		3.5	
Clayey water	SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$	3, 4 μM			[30]
	$\text{S}_4\text{O}_6^{2-}$, S^{2-}	4, 20 μM			
River water	O_2	20			[31]

^a PA: peak area; ^b t_m : migration time.

(trimethyl)ammonium bromide were used in the system. Nitrate and thiocyanate as petroleum tracers in subterranean waters by CE were performed by Song et al. [29]. Samples containing very high concentration of salts were determined by using 100 mM sodium chloride with CTAC as the carrier electrolyte solution. Motellier et al. [30] applied CE to the determination of sulfur species such as sulfate, thiosulfate, tetrathionate, and sulfide in a natural clayey water sampled from a drill hole. They adopted the indirect UV detection method using pyromellitate (1,2,4,5-benzenetetracarboxylate) and naphthalenesulfonate which have no oxidizing properties for sulfur species. Application of CE for the determination of dissolved oxygen in water samples was performed by Razee et al. [31]. The oxidation of pyrogallol in alkaline media by dissolved oxygen occurred during the electrophoretic run, and the reaction product was monitored at 440 nm. This approach showed the possibility of using CE for the determination of dissolved gases.

Validation data on the determination of inorganic species in river and ground water samples is summarized in Table 2.

4. Rainwater and snow

Some important characteristics of rainwater are

limited individual sample volumes and varied concentrations of components. CE can deal with very small volumes and it has been applied to the determination of inorganic ions, organic acids, metal ions in rain-, cloud-, fog-drops, snow, and rainwater. Determination of ions in individual and size-classified rain drops by CE has been performed by Bächmann and coworkers [32–36]. They trapped individual raindrops with a “Guttalgor”, mainly consists of a dewar vessel filled with liquid nitrogen. Röder and Bächmann [32] investigated the choice and concentration of electrolyte for indirect UV detection of inorganic anions and dicarboxylic acids. They described that the electrolyte system using *p*-aminobenzoate was most favorable for the analysis of those substances. They facilitated the separation of inorganic anions with the addition of barium ions. The separation of sulfate and nitrate was not possible without the addition of cations. Barium ions decreased the mobility of sulfate by forming ion pairs. Other cations (calcium, strontium, and lead) influenced the mobility of the dicarboxylic acids more than that of sulfate. Tenberken and coworkers [33,34] presented microanalytical investigations for the analysis of single and size-classified rain-, cloud-, and fog-drops by CE. They developed special sampling procedures and methods to store and to handle single rain- and fog-drops. Three techniques were described to ascertain the volume of single rain-

drops. The analysis of cations was performed by indirect UV detection with 4-N-methylaminophenol. For the analysis of organic and inorganic anions, *p*-aminobenzoate was used. The new electrolyte system for the analysis of organic acids and inorganic anions was reported by Mainka et al. [35]. They used the mixture of tris(hydroxymethyl)aminomethane (Tris), dodecyltrimethylammonium hydroxide (DoTAH), calcium, and barium ions as the electrolyte. Tris was used for buffering and its very low conductivity avoided the occurrence of disturbing Joule heating effects. DoTAH was used as the EOF modifier. The addition of calcium and barium ions affected the mobility of sulfate and dicarboxylic acids because of the formation of barely soluble substances. The best resolution was obtained adding 15 mM Tris and 400 μ M DoTAH. Tenberken and Bächmann [36] used hexadimethrine bromide instead of DoTAH as the EOF modifier. It was possible to separate chloride, sulfate, nitrate, and organic acids in a single run within 5 min.

Wen and Cassidy [37] determined electroactive metal ions, such as Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Cd(II), Hg(II), Tl(I), Pb(II) in snow samples with cathodic and anodic pulse amperometric detection by CE. HIBA and creatinine were used as the operating electrolyte. The detection methods were compared with atomic absorption spectrometry (AAS). On the determination of Cd(II) and Pb(II) in spiked samples and the determination of Zn in snow by standard addition calibration, the results showed good agreement among the three procedures. They studied sample stacking to enhance the detection of the metal ions. The LODs were more than tenfold smaller than those for nonstacking analysis.

Nguyen et al. [38] applied CE to the determination of fluoride, chloride, sulfate, nitrite, nitrate, and phosphate in rainwater samples. They used dichromate for indirect UV detection at 265 nm. Diethylenetriamine was used as the EOF modifier. They used direct injection of samples without addition of buffer. It led to a significant increase of sensitivity due to the solvent stacking. Using chlorate as the internal standard, linear calibration curves were obtained with an accuracy of better than 10%. Comparison of CE with IC and ion-selective electrode potentiometry for the analysis of fluoride in

rainwater was performed by van den Hoop et al. [39]. Hexane-1,6-bis(trimethyl)ammonium bromide was used for the preparation of an EOF modifier solution and ionic bromide was removed by using an OnGuard-A cartridge (Dionex). For the indirect UV detection, PMA was used. Fluoride concentrations in Dutch rainwater samples were determined by the three techniques. LODs were found to be somewhat higher for CE than for the other methods. The fluoride concentrations obtained by IC were significantly higher. They considered that the observed differences were most likely due to the presence of aluminum cations. Valsecchi et al. [40] developed a routine method for the determination of chloride, sulfate, and nitrate in rainwater by CE using an end-column nonsuppressed conductivity detector. The capillary was conditioned with a cetyltrimethylammonium bromide (CTAB) solution before each analysis in order to reverse the EOF. The running buffer was composed of 2-(*N*-cyclohexylamino)ethanesulfonic acid (CHES), lithium hydroxide, and Triton X-100. CHES and lithium hydroxide contributed to adjust the ionic strength and pH of the buffer solution. Triton X-100 decreased the surface tension of the coated layer with the modifier. The analytical parameters showed that the method could be applied to the monitoring of wet depositions. Determination of iron in rainwater by CE after precolumn complexation with 1,10-phenanthroline was performed by Xu and Ma [41]. Thioglycolic acid was added to the samples as a reductant of Fe(III) to Fe(II). They tested different buffer systems for the separation of the complex and the reagent. The optimum condition was pH 5 for the ammonium acetate–acetic acid buffer system. The absorbance of the complex was measured at 270 nm. The range of linear regression equation, LOD, and recovery of iron by the method were investigated. They concluded that the method could be quantitatively used for the determination of iron levels in natural waters.

Table 3 summarizes validation data on the determination of inorganic ions in rainwater and snow samples.

5. Seawater and brine water

There are not very many papers on the application

Table 3
Validation data of rainwater and snow samples

Sample	Ion	LOD (μM)	R.S.D. of PA ^a (%)	R.S.D. of t_m^b (%)	Ref.
Rain-drops	Cl ⁻ , SO ₄ ²⁻ , NO ₂ ⁻ , NO ₃ ⁻	30–40 nM			[32]
Rain-, cloud-, fog-drops	Na ⁺ , K ⁺ , NH ₄ ⁺ , Mg ²⁺ , Ca ²⁺ , Zn ²⁺ , Cl ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , SO ₃ ²⁻ , SO ₄ ²⁻	fmol range			[33]
Rain-drops	Na ⁺ , K ⁺ , NH ₄ ⁺ , Mg ²⁺ , Ca ²⁺ , Zn ²⁺	40–80 fmol			[34]
Rain-drops	Cl ⁻ , NO ₃ ⁻	0.330			[35]
	SO ₄ ²⁻	0.200			
Rain-, cloud-, fog-drops	Cl ⁻	70 fmol	4–9	0.61–0.87	[36]
	SO ₄ ²⁻	43 fmol			
	NO ₃ ⁻	69 fmol			
Snow	(Cathodic, nonstacking)				[37]
	Co(II), Ni(II), Zn(II), Tl(I), Pb(II)	2–3			
	Cd(II), Hg(II)	5–7			
	Ag(I), Cu(II)	11, 20			
	(Anodic, nonstacking)				
	Zn(II), Cd(II), Tl(I), Pb(II)	0.2–0.5			
	Co(II), Ni(II)	0.6–1.0			
	(Cathodic, with stacking)				
	Tl(I), Pb(II), Cd(II)	0.07, 0.1, 0.05			
	(Anodic, with stacking)				
	Tl(I), Pb(II), Cd(II)	0.05, 0.04, 0.01			
Rainwater	Cl ⁻ , SO ₄ ²⁻ , NO ₂ ⁻ , NO ₃ ⁻ , F ⁻ , PO ₄ ³⁻	4.8–19.8	12	4–5	[38]
Rainwater	F ⁻	0.6		0.8	[39]
Rainwater	Cl ⁻ , SO ₄ ²⁻	2 $\mu g/l$	1.7–5.1	3.1–3.3	[40]
	NO ₃ ⁻	3 $\mu g/l$			
Rainwater, lake, tap, waters	Total Fe	5 nM			[41]

^a PA: peak area; ^b t_m : migration time.

of CE to seawater analysis in comparison with the number of papers on other applications. The main reason for the lack of applications is the difficulty in eliminating the interference of high concentrations of matrix ions such as chloride, sulfate, sodium ions etc. in seawater. In order to eliminate the interference of the salts, Fukushi and Hiroyuki [42] used the complexation of magnesium and calcium ions with EDTA and injected 100-fold diluted seawater samples for the CZE determination of these ions in seawater. The effect of sodium chloride concentration in the sample solutions was examined. The proposed method was applied to the determination of magnesium and calcium ions in surface and bottom seawater samples. The results obtained by the stan-

dard addition method agreed closely with those obtained by the calibration graph method. The analysis time was less than 6 min. Tangen et al. [43] developed an indirect UV detection method for the determination of sodium, potassium, magnesium, and calcium ions in mixtures of seawater and formation water from oil wells to monitor the composition of the production water in situ. The migration order of the elements was changed by use of the carrier electrolyte containing methanol, 18-crown-6, and HIBA to solve the problem caused by the large excess of sodium and calcium ions in the samples. The samples were diluted by a factor of 100–1000 prior to analysis. The results of real samples obtained by the proposed method agreed well with those

obtained by ICP-atomic emission spectrometry (ICP-AES). A quaternary amine-coated capillary was used to reverse the EOF to prolong the residence time in the electric field for the separation of major cations in seawater by Schnierle and Hauser [44]. It was possible to completely remove the overlap of sodium and magnesium peaks at the higher concentrations of sodium ion. Four inorganic cations, potassium, sodium, calcium, and magnesium ions, in 100-fold diluted seawater were baseline-separated although the analysis time was somewhat prolonged. In order to evaluate the effectiveness of the quaternary amine-coated capillary precisely, the electrolyte composition in the coated capillary should be the same as that in an uncoated fused-silica capillary. Fukushi et al. [45] also proposed a tenfold diluted artificial seawater as the electrolyte to prevent interference from high concentrations of chloride ions for the determination of bromide ion in seawater. It was found that the peak area and migration time for bromide ion were almost constant, despite differences in the salinity of sample solutions. The method was also applied to the determination of bromide ion in coastal seawater samples. It is applicable to the determination of other ions, such as nitrite and nitrate ions in seawater, by improving the detection power and the resolution between nitrite and nitrate ions.

Salimi-Moosavi and Cassidy [46] showed that the direction and magnitude of EOF could be changed by using nonaqueous solvents (methanol–acetonitrile mixtures) and different kinds of electrolyte anions (chloride, perchlorate, and acetate). A unique separation selectivity for alkali, alkaline-earth, and ammonium ions was obtained. To evaluate the proposed system, it was applied to the separation of metal ions

in a brine solution sample containing sodium, potassium, calcium, and magnesium ions. All four metal ions contained in the sample were well resolved and the higher concentration of sodium and potassium ions (~100-times) did not interfere in the separation.

Matrix effects in CZE with several electrolytes and matrix ions were investigated by Boden and Bächmann [47]. They showed that analyte ions in the presence of a matrix ion could be determined by creating an isotachophoretic process in the initial state of a CZE separation without any modification of the CZE apparatus. The procedure seems to be very attractive for the application of CZE to seawater and brine water analyses. It may be useful for the determination of low concentrations of ions in these waters by adopting an electrolyte with suitable mobility and/or molar absorptivity and by adding matrix ions with suitable mobility to samples.

Validation data on the determination of inorganic ions in seawater and brine water samples is summarized in Table 4.

6. Waste water

It is important to monitor various pollutants in waste waters from the standpoint of environmental conservation. Tian and Schwedt [48] described the quantitative determination of chromate in leather-waste and -sludge by CE as well as ion pair chromatography and ion-exchange chromatography. Chromate migrated in the opposite direction to the EOF and was directly detected at 270 nm. The analytical results indicated that there were no differences evident among the three methods. A procedure for the simultaneous determination of Cr(III),

Table 4
Validation data of seawater and brine water samples

Sample	Ion	LOD ($\mu\text{g}/\text{l}$)	R.S.D. of PA ^a (%)	R.S.D. of t_m^b (%)	Ref.
Seawater	Mg ²⁺	130	0.8	0.1	[42]
	Ca ²⁺	260	1.2	0.1	
Seawater	Na ⁺ , K ⁺	140, 150			[43]
	Mg ²⁺ , Ca ²⁺	80, 80			
Seawater	Br ⁻	460	1.4	1.5	[45]
Brine water	Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺	7–20 μM		1	[46]

^a PA: peak area; ^b t_m : migration time.

Fe(III), Cu(II), and Pb(II) was developed by Baraj et al. [49]. These metals formed complexes with EDTA prior to the CZE analysis. Sample solutions were boiled for 10 min to accelerate the reaction of Cr–EDTA complexation. Waste waters from a tanning process were analyzed and only Cr(III) was found. Similarly Timerbaev et al. [50] developed a CE method for the simultaneous determination of Cr(III) and Cr(VI) using CDTA as the chelating agent instead of EDTA. Sample solutions were heated for 5 min on a water bath (70°C) to accelerate the formation of the Cr–CDTA complex. No EOF modifier was used in their work although it was usually used in anion analysis. The procedure was applied to the determination of both chromium species in industrial electroplating samples. The total chromium as determined by the proposed procedure agreed well with the values found by AAS. The mean recoveries of chromium ions in spiked samples were 99.4 and 98.9% for Cr(III) and Cr(VI), respectively. Padarauskas and Schwedt [51] also applied CZE to the separation of Co(III), Bi(III), Fe(III), Cr(III), V(IV), Pb(II), Hg(II), Co(II), Cu(II), and Ni(II) metal ions complexed with diethylenetriaminepentaacetic acid (DTPA). Better resolution was achieved using counterelectroosmotic conditions with 5 mM DTPA electrolyte at pH 8.5 and direct UV detection at 214 nm, but the resolution of Co(II), Cu(II), and Ni(II) chelates was poor. In order to evaluate the quantitative performance of the method, samples of alloyed Fe–Cr–Ni electroplating bath solution and waste water from an electroplating plant were analyzed using counterelectroosmotic and coelectroosmotic conditions, respectively. The CZE results were in a good agreement with those obtained by AAS and the spectrophotometric method. The rapid speciation of Fe–EDTA complex and free EDTA in the waste water from a photo-laboratory was also demonstrated using the coelectroosmotic condition.

Oehrle [52] performed the analysis of an inorganic anion and organic acids, and inorganic cations in nickel-plating baths by direct and indirect UV detection, respectively using different kinds of electrolytes. Chloride, citric acid, acetic acid, sodium, ammonium, and nickel in plating solutions prior to and after being used were determined. Schlegel et al. [53] applied CE to the separation of different inor-

ganic and organic arsenic and selenium compounds using two different detection systems, direct UV detection and conductivity detection. Monitoring the conductivity was suitable for direct detection of many ionic compounds in CE which were not UV-active. The LODs with conductivity detection were in the same range, slightly better in comparison with the direct UV detection as shown in Table 5. In a preliminary study presumably contaminated water samples of a tailing of tin ore processing were analyzed by the established method. Besides a number of yet unidentified peaks, only As(V) could be recognized and quantified by the standard addition technique. CE was investigated for the determination of sulfide in effluents and waste water samples from the leather industry by Font et al. [54]. Chloride and sulfate, which may exceed the concentration of sulfide by a factor of 500 in these samples, did not interfere with sulfide detection with direct UV detection at 229 nm. The LOD resulted in a fivefold improvement in sensitivity when compared to the chromate electrolyte. The R.S.D.s of the peak area and migration time for sulfide significantly improved by using molybdate as the internal standard. Real samples were analyzed by the CE, colorimetric, and iodometric methods. Spiking of the real samples gave recoveries between 102 and 111%. It was concluded that the CE method appeared to be an excellent alternative to classical procedures for determining sulfide in samples containing interfering substances that might give inaccurate or false negative results, by the iodometric and colorimetric methods. Masselter et al. [55] demonstrated the applicability of CE to the determination of various sulfur containing anions (sulfate, sulfite, sulfide, and thiosulfate) and other inorganic anions (hydroxide, chloride, oxalate, and carbonate) in Kraft pulping process liquors. A cationic polymer, 1,5-dimethyl-1,5-diazaundecamethylene polymethobromide (polybrene), was added to the chromate electrolyte (pH 11) as the EOF modifier to ensure short separation times. Acetonitrile was also used as the organic modifier to improve the selectivity of the anionic analytes. Simultaneous separation and detection of all species of interest was possible with indirect UV detection at 185 nm.

A CE method was developed to determine metal–cyano complexes from leaching solutions of au-

Table 5
Validation data of waste water samples

Sample	Ion	LOD ($\mu\text{g/l}$)	R.S.D. of PA ^a (%)	R.S.D. of t_m^b (%)	Ref.
Waste water	CrO_4^{2-}	500			[48]
Waste water	Cr(III), Fe(III) Cu(II), Pb(II)	16, 6.4 μM 15, 27 μM	<6	<1	[49]
Waste water	Cr(III) Cr(VI)	50 10	1.3 1.0		[50]
Waste water	V(IV), Cr(III), Fe(III), Co(II), Co(III), Ni(II), Cu(II), Hg(II), Pb(II), Bi(III)	2–8 μM	<5	<1.0	[51]
Waste water		(UV detection)			[53]
	As(III), As(V)	90, 60			
	DMA ^c , Se(IV)	120, 40			
		(Conductivity detection)			
	As(III), As(V)	76, 40			
	AsF ₆ (V), DMA ^c	45, 70			
	Se(IV), Se(VI)	85, 65			
Waste water	S ²⁻	41	0.7	0.04	[54]
Waste water	Metal–cyano complexes				[56]
	Fe(II), Ni(II), Cu(I)	10, 60, 11			
	Pd(II), Pt(II)	53, 18			

^a PA: peak area; ^b t_m : migration time; ^c DMA: dimethylarsinate.

tomobile catalytic converters by Aguilar et al. [56]. Fe(II)–, Cu(I)–, Ni(II)–, Pd(II)–, and Pt(II)–cyano complexes could be separated by adding tetrabutylammonium bromide and sodium cyanide to the buffer solution and detected with direct detection at 208 nm, but the Rh(III)–cyano complex could not be detected. LODs were obtained as a function of matrices and injection time. The lowest LOD for each metal–cyano complex is shown in Table 5. Both results by the CE method and ICP-AES for leaching solutions were almost similar.

Table 5 summarizes validation data for waste water samples.

7. Aerosol

The study of the chemical composition of aerosol particles in the atmosphere is of interest for understanding many atmospheric processes like cloud formation and solar and terrestrial solar radiation transfer [57]. Further, measurements of inorganic anions such as sulfate and nitrate in atmospheric aerosols provide information connected to acid rain

[58]. In addition, health effects of aerosols under polluted conditions are also influenced by particle composition [57]. Dabek-Zlotorzynska et al. [58] compared the CZE with the reverse-polarity mode and indirect UV detection using a pyromellitate-based electrolyte, IC, and photometric techniques for the analysis of sulfate and nitrate in high-volume sampled atmospheric aerosols. The comparative evaluation included response stability of instruments, LODs, accuracy, precision, analysis time, and other operational considerations. They concluded that CE could be applied very advantageously in a routine determination of sulfate, nitrate, and other anions in atmospheric aerosols. The long-term reliability of the above CE system was checked for chloride, sulfate, nitrite, and oxalate in the atmospheric aerosols over an 8-month period by Dabek-Zlotorzynska et al. [59]. The results showed the acceptable analytical performance of the CE system in the routine analysis of the major ions in atmospheric aerosols. The measurements from the CE and IC methods were in very good agreement at higher concentrations, but in poorer agreement for more diluted solutions.

Dabek-Zlotorzynska and Dlouhy [60] have dem-

onstrated the feasibility of using CE with a new electrolyte system for the analysis of alkali metal, alkaline-earth metal cations, and ammonium in atmospheric aerosols. 1,1'-Di-*n*-heptyl-4,4'-bipyridinium hydroxide was used as the UV-absorbing species, while glycine, 18-crown-6 ether, and methanol were employed to improve the separation. The CE results agreed quite well with the IC results, although the calcium IC concentrations were significantly larger than the calcium CE concentrations. CE was applied to the determination of mainly inorganic anions and cations in atmospheric aerosol samples to study the size distribution of the ions, the composition of particles, and correlations between concentrations and light scattering coefficient by Mihályi et al. [57]. Krivácsy et al. [61] also investigated not only the total concentrations of the inorganic ions and organic acids but also their size distributions in the aerosol samples. They carried out optimization of the composition of the background electrolytes, comparison of constant voltage and constant current separation modes, selection of the best wavelengths, and investigation of the matrix effect of inorganic anions on the separation of organic acids.

Validation data on the determination of inorganic ions in aerosol samples is summarized in Table 6.

Table 6
Validation data of aerosol samples

Sample	Ion	LOD ($\mu\text{g}/\text{l}$)	R.S.D. of PA ^a (%)	R.S.D. of t_m^b (%)	Ref.
Aerosol	Na ⁺ , K ⁺ , NH ₄ ⁺	132, 239, 152			[57]
	Mg ²⁺ , Ca ²⁺ , Cl ⁻	95.1, 211, 73.2			
	SO ₄ ²⁻ , NO ₃ ⁻ , PO ₄ ³⁻	101, 149, 202			
Aerosol	NO ₃ ⁻	35	3.33	2.65	[58]
	SO ₄ ²⁻	154	4.20	2.46	
Aerosol	Li ⁺	9	2.65	0.11	[60]
	Na ⁺	46	4.67	0.12	
	K ⁺	47	4.28	0.12	
	NH ₄ ⁺	42	1.92	0.13	
	Mg ²⁺	18	1.87	0.11	
	Ca ²⁺	42	2.81	0.12	
	Si ²⁺	38	3.64	0.11	
	Ba ²⁺	57	2.61	0.11	
	Mn ²⁺	39	3.17	0.18	
Aerosol	Na ⁺ , K ⁺ , NH ₄ ⁺	32, 74, 67	0.9–1.9	0.2–0.4	[61]
	Mg ²⁺ , Ca ²⁺	25, 30			
	Cl ⁻ , SO ₄ ²⁻ , NO ₃ ⁻	33, 48, 90			

^a PA: peak area; ^b t_m : migration time.

8. Other samples

CE has also been applied to other samples, e.g., thermal water, soil, and commercial detergent samples of environmental concern. The separation of selenite, selenate, selenocystine, and selenomethionine was achieved in a chromate buffer with trimethyltetradecylammonium hydroxide as an EOF modifier by Gilon and Potin-Gautier [62]. Selenate was determined as the only detectable source of selenium in a commercially available thermal water sample. The CE result was in good agreement with that of the differential-pulse cathodic stripping voltametric determination. They described the lack of selectivity, and sensitivity of the UV detector was a limit to its application to biological materials and other complex matrices.

The presence of metal ions of an aqueous soil sample extract, sodium, potassium, magnesium, calcium, is important since they play an important role not only as nutrients but also as catalysts in photosynthetic and other biological processes [63]. Howald et al. [64] determined sodium, potassium, ammonium, magnesium, calcium, manganese, and ferric ions in soil extracts using creatinine as the UV-absorbing background electrolyte. However, insufficient separation of magnesium and manganese,

and broad peak of ferric ion were obtained. They also determined chloride, sulfate, and nitrate in the soil extracts using chromate as the UV-absorbing background electrolyte and tetradecyldimethylammonium bromide as the EOF modifier. The separation of sulfate and nitrate (the concentration of which was ninefold higher than that of sulfate) was not sufficient. The effects of polyethylene glycols were examined in terms of electroosmotic mobility and electrophoretic mobilities of several metal ions with different charges and complexation properties by Stathakis and Cassidy [63]. The method was applied to the separation of sodium, potassium, ammonium, magnesium, and calcium ions in an aqueous soil extract and a fermentation broth sample. Michalke and coworkers [65,66] used online interfacing of CE with ICP-MS for the separation of Pt species such as PtCl_6^{2-} and PtCl_4^{2-} in aqueous extracts from Pt-treated soils and tunnel dust. The online CE-ICP-MS combination fulfils the requirement for low LOD ($\sim 1 \mu\text{g/l}$) which is necessary when dealing with environmental samples.

The separation and determination of builders in a formulated detergent are necessary not only for production monitoring and product quality control to guarantee cleaning effectiveness, but also for environmental protection [67]. Wang and Li [67] developed a CE method for the separation of polyphosphates and polycarboxylic acids which were used as builders in detergents. A carrier electrolyte

consisting of adenosine 5'-triphosphate as the UV chromophore for indirect detection at 260 nm and CTAB as the modifier to reverse the EOF was used. The changes in the effective mobilities of some solutes and common UV chromophores with pH were either predicted theoretically or determined experimentally. The method was applied to the determination of orthophosphate, pyrophosphate, and triphosphate in a commercial detergent.

Table 7 summarizes validation data for other samples such as thermal water, soil, fermentation broth, and detergent samples.

9. Conclusions

CE applications to inorganic species, mainly ions, in environmental samples were briefly reviewed from the standpoint of developments in sensitivity and matrix interference. As shown here, various procedures have been proposed for improving sensitivity and eliminating matrix interference. Consequently, CE has been widely used for the determination of inorganic ions in environmental samples. However, further studies on the sensitivity enhancement and the elimination of matrix interference are desirable for the wide recognition of CE as the analytical method for environmental monitoring. It is concluded that hyphenated techniques using CE with sensitive and element-selective detection techniques

Table 7
Validation data of other samples

Sample	Ion	LOD ($\mu\text{g/l}$)	R.S.D. of PA ^a (%)	R.S.D. of t_m^b (%)	Ref.
Thermal water	Se(IV)	5.7	3.0	3.7	[62]
	Se(VI)	16.4	1.8	3.2	
	Selenocystine	360		4.9	
	Selenomethionine	353		6.5	
Soil, fermentation broth	Na^+ , K^+ , NH_4^+ , Mg^{2+} , Ca^{2+}		0.2–9.2	0.46–0.64	[63]
Soil	PtCl_6^{2-}	~ 1			[65]
Soil	PtCl_6^{2-} , PtCl_4^{2-}	~ 1			[66]
Detergent	Orthophosphate	25 μM	5.6	1.4	[67]
	Pyrophosphate	20 μM	5.9	1.0	
	Triphosphate	50 μM	3.2	0.96	

^a PA: peak area; ^b t_m : migration time.

and preconcentration procedures appropriate to CE will be further developed in the near future.

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