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## Review

# Capillary electrophoresis of inorganic anions<sup>1</sup>

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### Abstract

This review deals with the separation mechanisms applied to the separation of inorganic anions by capillary electrophoresis (CE) techniques. It covers various CE techniques that are suitable for the separation and/or determination of inorganic anions in various matrices, including capillary zone electrophoresis, micellar electrokinetic chromatography, electrochromatography and capillary isotachopheresis. Detection and sample preparation techniques used in CE separations are also reviewed. An extensive part of this review deals with applications of CE techniques in various fields (environmental, food and plant materials, biological and biomedical, technical materials and industrial processes). Attention is paid to speciations of anions of arsenic, selenium, chromium, phosphorus, sulfur and halogen elements by CE. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Reviews; Isotachopheresis; Water analysis; Environmental analysis; Sample handling; Food analysis; Vegetables; Cosmetics; Soil; Pharmaceutical analysis; Inorganic anions

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<sup>1</sup>Dedicated to the memory of Professor Samo Stankoviánsky on occasion of his 90th birthday.

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## 1. Introduction

The first works dealing with the use of capillary electrophoresis (CE) techniques for the separation and/or analysis of inorganic anions were published more than 20 years ago (for a review see, e.g., [1]). In these works, capillary isotachopheresis (ITP) was the preferred CE technique and, in fact, in the first paper dealing with the separation of inorganic anions by capillary zone electrophoresis (CZE) [2], ITP instrumentation was used. The increase in interest in the use of CE techniques for the separation of inorganic anions in the 1990s is probably linked to the early works by Jones and co-workers [3–7]. At present, CE techniques are gaining general acceptance and are included in analytical guidebooks dealing with the determination of (inorganic) anions (see, e.g., [8]).

In this review (dealing primarily with works published in the 1990s and only, exceptionally, some earlier works), we provide a survey of various aspects of the CE separation and/or determination of inorganic anions. Following the concept of electrophoretic mobility of ions [9], we classify the separation mechanisms applied to the CE separation of

these anions. Although co-electroosmotic CZE is used mostly in the separation of inorganic anions, other CE techniques are also included in this review as, in many situations, they offer alternatives that should be considered by the analysts. Advances in the detection and sample preparation techniques are seen from many papers and, therefore, we paid special attention to these topics. Application works clearly outline fields in which CE techniques may expect wider use but also show their limitations in the light of real-life problems.

At present, ion chromatography (IC) has a dominant position in analytical laboratories involved in the separation and/or determination of inorganic anions present in various matrices. Therefore, CE techniques may become competitive in the area of inorganic analysis only when they offer carefully evaluated advantages. This may be a very complex task, as is apparent from recent reviews comparing CZE and IC [10,11].

Recently, several review articles dealing with the CE separation and speciation of metal cations [12,13] and environmental applications of CE [14,15] appeared in the literature. Therefore, these are suggested as suitable references on some topics

discussed in this review, in limited extents (e.g., oxoanions of metals).

## 2. Separation mechanisms in the CE of inorganic anions

With the exception of isoelectric focusing, differences in the effective mobilities of ionic constituents are essential for their separation by CE techniques. The effective mobility of an ionic constituent A ( $\bar{m}_A$ ) is defined as follows [9]:

$$\bar{m}_A = \sum_i \alpha_{A,i} \cdot \gamma_{A,i} \cdot m_{A,i,0} \quad (1)$$

where  $m_{A,i,0}$  is the absolute (limit) mobility of its  $i$ -th ionic form. Under actual separating conditions, it is necessary to take into account inter-ionic interactions in which the ionic form is involved. Therefore, it is convenient to define its actual (ionic) mobility ( $m_{A,i}$ ):

$$m_{A,i} = \gamma_{A,i} \cdot m_{A,i,0} \quad (2)$$

where  $\gamma_{A,i}$  is a coefficient representing a contribution of the inter-ionic interactions (ionic strength effect).  $\alpha_{A,i}$  is a molar ratio (distribution coefficient) characterizing a relative contribution of the  $i$ -th ionic form to the effective mobility of the constituent (A) under given separating conditions.

An electrophoretic (separative) transport of the separated constituents in CE can be accompanied by electroosmotic transport of the solution in which the separation is performed. Depending on the working conditions, the directions of the electroosmotic and electrophoretic transport may either be identical or opposite. To include electroosmotic transport, it is practical to define the apparent mobility of the constituent ( $m_{A,app}$ ):

$$m_{A,app} = \bar{m}_A + m_{EO} \quad (3)$$

where  $m_{EO}$  is the electroosmotic mobility.

### 2.1. Separations based on differences in the actual ionic mobilities

When the pH of the electrolyte system used for the CE separation is such that a given sample constituent is present only in one ionic form, then, from Eq. (1),

it is clear that its effective mobility is identical to the actual mobility of the ionic form in which the constituent exists. From the pK values of inorganic acids (Table 1) and from the pH values of the preferred electrolyte systems (Tables 4 and 5), we can see that this is a current situation in the CZE separation of inorganic anions and the separations due, mainly, to differences in the actual ionic mobilities of the dominant anionic forms are widely used.

Inter-ionic interactions of the dominant anionic forms of the analytes and, consequently, their actual mobilities (see Eq. (2)) can be influenced to some extent by the composition of the electrolyte systems in which the CZE separations are performed. This can be achieved in the following ways: (i) via a change of the concentration of the carrier electrolyte solution (a concentration-induced change in the ionic strength); (ii) via the use of the counter-ion of a proper charge number (a charge number-induced change in the ionic strength). Both alternatives were effective in the CZE separation of inorganic anions. For example, different migration orders of chloride, nitrate, nitrite and sulfate [5,16–18] can apparently be ascribed to differences in their actual mobilities due to different concentrations of chromate in the carrier electrolyte solutions (different ionic strength effects of the carrier electrolytes). The charge number of the counter-ion introduces analogous effects, with a less significant change of the ionic strength [19–21]. In this respect, it is necessary to note that some electroosmotic flow (EOF) modifiers [diethylenetriamine (DETA) and other multiply charged amines] act in this way in CZE separation a priori (see also Table 4).

From the works quoted, it is apparent that differences in the actual mobilities of the anionic forms can be influenced easily by ionic strength effects when these differ in their charge numbers. On the other hand, these effects may play marginal roles for the anionic forms of identical charge numbers (unless a selective ion association is involved).

### 2.2. Separations according to pK values

The pK values of inorganic acids (Table 1) show that the effective mobilities of some inorganic constituents depend on the pH at which the separation is

Table 1  
pK values, absolute ionic mobilities, and UV absorptivities of selected inorganic acids<sup>a</sup>

Acid	Formula	Step*	pK values	Mobility*	UV absorptivity*
Arsenic	H <sub>3</sub> AsO <sub>4</sub>	1	2.25 (2.18–2.25)	35.2	
		2	6.77 (6.77–6.96)	70	
		3	11.53 (11.23–11.60)		
Arsenious	H <sub>3</sub> AsO <sub>3</sub>	1	9.24 (9.13–9.40)		9500 (200 nm)
		2	13.52		5000 (210 nm)
		3			
Boric	H <sub>3</sub> BO <sub>3</sub>	1	9.14 (8.88–9.24)		
		2	12.74 (11.75–12.75)		
		3	13.8		
Bromic	HBrO <sub>3</sub>	1	–2	57.8 (50.8–58)	2000 (200 nm) 1100 (210 nm)
Carbonic	H <sub>2</sub> CO <sub>3</sub>	1	6.35 (6.16–6.38)	46.1	
		2	10.33 (10–10.38)	71.8 (62.2–76.7)	
Chloric	HClO <sub>3</sub>	1	–2.7	66.3 (56.9–67)	
Chlorous	HClO <sub>2</sub>	1	1.97 (1.95–2.31)	53.9	
Chromic	H <sub>2</sub> CrO <sub>4</sub>	1	0.75 (–0.2–0.98)	59.3	3600 (273 nm)
		2	6.50 (6.09–6.51)	74.6 (74–88.1)	4700 (372 nm)
Cyanic	HCNO	1	3.66 (3.47–3.66)	67 (56.8–67)	
Dichromic	H <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	1	0.75	47 (58.9)	
		2	1.64 (1.53–6.72)	82.1	
Dithionic	H <sub>2</sub> S <sub>2</sub> O <sub>6</sub>	1	0.2	48.2	
		2	3.4	96.4	
Dithionous	H <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	1	0.3	34.5	
		2	2.5 (2.46)	68.9	
Hydrobromic	HBr	1	–2	81.3 (65.5–81.3)	8900 (200 nm) 1900 (210 nm)
Hydrochloric	HCl	1	–2	79.1 (67.8–79.3)	
Hydrocyanic	HCN	1	9.31 (9.01–9.4)	80.8 (80.9)	
Hydrofluoric	HF	1	3.17 (2.40–3.45)	48.5 (47.9–57.4)	
		2	0.5 (0.59)	77.7	
Hydroiodic	HI	1	–2	79.7 (68.3–79.7)	12 100 (226 nm)
Hydrogen azide	HN <sub>3</sub>	1	4.72 (4.45–4.77)	72 (70.5–72)	6000 (200 nm) 1700 (210 nm)
		2			
Hexafluorophosphic	HPF <sub>6</sub>	1	0	59	
Hydrogen sulfide	H <sub>2</sub> S	1	7.04 (6.06–7.1)	67.4 (59.1)	8000 (230 nm)
		2	11.96 (11.44–14.7)		
Hypochlorous	HClO	1	7.53 (7.25–7.53)		
Hypophosphorous	H <sub>3</sub> PO <sub>2</sub>	1	1.23 (1–1.23)	45.2	
Iodic	HIO <sub>3</sub>	1	0.77 (0.72–0.85)	42 (35–43)	17 000 (200 nm) 3900 (210 nm)
		2			
Molybdenic	H <sub>2</sub> MoO <sub>4</sub>	1	2.54		10 000 (207 nm)
		2	3.86	77.2	5100 (227 nm)
Nitric	HNO <sub>3</sub>	1	–1.37	74 (63.9–74.1)	9300 (200 nm) 7800 (210 nm)
		2			
Nitrous	HNO <sub>2</sub>	1	3.16 (3.15–3.34)	74.6 (61.1–74.6)	5200 (209 nm) 5200 (210 nm)
		2			
Perchloric	HClO <sub>4</sub>	1	–2 (–7.3)	69.8 (60.4–71)	
Periodic	HIO <sub>4</sub>	1	1.55 (1.55–1.64)	56.5 (49–57.6)	
Permanganic	HMnO <sub>4</sub>	1	–2	63.4 (54.9–65.1)	
Phosphoric	H <sub>3</sub> PO <sub>4</sub>	1	2.12 (2–2.15)	34.2 (27.4–37.3)	
		2	7.21 (6.72–7.47)	59.1 (34.2–61.5)	
		3	12.32 (11.35–12.67)	71.5 (49)	

Table 1 (continued)

Acid	Formula	Step*	pK values	Mobility*	UV absorptivity*
Phosphorous	H <sub>3</sub> PO <sub>3</sub>	1	2 (1.51)	40	
		2	6.59 (6.5–7)	65.4	
Pyrophosphoric	H <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	1	0.85 (0.8–1.52)	24.9	
		2	2.1 (1.5–2.36)	57.9	
		3	6.6 (4.72–6.75)	75.3	
		4	9.3 (8.22–9.62)	88.8 (84.4–99.5)	
Selenic	H <sub>2</sub> SeO <sub>4</sub>	1	0 (–0.48)	41	
		2	1.92 (1.7–2.05)	78.5 (67.4–805)	
Selenious	H <sub>2</sub> SeO <sub>3</sub>	1	2.75 (2.27–2.75)	41.2	5100 (200 nm)
		2	8.5 (7.31–8.5)	60.5	2300 (210 nm)
Sulfuric	H <sub>2</sub> SO <sub>4</sub>	1	–3	51.8 (52)	
		2	1.92 (1.7–1.99)	82.9 (70.5–83.9)	
Sulfurous	H <sub>2</sub> SO <sub>3</sub>	1	1.77 (1.76–1.89)	51.8	
		2	6.99 (5.3–7.21)	74.6 (82.8)	
Telluric	H <sub>6</sub> TeO <sub>6</sub>	1	7.68 (7.61–7.81)		
		2	11 (10.33–11.29)		
		3	15 (15.6)		
Tellurous	H <sub>2</sub> TeO <sub>3</sub>	1	2.52 (2.46–2.68)		
		2	7.7 (5.37–9.8)		
Tetraphenylboronic	HB(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	1		21.8	
Thiocyanic	HSCN	1	0.85 (0.85–1)	68.4 (58.5–68.9)	5100 (200 nm)
					3200 (210 nm)
					3100 (215 nm)
					2800 (200 nm)
Thiosulfuric	H <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	1	0.6	44	3500 (210 nm)
		2	1.72 (1.3–2)	88.1 (88–90.6)	3800 (215 nm)
Tungstenic	H <sub>2</sub> WO <sub>4</sub>	1	2.2 (3.5)		6700 (200 nm)
		2	3.7 (4.6)	71.9 (61.1–71.9)	2700 (210 nm)
Ferrocyanic	H <sub>4</sub> [Fe(CN) <sub>6</sub> ]	3	2.25 (1.79–2.6)		
		4	4.25 (3.25–4.3)	115 (98.5–116)	
Ferricyanic	H <sub>3</sub> [Fe(CN) <sub>6</sub> ]	3		105 (88.2–105)	12 300 (200 nm)
					10 000 (210 nm)
					1000 (260 nm)
					1600 (303 nm)
Monofluorophosphoric	H <sub>2</sub> PO <sub>3</sub> F	1	0.55		1000 (420 nm)
		2	4.8 (4.47–5.12)	65.6	

\*Compiled from the data given in refs. [287–293].

The values with the largest frequency of occurrence are given; the span within which the data for a particular acid (anionic constituent) were found is given in parentheses.

Mobility data are given in the following units:  $10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ .

UV absorptivities are given in the following units:  $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ .

performed. Therefore, differences in the effective mobilities of these constituents can be linked with differences in their  $\alpha_{A,i}$  values (see Eq. (1)). Thus, a proper choice of pH for the electrolyte system in which the separation is performed (a relationship between pH,  $\text{p}K_A$  and  $\alpha_{A,i}$  is well known [9]) can be effective in some CE separations of inorganic anions.

However, from the compositions of the electrolyte systems used in the CZE separations of inorganic anions (Tables 4 and 5), we can see that this separation mechanism is seldom used in practice. Nevertheless, its use may be practical in the following situations: (i) in the resolution of groups of strong and weak acids and in the separation of weak

acids [22–24]; (ii) in reducing the numbers of sample matrix constituents migrating with effective mobilities close to those of inorganic anions [22,24].

### 2.3. Separations based on complex equilibria

Complex equilibria in which CE analytes are involved influence their effective mobilities. Assuming kinetic labilities of the equilibria, they influence the effective mobilities via the stability constants [these are explicitly included in the  $\alpha_{A,i}$  values (see Eq. (1))] and via the actual mobilities of the complex ionic forms in which the analytes migrate [25].

Complex formations of metal cations with suitable ligands are probably the key equilibria employed in the CE separation of metal cations (see, e.g. [12] and references therein). By using suitable metal cations in the electrolyte systems, they are also applicable to the separation of inorganic anions. So far, however, the use of complex equilibria for these purposes in CZE is rare [2,26,27]. In the ITP separation of inorganic anions, they were used more often (for a review see, e.g. [1,28]).

Probably the first work dealing with the use of host–guest complex equilibria in CE separations [29] showed that cyclodextrins may be useful complexing agents in the separation of inorganic anions. Detailed investigations carried out in this respect with  $\alpha$ -cyclodextrin proved its suitability in the ITP [30] and CZE [31] separation of common inorganic anions.

### 2.4. Ion-pairing of inorganic anions with amphiphilic cations

Quaternary ammonium cations are currently the preferred modifiers of EOF in the CZE separation of inorganic anions (see Section 3.1.1 and Table 2). These amphiphilic cations tend to form ion-pairs with less hydrated (hydrophobic) inorganic anions [285]. These association processes influence the effective mobilities of the anions, formally, in the same way as complex equilibria do (see Section 2.3).

From CZE experiments using different types of quaternary ammonium cations, it is apparent that the cations or their concentrations in the carrier electrolyte solution are responsible for the different separation selectivities of some inorganic anions in CZE. Jones and Jandik [5] showed that, in this way,

it is possible to significantly influence the effective mobilities of bromide, sulfate and nitrate. From the work of Guan et al. [32], it can be concluded that cetyltrimethylammonium (CTA<sup>+</sup>) cation is a more effective ion-pairing agent for these anions than the cation(s) present in the Nice-Pak OFM Anion-BT preparation [5], as a 1.1-mmol/l concentration of CTA<sup>+</sup> in the carrier electrolyte solution was sufficient to obtain the migration order: nitrite–bromide–nitrate. CTA<sup>+</sup> also influences the effective mobilities of thiosulfate, iodide and thiocyanate [33]. A combination of 10 mmol/l chromate with 2.3 mmol/l CTA<sup>+</sup> in the carrier electrolyte solution gave the migration configuration: chloride, bromide, nitrite, sulfate, thiosulfate and nitrate [34]. In this instance, the ion-pairing effects were undoubtedly accompanied by changes in the actual mobilities of the double charged anions induced by the ionic strength effects (see Section 2.1), as this is a very differing migration configuration of the anions compared to that obtained in current chromate electrolyte systems (see Table 4).

A binary mixture of amphiphilic cations [tetradecyltrimethylammonium (TTA<sup>+</sup>) and dodecyltrimethylammonium (DTA<sup>+</sup>)], which differ in their influences on the effective mobilities of anions, was studied in conjunction with the CZE separation of anions present in Bayer liquor [35]. It was shown that the migration order of the inorganic anions depended not only on the total concentration of amphiphilic cations but also on their concentration ratio in the carrier electrolyte solution [36].

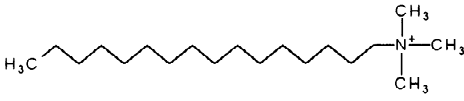
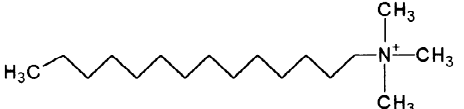
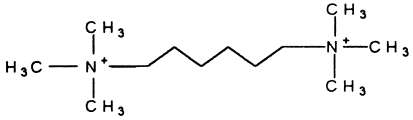
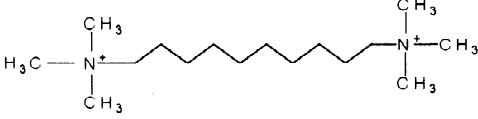
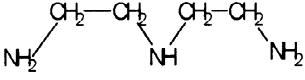
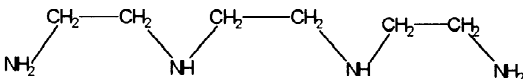
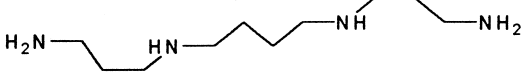

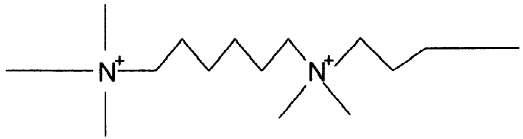
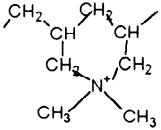
The use of amphiphilic cations as co-counter-ions in the leading electrolyte was also found to be effective in the ITP separation of inorganic anions [37].

### 2.5. Separations based on interactions of the anions with electroneutral and positively charged water-soluble polymers

Electroneutral, water-soluble polyvinylpyrrolidone (PVP) was found to influence the effective mobilities of inorganic anions in a differentiating way [38]. Its influence on the migration properties of iodide, thiocyanate, perchlorate and chromate was the largest. It also significantly influenced the effective mobilities of nitrate, chlorate, bromide, thiosulfate,

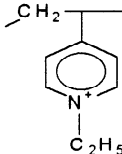
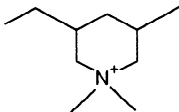
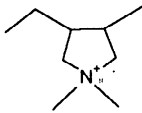
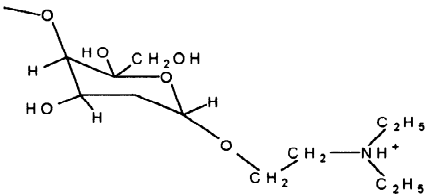
Table 2

Electroosmotic flow modifiers used in co-electroosmotic the CZE separation of inorganic anions

Modifier	Structure	Concentration <sup>a</sup> [mmol/l]
Cetyltrimethylammonium = CTA		0.002–2.3
Tetradecyltrimethylammonium = TTA		0.1–100
OFM Anion-BT Hexane-1,6-bis(trimethyl)- ammonium = hexamethonium		0.3–5 0.75–2.13
Decane-1,10-bis(trimethyl)- ammonium = decamethonium		
Diethylene triamine		0.2–20; 0.02% (v/v)
Triethylenetetramine		0.25–4
Spermine		
Hexanediamine		
Poly( <i>N,N,N',N'</i> -tetramethyl- <i>N</i> - trimethylene-hexamethylene- diammonium) = polybrene = hexadimethrin		2.67; 0.001%–0.6% (w/v)
PDADMA (poly- (diallyldimethylammonium))		5.35

(continued on next page)

Table 2 (continued)

Modifier	Structure	Concentration <sup>a</sup> [mmol/l]
PVPy (poly-( <i>N</i> -ethyl-4-vinylpyridinium))		0.1% (w/v)
Poly(1,1-dimethyl-3,5-dimethylenepiperidinium)		0.004–0.6% (w/v)
Poly(1,1-dimethyl-3,5-dimethylenepyrrolidinium)		0.004–0.6% (w/v)
DEAED ((diethylamino)-ethyl-dextran)		0.004–0.6% (w/v)

<sup>a</sup>Table was compiled from the references summarized in Tables 4 and 5. Concentration in the carrier electrolyte solution.

pyrophosphate and nitrite, while the effective mobilities of chloride, sulfate, orthophosphate, selenite, fluoride, bromate and arsenate were not influenced in the presence of PVP in the electrolyte system. The use of the polymer was very effective in the CZE separation of a group of common inorganic anions present in various sample matrices [22]. From the point of view of electrophoretic separations, it is also important that this electroneutral polymer does not contribute to the conductances of the electrolyte systems so that it can be used at very high concentrations.

A group of cationic, water-soluble polymers was investigated in the CZE separation of common inorganic anions [39,40]. These EOF-reversing polymers selectively influenced the effective mobilities of some anions (sulfate, phosphate, bromide, nitrate). Two of the polymers were studied in the separation

of anions in water–methanol and water–acetonitrile solvent mixtures. Methanol and acetonitrile were found to have different influences on the effective mobilities of common inorganic anions in the presence of the polymers. The effect of acetonitrile, even at low concentrations, was remarkable.

Three water-soluble cationic polymers were investigated in the CZE separation of inorganic anions [41]. The results from this investigation showed that they differ in their association abilities with the anions and exhibit, to some extent, different separation selectivities for the anions.

## 2.6. Separations in organic solvents and in mixtures of them with water

Organic solvents and mixtures of them with water were employed to separate inorganic anions even in



early CE works (for reviews, see [1,42]). From the cited works, it is apparent that changing the solvent in which the separation is performed is accompanied by complex changes in the effective mobilities of the separated constituents. In general, such a solvent change is linked with all of the parameters that determine the effective mobilities (see Eq. (1)): (i) identical anionic forms of constituents have different absolute mobilities in different solvents (solvent mixtures) due to differences in their solvations; (ii) acid–base properties of the separated constituents ( $pK$  values) are changed; (iii) different inter-ionic interactions of the anionic forms of the analytes with the electrolyte system's constituents are involved; (iv) in some instances, the anionic forms of the analytes can participate in the formation of ion-associates.

Detailed investigations of the CZE separation of eleven inorganic anions in methanol and dimethylformamide revealed significant changes in their migration order relative to those in aqueous systems [43]. For example, the change was dramatic for thiocyanate (the second slowest in water, became the second fastest in methanol); the migration order of halides in methanol was changed and, as could be expected, the effective mobilities of the doubly charged anions were much lower in methanol (ion-association effects).

However, the use of pure organic solvents is rare in the CE of inorganic anions and water–organic solvent mixtures are mostly employed to implement solvent effects in the separations. In some instances, relatively low concentration of organic solvent can selectively influence the effective mobilities of inorganic anions. For example, iodide and chloride were not resolved when their CZE separations were carried out in electrolyte systems based on separation according to differences in their actual ionic mobilities in water. The same applied for perchlorate and azide. Significant improvements in the separation of these pairs were achieved when a carrier electrolyte containing methanol (15%, v/v) was used [44]. In this context, we should also mention other combinations of organic solvents (acetonitrile, methanol, acetone, tetrahydrofuran and ethylene glycol) with water, as used in the separation of inorganic anions by Buchberger and Haddad [33]. The influences of methanol and acetonitrile on the

effective mobilities of common inorganic anions in the presence of cationic polymers were investigated by Stathakis and Cassidy [40]. The effect of acetonitrile on the effective mobilities of some anions (nitrate, sulfate, thiocyanate) was found to be very significant and it differed from that observed for acetonitrile in the presence of amphiphilic cations in the carrier electrolyte solution [33]. This indicates that polymer properties (solvation, structural conformation) also contributed to the overall selectivity effect.

### 3. Separation of inorganic anions by various CE techniques

In spite of the fact that ITP was the first of the CE techniques used in the separation of inorganic anions (for a review of pioneering works, see, e.g., [1]), at present, the use of CZE is dominating. In this context, we should note that, with the probable exception of isoelectric focusing, inorganic anions can be separated by all current CE techniques in capillary tubes made of fused-silica or suitable plastic materials [22,45].

#### 3.1. Capillary zone electrophoresis

In the CZE separation of inorganic anions, the electrophoretic separation process itself is combined with various electroosmotic regimes in the column [46,47]. Therefore, it is convenient to distinguish between three basic CZE alternatives, as discussed below.

##### 3.1.1. Co-electroosmotic capillary zone electrophoresis

In the co-electroosmotic CZE mode, the directions of the EOF and the electrophoretic (separative) transport are identical. The analytes migrate through the detector in the order of decreasing effective mobilities and, for their apparent mobilities (see Eq. (3)), the following relationship is valid:

$$m_{A,app} = |\bar{m}_A| + |m_{EO}| \quad (4)$$

EOF in capillary tubes with untreated inner surfaces is directed towards the cathode. Its anodic

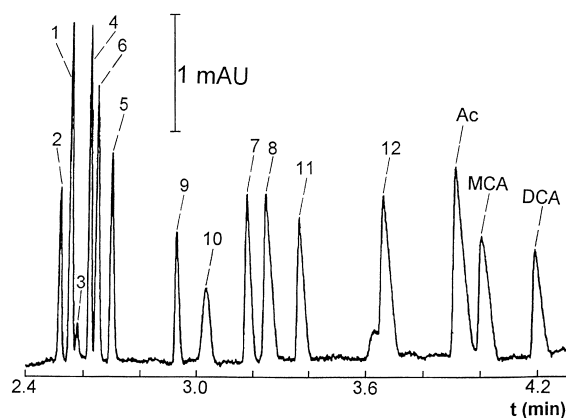


Fig. 1. Separation of inorganic anions and organic halides by co-electroosmotic CZE. Peaks: 1=chloride, 2=bromide, 3=iodide, 4=sulfate, 5=nitrate, 6=nitrite, 7=fluoride, 8=phosphate, 9=chlorate, 10=perchlorate, 11=chlorite, 12=carbonate, Ac=acetate, MCA=monochloroacetate and DCA=dichloroacetate. The carrier electrolyte was 5 mmol/l chromate and 0.3 mmol/l OFM Anion-BT, adjusted to pH 8.0. The applied driving potential was 20 kV (negative polarity). Capillary dimensions were: a 60-cm total length (52 cm to the detector) and a 75- $\mu$ m I.D. The sample (containing the anions at low ppm concentrations) was injected hydrostatically (10 cm for 30 s). Adapted from ref. [100] with permission.

inversion is needed for the co-electroosmotic mode of separation (see also Fig. 1). This requires a change in the polarity of the  $\zeta$ -potential, e.g., by using a suitable amphiphilic cation (EOF modifier) in the carrier electrolyte solution [48]. Various aspects of this approach to EOF inversion were studied in detail [16,46,47,49–51]. A proprietary alkyl quaternary amine, better known as CIA-Pak OFM Anion-BT [46,47,52–55],  $\text{CTA}^+$ ,  $\text{TTA}^+$  and dodecyltrimethylammonium ( $\text{DTA}^+$ ) cations are probably the mostly used amphiphilic EOF modifiers (see Tables 2,4 and 5). Amphiphilic quaternary alkylphosphonium cations [16] may be considered as alternatives to alkylammonium cations.

Memory effects of amphiphilic EOF modifiers on capillary walls are usually strong enough so that the walls can be modified before the separation and then the modifiers need not be added to the carrier electrolyte solution [56]. On the other hand, the separation of some samples containing strongly adsorbing constituents can adversely affect the reproducibility of the EOF unless a convenient capillary cleaning procedure is applied between runs. An

example, using a brewed coffee sample [47], may serve as an illustration of these problems. In this context, we should note that CZE experiments performed by the same author with the same sample type in a different carrier electrolyte (with hexamethonium used for EOF inversion) clearly indicated that some EOF modifiers can be more effective in preventing instabilities of EOF than amphiphilic cations [47].

The use of di- and multivalent organic bases in carrier electrolyte solutions is another alternative for EOF inversion towards the anode. DETA [20,21,57–60], triethylenetetraamine (TETA) [60], hexamethonium [16,44,61–66], decamethonium [16], spermine [26], cryptand-22 [19] and hexanediamine [67] are polyamines that have been used successfully for this purpose.

A group of water-soluble cationic polymers was shown to reverse the EOF in the separation of inorganic anions [39–41,68,69]. These polymers adsorb to the surface of the capillary and produce stable EOFs towards the anode when present in the carrier electrolyte at relatively low concentrations [39,68]. However, the actual size of the flow depends on the carrier anion employed in the electrolyte system. For example, it was found that chromate, combined with a polymeric EOF modifier, was responsible for a significant reduction in the EOF, compared to other carrier anions [40]. This phenomenon was ascribed to stronger interactions of chromate with the polymers, with a concomitant reduction in the  $\zeta$ -potential. Such an EOF decrease is even stronger when organic modifiers (acetonitrile or methanol) are present in the carrier electrolyte. The adsorption of some cationic polymers to the capillary surface is very strong and they can form coatings that are stable enough that polymers need not be added to the carrier electrolyte solutions [68].

Some polymers can be chemically bound to the inner wall of the capillary to give a permanent positive charge on the surface. Such a surface modification leads to the anodic direction of the EOF without the use of modifiers. This approach in the co-electroosmotic CZE of inorganic anions was studied by Burt et al. [70], who used a polyamide resin for the capillary coating. However, the quality of the coating attained was not acceptable for routine use. Hauser et al. [71] coated a capillary surface with

polyacrylamide incorporating a quaternary amine. The results with this type of coating appeared to be less favourable in comparison with a common chromate electrolyte system. A 24-membered macrocyclic polyamine based on a propylene-1,3-diamine unit was used as a capillary coating [72]. Its use, in combination with 5 mmol/l sodium chromate at pH 10, gave separation times of about 10 min for common inorganic anions. This undoubtedly indicates that the EOF velocity corresponding to this coating was much lower than that found for EOF modifiers added to the carrier electrolyte solutions. The work by Corr and Anacleto [73] showed that coating a capillary with strong anion-exchange sites is advantageous when mass spectrometry is used for the detection of inorganic anions, as current EOF modifiers increase background noise and mass spectral complexity.

### 3.1.2. Capillary zone electrophoresis without electroosmotic flow

EOF can be suppressed to values close to zero [48,74–76] and, under these conditions, anions migrate through the detector in order of decreasing effective mobilities (the same migration order as in the co-electroosmotic mode). In this instance, the electrophoretic migration of the anions is the only electrokinetic transport process involved and, for their apparent mobilities, the following relationship is valid:

$$m_{A,\text{app}} = \bar{m}_A \quad (5)$$

CZE separations carried out at low pH values are associated with very low values of the  $\zeta$ -potential [48]. To perform a CZE separation under such separating conditions is, in fact, the simplest way of minimizing the EOF ( $\zeta$ -potential  $\sim 0$ ). Such an approach was used in the CZE separation of inorganic anions, e.g., in works by Takayanagi et al. [77,78] and Thornton and Fritz [79].

Suppression of the EOF in the way currently used in ITP separations, in a hydrodynamically closed separation compartment (by adding a suitable polymer that is soluble in the electrolyte solution in which the separation is performed), is another alternative that is convenient for this purpose (see Fig. 2). It was found to be very effective in the CZE

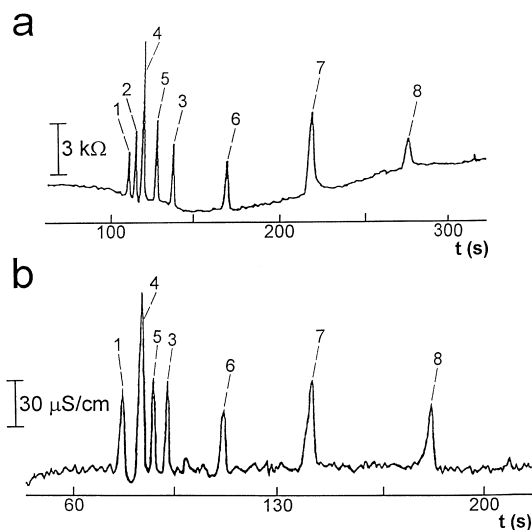


Fig. 2. Separation of model mixtures of common inorganic anions by CZE without EOF. Peaks: 1 = chloride, 2 = bromide, 3 = iodide, 4 = sulfate, 5 = nitrate, 6 = nitrite, 7 = fluoride, 8 = phosphate. In both instances, the samples were injected with the aid of a CZE injection valve using a 200-nl sample loop. The separations were carried out in 300  $\mu\text{m}$  I.D. capillary tubes with a total length of 28 cm (ca. 20 cm to the detector) and made of fluoroplastics. a = signal provided by a contact conductivity detector (the concentrations of the sample constituents in the injected sample were 2  $\mu\text{mol/l}$ , with the exception of fluoride, which was present at a concentration of 10  $\mu\text{mol/l}$ ); b = signal provided by a contactless conductivity detector (the concentrations of the sample constituents in the injected sample were 10  $\mu\text{mol/l}$ , with the exception of fluoride, which was present at a concentration of 20  $\mu\text{mol/l}$ ). The separations were carried out in a carrier electrolyte consisting of 7 mmol/l succinic acid, 5% (w/v) PVP and bis-Tris propane (to adjust the pH 3.5). Methylhydroxyethylcellulose (0.2%) in the carrier electrolyte solution served as an EOF suppressor. The driving current was stabilized at 30  $\mu\text{A}$ .

separation of inorganic anions when performed in a column with enhanced sample loadability [22]. The results of a detailed study dealing with this group of EOF suppressors [74] show that they can be applied in various ways (dynamic coating of the surface, stable physical coating of the surface, mixed layers of polymers formed on the surface).

The  $\zeta$ -potential can be reduced to a value approaching zero by using a suitable amphiphilic cation at an appropriate concentration in the electrolyte system [48] or by the simultaneous use of such a cation with an electroneutral water-soluble polymer [80].

Chemical modification of the inner wall of the capillary can form a permanent coating, eliminating EOF [81,82]. A bonded polyacrylamide coating used for this purpose in the separation of inorganic anions was claimed to provide very reproducible separations in a large series of analyses when the pH of the carrier electrolyte was in the range of two–eight [83]. A series of commercially available coated capillaries was tested, by Tindall and Perry [18], in this context in the CZE separation of common inorganic anions.

### 3.1.3. Counter-electroosmotic capillary zone electrophoresis

EOF transports the carrier electrolyte solution to the cathode, i.e., in the opposite direction to the migration of the anionic constituents. Under these conditions, the separated anions migrate through the detector in the order of increasing effective mobilities. The following relationship is valid for determining the apparent mobilities of the anionic constituents:

$$m_{A,app} = |m_{EO}| - |\bar{m}_A| \quad (6)$$

For known reasons [46], counter-electroosmotic CZE is a less favoured alternative for the separation of inorganic anions. However, the results obtained with suppressed conductivity detectors [17,84,85] and bipolar pulse conductivity detection [86] show that, using a carrier electrolyte solution of suitable composition, even the most mobile anions can reach the detector in reasonable migration times. Using the counter-electroosmotic mode of separation, it was shown [17] that, by choosing the working temperature carefully, the analysis time could be reduced (also, see Fig. 3).

### 3.2. Micellar electrokinetic chromatography and electrochromatography

To date, both micellar electrokinetic chromatography (MEKC) and electrochromatography (EC) with packed columns have been used only rarely for the separation of inorganic anions [87–91]. As shown in the work by Bjerregaard et al. [87], the use of MEKC may have practical potential, especially in the analysis of these anions in biological fluids. On

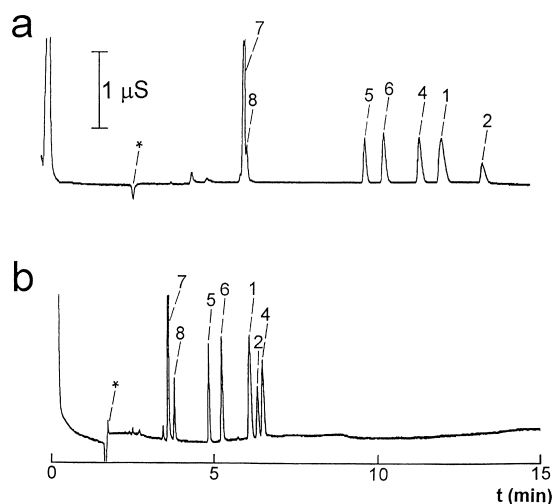


Fig. 3. Separation of a model mixture of common inorganic anions by counter-electroosmotic CZE at different temperatures. a = 21.1°C; b = 54.4°C. Peaks: 1 = chloride, 2 = bromide, 3 = iodide, 4 = sulfate, 5 = nitrate, 6 = nitrite, 7 = fluoride, 8 = phosphate (the concentrations of the analytes were 1 ppm). In both instances, the sample was injected hydrostatically (40 mm/5 s). Capillary, 60 cm × 75 μm fused silica; detection, suppressed conductivity (5 mmol/l sulfuric acid as a regenerant); driving voltage, 24 kV (the detector end cathodic). Adapted from ref. [17] with permission.

the other hand, although the use EC is still in the developmental stages, its potential in the analysis of inorganic anions appears promising, as it can provide new analytical possibilities by combining various selectivity effects resulting from the simultaneous use of chromatography and electrophoretic separation principles [89,90].

### 3.3. Capillary isotachopheresis

The use of ITP for the analysis of inorganic anions has attracted less attention within the last few years. On the other hand, this basic electrophoretic technique has become a subject of interest as a promising sample pretreatment technique (see below).

In contrast to CZE, ITP separations are carried out almost exclusively without EOF. Although this is not essential [92–94], different ζ-potentials in the ITP zones (linked with large differences in the relevant physico-chemical properties of the zones) are responsible for large changes of the EOF velocities within the ITP run. Adequate modification of the CE instrumentation is necessary to correct for these EOF

changes in order to obtain reliable ITP data [95]. EOF in ITP separations is eliminated (minimized) by the use of water-soluble polymers (e.g., hydroxyethylcellulose, polyvinylalcohol) or electroneutral surfactants (e.g., Triton X-100) in the leading electrolytes [28,96].

The high sample load capacity in ITP separation systems is linked not only with their volumes but also with an efficient use of the electric charge delivered to the separation of the samples [28,96]. This presents the possibility of injecting sample volumes as large as several hundred microliters. As shown recently by Meissner et al. [97,98], this capability of ITP can lead to unprecedented analyte-to-excess ratios in CE analysis ( $1:3 \cdot 10^5$ – $1:4 \cdot 10^7$ ). Due to this, trace inorganic anions present in technically important chemicals at  $2.5 \cdot 10^{-6}$ – $1 \cdot 10^{-3}$ % concentrations could be determined directly without any pre-column sample pretreatment.

#### 4. Detection in CE

Direct and, especially, indirect photometric detection is the favoured detection technique in the CZE of inorganic anions, while in ITP, various conductivity detection methods are preferred for this purpose.

##### 4.1. Direct UV photometric detection

From the data in Table 1, it is apparent that only a limited number of common inorganic anions are detectable by direct photometric detection. Although seldom giving limits of detection for these anions of lower than  $1 \mu\text{mol/l}$ , the main advantages of the direct mode of photometric detection in practical CZE applications are associated with its compatibility with (highly) concentrated carrier electrolyte solutions (see Tables 4 and 5 for examples).

Direct photometric detection offers very low concentration limits of detection for ITP analytes when these are determined in the spike mode of detection [28,96]. This detection approach is very useful in the trace analysis of inorganic anions present in complex ionic matrices. Isotachopherograms from the determination of iodide present in mineral water samples containing chloride at a  $10^4$ – $10^5$  molar excess (Fig.

4) illustrate its analytical utility [38]. The same approach provided a very sensitive and selective method for the determination of Cr(VI) in water without any sample pretreatment [99].

##### 4.2. Indirect UV photometric detection

This method was probably used for the first time in CZE by Hjertén et al. [81]. However, it was first used for the CZE analysis of inorganic anions by Jones and Jandik [3,5,100]. At present, this is the key detection technique in the CZE analysis of these anions and its basic aspects, in conjunction with its use in inorganic analysis, are discussed in the literature (see, e.g., [47,101,102]).

There is a direct link between the limit of detection for an analyte ( $c_{A,LOD}$ ) and the concentration

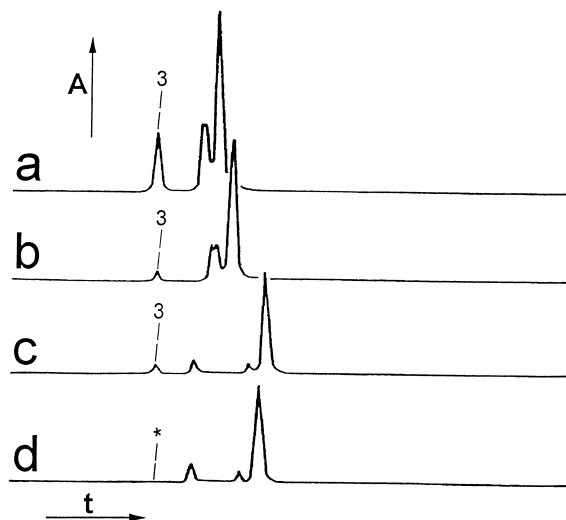


Fig. 4. Isotachopherograms from the determination of iodide (3) in mineral water samples by ITP with the spike mode of photometric detection (254 nm). A 6% (w/v) concentration of PVP was used in the leading electrolyte. Sulfate and fluoride, added to the samples at concentrations of 0.1 mmol/l, served as discrete spacers for iodide. a, b=analysis of samples of mineral water (diluted tenfold with water); c=analysis of a model sample containing iodide at  $1 \mu\text{mol/l}$ ; d=blank run with the spacing constituents (an asterisk indicates the migration position of iodide). Leading electrolyte, 10 mmol/l HCl, 6% (w/v) PVP, histidine was added to bring the pH to 6.0; EOF suppressor, 0.2% MHEC (w/v) in the leading electrolyte; Terminating electrolyte, 5 mmol/l MES. The driving current was stabilized at  $50 \mu\text{A}$ . Adapted from ref. [38] with permission.

of the visualization (carrier) ion in the carrier electrolyte solution ( $c_C$ ), in indirect detection [103]:

$$c_{A,LOD} = \frac{c_C}{DR \cdot TR} \quad (7)$$

where TR is a symbol for the transfer ratio and DR is the dynamic reserve. This relationship shows that favourable  $c_{A,LOD}$  values for analytes require a low concentration of the visualization ion in the carrier electrolyte solution, while the DR and TR parameters are to be maximized. The wide use of this detection technique in the analysis of inorganic anions stimulated a search for suitable visualization anions and, in this context, various constituents were tested (see Table 3). From the works dealing with the CZE separation of various combinations of anions (Table 4 and Table 5), it is apparent that the use of chromate is dominant. This can be, at least in part, ascribed to its favourable light absorption properties in a wide range of light spectra. In addition, the effective mobility of chromate offers a good match with the effective mobilities of many inorganic anions so that their electromigration dispersions [104,105] can be tolerable in some critical situations (very different concentrations of analytes in the injected sample).

#### 4.3. Conductivity detection

Conductivity detection is a key detection technique in ITP (for details see, e.g., [28,96]). Although it was used in the first work dealing with the CZE separation of inorganic anions [2], its use for this purpose in CZE is, in general, rare [17,22,56,84–86,106–108].

There are links between the sensitivity of conductivity detection and the composition of the carrier electrolyte in CZE [104,105,109]. For strong monovalent ions, this is expressed by the following relationship [109]:

$$s_A = F(\bar{m}_A + \bar{m}_{CO}) \left( 1 - \frac{\bar{m}_{CA}}{\bar{m}_A} \right) \quad (8)$$

where,  $s_A$  is the molar response of the detector for the analyte (sensitivity of the detector),  $F$  is the Faraday constant,  $\bar{m}_A$ ,  $\bar{m}_{CO}$  and  $\bar{m}_{CA}$  are the effective mobilities of the analyte, counter-ion and carrier ion, respectively. Eq. (8) explicitly shows that high

sensitivity of the conductivity detector requires that the effective mobilities of the analytes and the carrier ion differ as much as possible. However, such a requirement cannot be strictly followed as it can lead to significant electromigration dispersions of the analyte peaks [104,105]. Therefore, in the use of conductivity detection, a compromise has to be found between these contradictory requirements. Highly efficient separations, as obtained for inorganic anions, clearly suggest that this is possible with detectors of different constructions and with capillary tubes of different I.D.s (for relevant references, see below).

##### 4.3.1. Contact and contactless conductivity detections

On-column [28,96,110,111] and post-column [56,108,114] conductivity sensors, with measuring electrodes in direct contact with the electrolyte solution in which the separation is performed, are preferred at present in CZE and ITP. This contact mode of detection requires that the construction of the detector minimizes some specific phenomena that can occur in the conductivity measurement in the driving d.c. electric field, as these may adversely affect analytical data provided by the detector (for details see, e.g., [96]).

In the early 1980s, Gaš et al. [112,115–117] designed a high-frequency contactless conductivity detector for CE, solving the problems associated with the use of contact conductivity sensors. This contactless conductivity detector was intended for ITP where the differences in the conductances of the zones are much higher than those linked with CZE zones. It was shown recently [31] that this detection technique offers promising detection possibilities in the CZE separation of inorganic anions. From electropherograms comparing the contact and contactless conductivity detectors for these anions, under very close working conditions (Fig. 2), we can see that the latter detector was less sensitive. Nevertheless, this need not be conclusive as no attempts to improve its noise parameters (responsible for the lower sensitivity) have been undertaken to date.

A different measuring principle for contactless conductivity detection in CE was recently introduced by Zemann et al. [113,118]. In this instance, the detector was tested in conjunction with the CZE

Table 3

Visualisation of anions for indirect photometric detection in the CZE separation of inorganic anions

Anion	Detection wavelength <sup>a</sup> (nm)	Concentration <sup>a</sup> (mmol l <sup>-1</sup> )	pH <sup>a</sup>
<i>Benzoic acid and its derivatives</i>			
Benzoate	228; 254 (+)	5–20	5.6–9.1
<i>p</i> -Aminobenzoate	264	7.5	9.4
<i>p</i> -Hydroxybenzoate	254	5	6; 9.37
<i>o</i> -Benzylbenzoate	228	20	6.5
4-Methoxybenzoate ( <i>p</i> -anisate)	254	5	6
Phthalate	210; 214 (++); 228; 254 (++)	3–20	4.3–9.3
Trimellitate	254	2–10	5.6–9.3
Pyromellitate	214 (++); 220; 250 (++); 254 (++)	1.13–5	3.5–8
Trimesate	230; 254	5	6
Salicylate	220; 254	5; 20	6; 8.1
Naphthalene-2,6-dicarboxylate	280	2	10.9
3,5-Dinitrobenzoate	254	1.25–10	4–9
<i>Arylsulfonic acids</i>			
2-Sulfobenzoate	228	20	6.5
1,3-Benzenedisulfonate	214 (++)	3	8.05
1,2-Dihydroxybenzene-3,5-disulfonate (Tiron)	293	5	3.5–8.8
Naphthalenemonosulfonate	254; 274 (++)	4–10	8–10
1,5-Naphthalenedisulfonate	214 (+++)	3	8.1
Naphthalenedisulfonate	288 (+++)	4 (8.3)	8
1,3,6-Naphthalenetrisulfonate	214 (+++)	2	8
Naphthalenetrisulfonate	284 (++)	3 (8.3)	8
1-Nitroso-2-naphthol-6-sulfonate (126 NNS)	254 (260)	0.5	8
2-Nitroso-1-naphthol-6-sulfonate (216 NNS)	254 (260)	0.5	8
1-Nitroso-2-naphthol-3,6-disulfonate	254 (260)	0.5	8
<i>p</i> -Toluenesulfonate	195	5	3
<i>Nucleotides</i>			
5'-AMP	259 (++)	5	6.8–8.3
5'-ADP	259 (++)	5	7.8
5'-ATP	260	5–10	3–9
5'-CMP	271 (++)	5	7.8
5'-GMP	254 (++)	5	7.8
5'-UMP	261 (++)	5	7.8
<i>Other organic acids</i>			
Pyridine-2,6-dicarboxylate	254	3–15	3–7.8
Picrate	357	2–10	2.5–12.6
Sorbate	254	5–6	6; 7.64; 12.2
EDTA	210	5	10.3
Fluorescein disodium salt	238	1	11
<i>Inorganic acids</i>			
Chromate	185; 205; 214; 229; 254 (++) ; 260 (++) ; 262; 265; 270; 275; 280; 313; 365; 372; 405; 436; 546;	1.8–10	2–12
Nitrate	214	2.1–10	4–9
Iodide	226	7.5	?
Molybdate	211	8–12	6.7
Sodium vanadate	254	7.5	?

<sup>a</sup>Table was compiled from the references summarized in Tables 4 and 5. Molar absorptivity scale: + = low; ++ = medium; +++ = high. Concentration in the carrier electrolyte solution. pH span within which the anion was used.

Table 4  
CZE separation and analysis of common inorganic anions

Anions	Sample	Electrolyte system	Detection	Reference
<i>Model mixture</i>				
Chloride perchlorate <sup>a</sup> , chlorate, carbonate and inorganic cations	Model mixture (simultaneous cations and anions)	0.5 mmol/l cerium(III) sulfate, 0.5 mmol/l 2,5-dihydroxybenzoic acid, pH 3.4	Indirect FD (314/389 nm)	[270]
Bromide chloride, sulfate, nitrite, nitrate, molybdate, azide, chlorate, fluoride, formate, chlorite and carbonate <sup>a</sup>	Model mixture	5 mmol/l sodium chromate, 30 μmol/l OFM Anion-BT, 4% 1-butanol, pH 8	Indirect UV (254 nm)	[266]
(a) Thiosulfate, bromide, chloride, iodide, sulfate, nitrite, nitrate, chlorate, thiocyanate and fluoride <sup>a</sup> (b) Bromide, iodide, nitrite, nitrate and thiocyanate <sup>a</sup> (c) Thiosulfate, bromide-iodide, chloride, nitrate, nitrite, sulfate, chlorate, thiocyanate and fluoride <sup>a</sup>	Model mixture	(a) 5 mmol/l sodium chromate, 0.5 mmol/l TTAB (b) 5 mmol/l sodium chloride (potassium sulfate), 0.5 mmol/l TTAB (c) 5 mmol/l sodium chromate, 0.5 mmol/l TTAB, 30% methanol	(a) Indirect UV (254 nm) (b) Direct UV (214 nm) (c) Indirect UV (254 nm)	[33]
Bromide chloride, sulfate, nitrate, fluoride and phosphate <sup>a</sup>	Model mixture	2.25 mmol/l PMA, 1.6 mmol/l TEA, pH 7.9 (sodium hydroxide)	Indirect UV (250 nm)	[70]
Bromide chloride, nitrite, sulfate, nitrate, azide, chlorate, fluoride, phosphate, carbonate and iodate <sup>a</sup>	Model mixture	10 mmol/l sodium chromate, 0.5 mmol/l TTAB, pH 9	Indirect UV (254 nm)	[271]
Thiosulfate, chromate, bromide, chloride, sulfate, selenate, molybdate, chlorate, bromate, arsenate, chlorite, selenite, perchlorate, phosphonate and iodate	Model mixture	2.5 mmol/l PMA, 20% methanol, pH 7.8	IS-MS	[73]
Bromide chloride, sulfate, fluoride, phosphate and citrate <sup>a</sup>	Model mixture	5 mmol/l sodium chromate, OFM Anion-BT, pH 8	Indirect UV (254 nm)	[272]
Bromide chloride, sulfate, nitrite, nitrate and phosphate <sup>a</sup>	Model mixture	(a) 5 mmol/l sodium chromate, 0.4 mmol/l HM, pH 8 (b) 5 mmol/l sodium chromate, 0.2 mmol/l TTA, pH 8 (c) 5 mmol/l sodium chromate, 20 μmol/l CTA, pH 8 (d) 5 mmol/l sodium chromate, 0.2 μmol/l HDM, pH 8	Indirect UV (254 nm)	[49]



Table 4 (continued)

Anions	Sample	Electrolyte system	Detection	Reference
Chloride nitrate, sulfate, bromate and organic acids <sup>a</sup>	Model mixture	1 mmol/l 2,5-dihydroxybenzoic acid, 0.5 mmol/l lead(II) acetate, pH 4.3	Indirect FD (314/389 nm)	[26]
Chloride sulfate, nitrate, vanadate 1, chlorate, vanadate 2 and fluoride <sup>a</sup>	Model mixture	5 mmol/l disodium 1,2-dihydroxy-3,5-disulfonate, pH 5.3	Indirect/direct UV (293 nm)	[273]
Bromide chloride, sulfate, nitrite, nitrate and molybdate <sup>a</sup>	Model mixture	2.25 mmol/l PMA	Indirect UV (250 nm)	[56]
Chloride bromide (as a system peak), sulfate, phosphate and carbonate <sup>a</sup>	Model mixture	5 mmol/l sodium chromate, 2.6 mmol/l TTAB, pH 8.8	Indirect UV (254 nm)	[274]
(a) Bromide, nitrate, permanganate and arsenate <sup>a</sup> (b) Chromate, molybdate, tungstate and vanadate <sup>a</sup>	Model mixture	(a) potassium phosphate, pH 2.5 (phosphoric acid) (b) Tris, pH 8.75 (hydrochloric acid)	direct UV (200 nm)	[267]
Fluoride phosphate, nitrate, nitrite, sulfate, chloride and bromide <sup>a</sup>	Model mixture	(a) 2 mmol/l sodium tetraborate, pH 9.2 (b) 4 mmol/l sodium glycinate, pH 10.5	Cd	[17]
(a) Dithionate, thiosulfate, bromide, chloride, sulfate, nitrite, nitrate, molybdate, azide, thiocyanate, chlorate, fluoride, bromate, phosphate and organic acids <sup>a</sup> (b) Iodide, chloride, perchlorate and azide <sup>a</sup>	Model mixture	(a) 2.5 mmol/l PMA, 6.5 mmol/l sodium hydroxide, 0.75 mmol/l HMOH, 1.6 mmol/l TEA, pH 7.7 (b) 2.5 mmol/l PMA, 6.5 mmol/l sodium hydroxide, 0.75 mmol/l HMOH, 1.6 mmol/l TEA, 15% methanol (v/v), pH 7.7	Indirect UV (250 nm)	[44]
Bromide chloride, sulfate, nitrite, nitrate, fluoride, phosphate and carbonate <sup>a</sup>	Model mixture	5 mmol/l sodium chromate, 0.5 mmol/l OFM-BT, pH 8.1	Indirect UV (254 nm)	[3]
Thiosulfate bromide, chloride, sulfate, nitrite, nitrate, molybdate, tungstate, fluoride, phosphate and carbonate <sup>a</sup>	Model mixture	5 mmol/l sodium chromate, 0.5 mmol/l OFM Anion-BT, pH 8.0	Indirect UV (254 nm)	[275]
Thiosulfate bromide, chloride, sulfate, nitrite, nitrate, molybdate, azide, tungstate, monofluorophosphate, chlorate, fluoride, phosphate, phosphite, chlorite, carbonate and organic acids <sup>a</sup>	Model mixture	5 mmol/l sodium chromate, 0.5 mmol/l NICE-Pak OFM Anion-BT, pH 8.0	Indirect UV (254 nm)	[5]
(a) Thiosulfate, bromide, chloride, sulfate, nitrite, nitrate, molybdate, azide, tungstate, monofluorophosphate, chlorate, fluoride, phosphate, phosphite, chlorite, carbonate and organic acids <sup>a</sup>	Model mixture	(a) 5 mmol/l sodium chromate, 0.4 mmol/l OFM Anion-BT, pH 8.0 (b) 5 mmol/l sodium chromate, 0.3 mmol/l OFM Anion-BT, pH 8.0 (c, d) 5 mmol/l sodium chromate, pH 11 (lithium hydroxide)	(a, b, c, d) Indirect UV (254 nm) (e) Direct UV (214 nm)	[100]

(continued on next page)

Table 4 (continued)

Anions	Sample	Electrolyte system	Detection	Reference
(b) Bromide, chloride, iodide, sulfate, nitrite, nitrate, chlorate, perchlorate, fluoride, phosphate, chlorite, carbonate and organic acids <sup>a</sup>		(e) 25 mmol/l sodium chloride, 0.5 mmol/l OFM Anion-BT-Cl, pH 8		
(c) Fluoride, carbonate, nitrite, nitrate, sulfate, chloride, bromide and persulfate <sup>a</sup>				
(d) Hypochlorite, carbonate, chlorate and chloride <sup>a</sup>				
(e) Bromide, nitrite and nitrate <sup>a</sup>				
Bromide iodide, chloride, nitrate, nitrite, perchlorate and thiocyanate <sup>a</sup>	Model mixture	10 mmol/l potassium sulfate	ISE	[119]
Bromide chloride, iodide, nitrite, nitrate, sulfate, perchlorate, fluoride, phosphate, carbonate, acetate and metal-PAR chelates <sup>a</sup>	Model mixture (simultaneous)	5 mmol/l potassium chromate, 0.05% (w/w) Polybrene, pH 8.9	Indirect UV (254 nm), for chelates Direct UV (490 nm)	[41]
Nitrite, nitrate, bromide, thiocyanate, chromate and metal-EDTA complexes <sup>a</sup>	Model mixture	5 mmol/l sodium sulfate, 10 mmol/l sodium acetate, 53.5 mmol/l PDMACl, pH 8.0	Direct UV (220 nm)	[276]
Bromide chloride, sulfate, nitrite, nitrate, molybdate, chlorate, fluoride and acetate <sup>a</sup>	Model mixture	5 mmol/l sodium chromate, pH 8.4–11.5	Indirect UV (254 nm)	[45]
(a) Cyanide <sup>a</sup>	Model mixture	0.1 mmol/l fluorescein, potassium hydroxide, pH 10	Indirect UV (238 nm), Indirect LIF	[277]
(b) Cyanate, thiocyanate, nitrate, chloride and sulfate <sup>a</sup>				
(a) Chloride, sulfate and inorganic cations <sup>a</sup>	Model mixture (simultaneous cations and anions)	(a) 5 mmol/l imidazole, 2 mmol/l nitric acid, pH 4 (fumaric acid) (b) 2.5 mmol/l copper(II) nitrate, 5 mmol/l EDA, 1 mmol/l fumaric acid, pH 8.5 (TEAOH)	Indirect UV (214 nm)	[278]
(b) Chloride, sulfate, carbonate and inorganic cations <sup>a</sup>				
Thiosulfate bromide, chloride, sulfate, nitrite, nitrate, fluoride and phosphate <sup>a</sup>	Model mixture	5 mmol/l sodium chromate, 0.5 mmol/l TTAB, 5 mmol/l boric acid, pH 8	Indirect UV (272 nm)	[61]
Bromide chloride, iodide, sulfate, nitrite, nitrate, chlorate, perchlorate, fluoride, phosphate, chlorite, carbonate and organic acids <sup>a</sup>	Model mixture	5 mmol/l sodium chromate, 0.3 mmol/l CIA-Pak OFM Anion-BT, pH 8	Indirect UV (254 nm)	[279]
(a) Iodide, thiocyanate, nitrate, bromide, nitrite, azide, chloride, fluoride, oxalate, thiosulfate and sulfate <sup>a</sup>	Model mixture	(a) 10 mmol/l potassium hydrogenphthalate, 20 mmol/l <i>n</i> -butylamine, 2% (v/v) water in methanol (b) 50 mmol/l TEAP in	(a) Indirect UV (254 nm) (b,c) Amperometric	[43]

Table 4 (continued)

Anions	Sample	Electrolyte system	Detection	Reference
(b) Thiocyanide, azide, iodide, nitrite and chloride <sup>a</sup> (c) Nitrite, iodide and bromide <sup>a</sup>		DMFA (c) 100 mmol/l TBAHP in DMFA		
Bromide chloride, sulfate, nitrate, fluoride, phosphate and carbonate <sup>a</sup>	Model mixture	5 mmol/l sodium chromate, 0.1% (w/w) Praestol 185 K (EOF modifier), pH 8	Indirect UV (254 nm)	[68]
(a) Bromide, chloride, nitrite, nitrate, sulfate, dithionate, chlorate, cyclic trimetaphosphate–bromate <sup>a</sup> (b) Bromide, chloride, nitrite, nitrate, sulfate, dithionate, chlorate, cyclic trimetaphosphate, bromate, fluoride, chlorite, orthophosphate and organic acids <sup>a</sup>	Model mixture	(a) 100 mmol/l boric acid, 5 mmol/l disodium tetraborate, 2 mmol/l DETA, 4–8.3 mmol/l NDS, pH 8 (b) 100 mmol/l boric acid, 5 mmol/l disodium tetraborate, 2 mmol/l DETA, 4 mmol/l NTS, pH 8	(a) Indirect UV (288, 214 nm) (b) Indirect UV (284, 214 nm)	[21]
(a) Phosphate, fluoride, phosphonate, nitrate, nitrite, chloride and sulfate <sup>a</sup> (b, c) Phosphate, phosphonate and clodronate <sup>a</sup>	Model mixture	(a) 0.5 mmol/l Nitroso-R salt, pH 8 (b) 0.5 mmol/l Nitroso-R salt, pH 8 (c) 0.5 mmol/l 126NNS, pH 8	(a) Indirect UV (254 nm) (b, c) UV (260 nm)	[280]
Bromide iodide, chromate, nitrate, thiocyanate, molybdate, tungstate, bromate, chlorite, arsenate and iodate <sup>a</sup>	Model mixture	20 mmol/l phosphate, pH 8.0	Direct UV (200 nm)	[281]
Bromide chloride, nitrite, nitrate, sulfate, fluoride and phosphate <sup>a</sup>	Model mixture	5 mmol/l sodium chromate, 0.14% (w/v) PDDPiCr	Indirect UV (254 nm)	[39]
Bromide, nitrite, nitrate, molybdate and tungstate		4 mmol/l sodium sulfate, TTAB	Direct UV (214 nm)	[77]
Nitrite, nitrate and organic acids		sodium sulfate	Direct UV	[78]
(a) Metal–chloro complexes (b) Permanganate, chromium oxalate, perhenate, vanadate and chromate <sup>a</sup> (c) Iodide, nitrate, thiocyanate, periodate and iodate <sup>a</sup>	Model mixture	(a, b) 4 mmol/l hydrochloric acid, 25 mmol/l sodium chloride, pH 2.4 (c) 25 mmol/l perchloric acid, pH 2.4	Direct UV (214 nm)	[79]
Chloride sulfate, nitrite, nitrate, molybdate, azide, fluoride, formate and phosphate <sup>a</sup>	Model mixture	2.25 mmol/l PMA, 6.5 mmol/l sodium hydroxide, 0.75 mmol/l HMOH, 1.6 mmol/l TEA, pH 7.7	Indirect UV	[66]
Chloride, chlorate, perchlorate, nitrite, nitrate, bromide and bromate	Model mixture	potassium chromate, OFM	Indirect UV	[265]
Thiosulfate chloride, sulfate, oxalate, sulfite and carbonate <sup>a</sup>	Model mixture	5 mmol/l chromate, 0.001% hexadimethrine bromide 20% acetonitrile, pH 11	Indirect UV (185 nm)	[69]

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Table 4 (continued)

Anions	Sample	Electrolyte system	Detection	Reference
<i>(A) Drinking, ground and surface water</i>				
Chloride nitrite, nitrate, sulfate, bromate and phosphate <sup>a</sup>	Water purification plant and mineral water	2 mmol/l potassium dichromate, 2 mmol/l DETA, pH 7.5	Indirect UV (265 nm)	[20]
Chloride bromide, sulfate, nitrate, iodide, nitrite, fluoride, phosphate and organic acids <sup>a</sup>	Model mixture; drinking, river and rain water	7 mmol/l succinate, BTP, 5% PVP, 0.2% MHEC, pH 3.55	Cd	[22]
Thiosulfate bromide, chloride, sulfate, nitrite, nitrate, tungstate, molybdate, fluoride, phosphate, carbonate, organic acids and inorganic cations <sup>a</sup>	Model mixture; tap and rain water	6 mmol/l 4-aminopyridine, 2.7 mmol/l chromic acid, 30 μmol/l CTAB, pH 8	Indirect UV (262 nm)	[162]
Nitrite and nitrate	Water	Sodium chloride, OFM Anion-BT	Direct UV (210 nm)	[181]
Bromide chloride, sulfate, nitrite, nitrate, fluoride and phosphate <sup>a</sup>	Model mixture; drinking, ground and waste water	4 mmol/l sodium chromate, 0.3 mmol/l CIA-Pak OFM Anion-BT, pH 8.1	Indirect UV (254 nm)	[163]
Chloride, bromide, nitrate, sulfate, perchlorate, fluoride, phosphate and carbonate	River, rain, tap and waste water	Organic photometric reagent	Indirect UV	[164]
Bromide chloride, nitrite, sulfate, nitrate, chlorate, fluoride, phosphate and carbonate <sup>a</sup>	Model mixture; mineral water	5 mmol/l potassium dichromate, 1.6 mmol/l TEA, 0.1 mmol/l DMOH (DMBr), pH 8	Indirect UV (260 nm)	[16]
Nitrate chloride, sulfate and nitrite <sup>a</sup>	Model mixture; drinking water	Cadmium acetate (4 mmol/l, cadmium nitrate, 10 mmol/l, acetic acid)	Cd	[2]
Nitrate and nitrite <sup>a</sup>	Model mixture; well water	25 mmol/l sodium phosphate, 0.5% DMMAPS, 1% Brij-35, pH 3	Direct UV (214 nm)	[24]
Nitrite and nitrate	Mineral and well water	Borate, 0.4 mmol/l CTAB, pH 8.2		[165]
Bromide iodide, nitrate, selenate, bromate, iodate, nitrite and selenite <sup>a</sup>	Model mixture; river water	25 mmol/l sodium/disodium phosphate, 25 mmol/l phosphoric acid, pH 3	Direct UV (200 nm)	[23]
Nitrite, bromide and nitrate <sup>a</sup>	Tap and river water	20 mmol/l sodium tetraborate, 1.1 mmol/l CTAC, pH 8.94	Direct UV (200 nm)	[32]
(a) Bromide, chloride, sulfate, nitrite, nitrate, fluoride, phosphate and carbonate <sup>a</sup> (b) Nitrite and nitrate <sup>a</sup>	(a) Model mixture; estuarine water (b) estuarine water	(a) 5 mmol/l sodium chromate, 0.5 mmol/l CIA-Pak OFM Anion-BT, pH 8 (b) 10 mmol/l sodium sulfate, 0.5 mmol/l CIA-Pak OFM Anion-BT	(a) Indirect UV (254 nm) (b) Direct UV (214 nm)	[171]
Thiosulfate chloride, sulfate, nitrate, suiphide, sulfite, fluoride, phosphate, carbonate, hydroxide and organic acids <sup>a</sup>	Model mixture; tap water	6 mmol/l sodium chromate, 3 mmol/l boric acid, 32 μmol/l CTAB, pH 8 (sodium bromate)	Indirect UV (372 nm)	[140]
Thiosulfate chloride, sulfate, nitrate and carbonate <sup>a</sup>	Tap water	6 mmol/l potassium chromate, 3 mmol/l boric acid, 30 μmol/l CTAB, pH 8	Indirect UV (372 nm)	[142]

Table 4 (continued)

Anions	Sample	Electrolyte system	Detection	Reference
Chloride, nitrate, sulfate, fluoride, phosphate and carbonate <sup>a</sup>	Lake water	10 mmol/l sodium chromate, 1 mmol/l TTAB	Indirect UV	[172]
Thiosulfate bromide, chloride, sulfate, nitrite, nitrate, fluoride and phosphate <sup>a</sup>	Model mixture; tap water	2.25 mmol/l PMA, 6.5 mmol/l sodium hydroxide, 0.75 mmol/l HMOH, 1.6 mmol/l TEA, pH 7.7	Indirect UV (250 nm)	[61]
Bromide nitrite, nitrate, iodide and thiocyanate <sup>a</sup>	Model mixture; subterranean water	100 mmol/l sodium chloride, 2.0 mmol/l CTAC	Direct UV (214 nm)	[182]
Bromide chloride, sulfate, nitrate, fluoride, phosphate and carbonate <sup>a</sup>	ground and surface water, stemflow	1.13 mmol/l PMA, 0.8 mmol/l TEA, 2.13 mmol/l HMOH, pH 7.7	Indirect UV (254 nm)	[63]
Nitrate and chlorate	swimming pool water	(a) 10 mmol/l chromate, 0.1 mmol/l CTAB (b) 10 mmol/l sulfate, 0.1 mmol/l CTAB	(a) Indirect UV (254 nm) (b) Direct UV (214 nm)	[173]
<i>(B) Sea water</i>				
Bromide nitrite and nitrate <sup>a</sup>	Sea water, pH 7	Tenfold-diluted artificial sea	direct UV (200 nm)	[174]
<i>(C) Waste water</i>				
(a) Thiosulfate, iodide, and biphthalate <sup>a</sup>	(a) Effluent sample	10 mmol/l sodium sulfate, 0.5 mmol/l CIA-Pak OFM-OH, pH 11.4 (sodium hydroxide)	Direct UV (229 nm)	[177]
(b) Thiosulfate, nitrite, nitrate, sulfide and molybdate <sup>a</sup>	(b) Waste water			
Chloride, sulfate, nitrate, phosphate and carbonate <sup>a</sup>	Waste water	4.5 mmol/l sodium chromate, 0.5 mmol/l CIA-Pak OFM Anion-BT, pH 8.1	Indirect UV (254 nm)	[178]
Chloride sulfate, nitrite, nitrate, fluoride, phosphate, carbonate and organic acids <sup>a</sup>	Waste water	9 mmol/l PDC, 0.5 mmol/l TTAB, pH 7.8 (sodium hydroxide)	Indirect UV (254 nm)	[179]
<i>(D) Rain water and atmospheric aerosols</i>				
Chloride nitrate, sulfate, carbonate and organic acids <sup>a</sup>	Model mixture; single cloud, fog and rain drops	20 mmol/l salicylic acid, 32 mmol/l Tris, 0.001% Polybrene, pH 8.1	Indirect UV (220 nm)	[175]
(a) Chloride, nitrate, sulfate, carbonate and organic acids <sup>a</sup>	rain sample	(a) 7.5 mmol/l <i>p</i> -aminobenzoate, 0.75 mmol/l barium hydroxide, 0.1 mmol/l TTAH, pH 9.4	(a) Indirect UV (264 nm) (b) Amperometric	[27]
(b) Nitrite and sulfite <sup>a</sup>		(b) 5 mmol/l sodium/disodium phosphate, pH 6.7		
Bromide chloride, nitrite, nitrate, sulfate, sulfite, fluoride, phosphate, carbonate and organic acids <sup>a</sup>	Model mixture; rain water	100 mmol/l CHES, 40 mmol/l lithium hydroxide, 0.02% Triton X-100, pH 9.3	Cd	[106]
Fluoride <sup>a</sup>	Rain water	1.13 mmol/l PMA, 0.8 mmol/l TEA, 2.13 mmol/l HMOH, pH 7.7	Indirect UV (254 nm)	[64]
Bromide chloride, sulfate, nitrite, nitrate and oxalate <sup>a</sup>	Model mixture; atmospheric aerosols	2.25 mmol/l PMA, 0.75 mmol/l HMOH, 6.5 mmol/l sodium hydroxide, 1.6 mmol/l TEA, pH 7.7–7.9	Indirect UV (254 nm)	[183] [184] [185]
Chloride, sulfate, nitrate and organic acids <sup>a</sup>	Model mixture; atmospheric aerosols	6 mmol/l sodium chromate, 2.5% (v/v) OFM Anion-BT, pH 8–8.1	Indirect UV (254 nm)	[186]

(continued on next page)

Table 4 (continued)

Anions	Sample	Electrolyte system	Detection	Reference
Chloride, sulfate, nitrate, phosphate and organic acids <sup>a</sup>	atmospheric aerosols	sodium chromate, Tris, TTAB, potassium phthalate, pH 8 (sulfuric acid)	Indirect UV (254 nm)	[187]
<i>(E) Soil</i>				
Bromide chloride, sulfate, nitrite, nitrate, fluoride, phosphate and carbonate <sup>a</sup>	Model mixture; phosphate extract of a soil	5 mmol/l sodium chromate, 0.5 CIA-Pak OFM Anion-BT, pH 8	Indirect UV (254 nm)	[171]
Bromide chloride, sulfate, nitrite, nitrate, chlorate, perchlorate, fluoride, formate and carbonate <sup>a</sup>	Model mixture; soil extract	5 mmol/l sodium chromate, 0.2 mmol/l TTAB, pH 8.2 (sulfuric acid)	Indirect UV (275 nm)	[189]
(a) Chloride, sulfate, nitrate and oxalate <sup>a</sup> (b) Chloride, phosphate and organic acids <sup>a</sup>	Soil solutions	(a) 3 mmol/l TMA, 0.02% (v/v) DETA, pH 5.8 (sodium hydroxide) (b) 8 mmol/l Tris, 2 mmol/l TMA, 0.3 mmol/l TTAB, pH 7.6	Indirect UV (254 nm)	[190]
<i>(F) Food, vegetable and plant materials, cosmetics</i>				
Chloride, nitrate, sulfate, phosphate and organic acids <sup>a</sup>	Model mixture; wines and fruit juices	3 mmol/l PMA, 3 mmol/l DETA, pH 7.5	Indirect UV (220 nm)	[57]
(a) Bromide, chloride, ferrocyanide, nitrite, nitrate, sulfate, azide, molybdate, tungstate, fluoride, selenite, phosphate, carbonate and organic acids <sup>a</sup> (b) Bromide, chloride, iodide, nitrite, nitrate and sulfate <sup>a</sup>	(a) model mixture; soft drink (b) multivitamin supplement	(a) 50 mmol/l CHES, 20 mmol/l lithium hydroxide, 0.03% Triton X-100, pH 9.2 (b) 75 mmol/l boric acid, 30 mmol/l lithium hydroxide, 0.75 mmol/l HMOH, pH 8.95	Cd	[56]
Chloride bromide, nitrite, sulfate, thiosulfate, nitrate, molybdate, carbonate, tungstate, fluoride, phosphate, borate and organic acids <sup>a</sup>	Model mixture; vegetables	10 mmol/l chromate, 2.3 mmol/l C TAB, pH 11.5 (sodium hydroxide)	Indirect UV (254 nm)	[34]
Thiosulfate chloride, sulfate, nitrate, suiphide, sulfite, fluoride, phosphate, carbonate, hydroxide and organic acids <sup>a</sup>	Model mixture; mud, juice and milk	6 mmol/l sodium chromate, 3 mmol/l boric acid, 32 μmol/l CTAB, pH 8 (sodium borate)	Indirect UV (372 nm)	[140]
Thiosulfate bromide, chloride, sulfate, nitrite, nitrate, tungstate, molybdate, fluoride, phosphate, carbonate, organic acids and inorganic cations <sup>a</sup>	Model mixture; mud and milk	6 mmol/l 4-aminopyridine, 2.7 mmol/l chromic acid, 30 μmol/l CTAB, pH 8	Indirect UV (262 nm)	[162]

Table 4 (continued)

Anions	Sample	Electrolyte system	Detection	Reference
(a) Chloride, sulfate, phosphate, carbonate and organic acids <sup>a</sup> (b) Sulfite, carbonate and acetate <sup>a</sup>	(a) Juice and milk (b) Wine and vinegar	6 mmol/l potassium chromate, 3 mmol/l boric acid, 30 μmol/l CTAB, pH 8	Indirect UV	[142]
Nitrite and nitrate	Food and meat products	OFM Anion-BT/sodium chloride	Direct UV (210 nm)	[181]
Chloride sulfate, phosphate, carbonate and organic acids <sup>a</sup>	milk	Chromate, OFM Anion-BT	Indirect UV (254 nm)	[194]
Chloride sulfate, phosphate and organic acids <sup>a</sup>	Model mixture; beer	5 mmol/l PDC, 0.5 mmol/l CTAB, pH 5.6 (sodium hydroxide)	Indirect UV (350 nm)	[192]
Chloride, sulfate, nitrate, phosphate, carbonate and organic acids <sup>a</sup>	Prenatal vitamin tablet	5 mmol/l chromate, 0.4 mmol/l CIA-Pak OFM anion BHT, pH 8	Indirect UV (254 nm)	[282]
Sulfite (as a sulfate)	Food and beverages	5 mmol/l sodium chromate, 0.5 mmol/l OFM anion-BT reagent, pH 8	Indirect UV (254 nm)	[196]
Fluoride and phosphate	Toothpaste	chromate	Indirect UV	[206]
Chloride sulfate, nitrate, tungstate, monofluorophosphate, fluoride and phosphate <sup>a</sup>	Model mixture; toothpaste	10 mmol/l sodium chromate, 0.1 mmol/l CTAB, pH 9.37	Indirect UV (254 nm)	[205]
<i>(G) Biological, biomedical, pharmaceutical and forensic samples</i>				
Bromide nitrite and nitrate <sup>a</sup>	Model mixture; serum, cerebrospinal fluid, urine and tissue	Sodium/disodium phosphate, 1.4% sodium chloride, 0.1% PEG 8000	Direct UV (214 nm)	[149]
Chloride nitrite, nitrate, sulfate, phosphate and carbonate <sup>a</sup>	Rat lung airway surface fluid	100 mmol/l CHES, 40 mmol/l lithium hydroxide/2-propanol 92:8 (v/v), 80 μmol/l spermine, pH 9.3	Cd	[268]
Chloride nitrate, sulfate, carbonate and organic acids <sup>a</sup>	Urine	100 mmol/l CHES, 40 mmol/l lithium hydroxide, 3 mmol/l HMOH, pH 9.2	Cd	[56]
Nitrate and nitrite <sup>a</sup>	Model mixture; urine	25 mmol/l sodium phosphate, 0.5% DMMAPS, 1% Brij-35, pH 3	Direct UV (214 nm)	[24]
Nitrite and nitrate <sup>a</sup>	Urine, plasma and brain tissue	10 mmol/l sodium sulfate, OFM-OH	Direct UV (214 nm)	[207]
Bromide chloride, sulfate, nitrite, fluoride, phosphate, carbonate and organic acids <sup>a</sup>	Model mixture; drugs	Sodium chromate, sulfuric acid, OFM Anion-BT	Indirect UV (254 nm)	[202]
Bromide, chloride, fluoride, nitrite, sulfite, sulfate, perchlorate, chlorate and chlorite	Urine and post-mortem blood	5 mmol/l ammonium dichromate, 10 mmol/l ammonium acetate, 20 mmol/l DETA, 10% methanol, pH 9.3	Indirect UV	[59]

(continued on next page)

Table 4 (continued)

Anions	Sample	Electrolyte system	Detection	Reference
Thiosulfate bromide, chloride, sulfate, nitrite, nitrate, fluoride and phosphate <sup>a</sup>	Model mixture; urine and serum	2.25 mmol/l PMA, 6.5 mmol/l sodium hydroxide, 0.75 mmol/l HMOH, 1.6 mmol/l TEA, pH 7.7	Indirect UV (250 nm)	[61]
Chloride sulfate, phosphate and organic acids <sup>a</sup>	Model mixture; dental plaque extract and human saliva	5 mmol/l potassium phthalate, Nice-Pak OFM Anion-BT, pH 5.6	Indirect UV (254 nm)	[6]
Nitrite, nitrate and iodide <sup>a</sup>	plasma	200 mmol/l lithium chloride, 0.7–10 mmol/l TTAB, 5 mmol/l TEA, pH 11.3–12	Direct UV (200 nm)	[150]
Nitrite and nitrate	Plasma	75 mmol/l sodium chloride, 5% Nice-Pak OFM Anion-BT	Direct UV (214 nm)	[151]
(a) Bromide, chloride, sulfate, nitrite, nitrate, fluoride, phosphate and carbonate <sup>a</sup> (b) Chloride, sulfate, nitrite, nitrate, phosphate, arsenate, carbonate and arsenite <sup>a</sup>	Model mixture; urine	(a) sodium chromate, NICE-Pak OFM Anion-BT, pH 8 (b) sodium chromate, NICE-Pak OFM Anion-BT, pH 10	Indirect UV (254 nm)	[7]
Chloride, sulfate, nitrate phosphate, carbonate and organic acids <sup>a</sup>	Model mixture; heroin	(a) 2.25 mmol/l PMA, 6.5 mmol/l sodium hydroxide, 0.75 mmol/l HMOH, 1.6 TEA, pH 7.7 (b) Anitron kit (trimesic acid as a co-ion and Micro-Coat capillary charge-reversal agent)	(a) Indirect UV (250 nm) (b) Indirect UV (230 nm)	[204]
<i>(H) Industrial applications</i>				
(a) Thiosulfate, chloride, sulfate, nitrate, chlorate and fluoride <sup>a</sup> (b) Bromide, chloride, sulfate, nitrate, chlorate and fluoride <sup>a</sup> (c) Bromide, chloride, sulfate, nitrite, nitrate and fluoride <sup>a</sup> (d) Bromide, chloride, sulfate, nitrite, oxalate, nitrate and fluoride <sup>a</sup>	(a, b) Model mixture with hydrofluoric acid (c, d) Silicon wafer with an excess of fluoride solution	(a) 5 mmol/l sodium molybdate, pH 6.7 (b) 7.5 mmol/l potassium chromate, 2 mmol/l TTAOH, pH 8.5 (c) 7 mmol/l sodium molybdate, pH 6.7 (d) 6 mmol/l potassium chromate, 70 μmol/l TTAOH, pH 8.1	(a, c) Indirect/direct UV (211 nm) (b, d) Indirect UV (254 nm)	[217]
Bromide, sulfate, tetrafluoroborate, fluoride, monofluorophosphate and phosphate <sup>a</sup>	Borophosphosilicate thin film etched with hydrofluoric acid	10 mmol/l sodium chromate, 50 μmol/l OFM Anion-BT, pH 7.93 (sulfuric acid)	Indirect UV (254 nm)	[218]
Chloride, sulfate, nitrate, fluoride, phosphate and organic acids <sup>a</sup>	Model mixture; water extracts of head gimbal assemblies	(a) 10 mmol/l sodium chromate, 1.5 mmol/l OFM-OH, pH 11 (b) 7 mmol/l sodium chromate, 0.5 mmol/l OFM-OH, pH 8	Indirect UV (254 nm)	[220]



Table 4 (continued)

Anions	Sample	Electrolyte system	Detection	Reference
Bromide, chloride, sulfate, nitrite, nitrate, phosphate and fluoride <sup>a</sup>	Model mixture; silicone coatings	2.25 mmol/l PMA, 6.5 mmol/l sodium hydroxide, 0.75 mmol/l HMOH, 1.6 mmol/l TEA	Indirect UV (250 nm)	[65]
Bromide, chloride, sulfate, nitrate, chlorate, fluoride, phosphate and organic acids <sup>a</sup>	Model mixture; boric acid	5 mmol/l sodium chromate, 10 µmol/l TTAB, pH 8.1	Indirect UV (254 nm)	[147]
Bromide, chloride, sulfate, nitrite, nitrate, fluoride, phosphate and organic acids <sup>a</sup>	Model mixture; pure water, boric acid and morpholine	10 mmol/l sodium chromate, 0.5 mmol/l NICE-Pak OFM Anion-BT, pH 8 (sulfuric acid)	Indirect UV (254 nm)	[146]
Bromide, chloride, sulfate, nitrite, nitrate, fluoride, phosphate and carbonate <sup>a</sup>	Model mixture; boiler water and ink-jet dye	5 mmol/l sodium chromate, Nice-Pak OFM Anion-BT, pH 8	Indirect UV (254 nm)	[228]
(a) Chloride, sulfate, nitrate and carbonate <sup>a</sup> (b) Chloride, sulfate and phosphate <sup>a</sup>	(a) Model mixture; boiler water (b) Model mixture; dyes	(a) 7 mmol/l sodium chromate, 0.7 mmol/l CIA-Pak OFM anion-OH (b) 4.5 mmol/l sodium chromate, 0.5 mmol/l CIA-Pak OFM anion-BT, pH 8.1	Indirect UV (254 nm)	[224]
(a) Chloride, sulfate and citrate <sup>a</sup> (b) Chloride and sulfate <sup>a</sup> (c) Fluoride, carbonate, nitrate, nitrite, sulfate, chloride, bromide and persulfate <sup>a</sup> (d) Hypochlorite, carbonate, chlorate and chloride <sup>a</sup>	(a) Citrate (b) Sulfate (c) Persulfate (d) Hypochlorite	(a, b) 5 mmol/l sodium chromate, 0.5–1.5 mmol/l OFM Anion-BT, pH 8.0 (acetic acid) (c, d) 5 mmol/l sodium chromate, OFM Anion-BT, pH 11 (lithium hydroxide)	Indirect UV (254 nm)	[100]
Bromide and sulfate <sup>a</sup>	Detergents	5 mmol/l sodium chromate, sulfuric acid, 0.5 mmol/l CIA-Pak OFM Anion-BT, pH 8.0 (sodium hydroxide)	Indirect UV (254 nm)	[226]
Chloride, sulfate and nitrate	Detergents	PMA, HMC1	Indirect UV (254 nm)	[283]
Bromide, chloride, sulfate, nitrite, nitrate, chlorate, perchlorate, fluoride, formate and carbonate <sup>a</sup>	Model mixture; halone after chemical decomposition	5 mmol/l chromate, 0.2 mmol/l TTAB, pH 8.2 (sulfuric acid)	Indirect UV (275 nm)	[189]
Chloride, bromide and sulfate <sup>a</sup>	Potash (potassium chloride)	5 mmol/l sodium chromate 0.154% (w/v) PDDPiCr, pH 8.0	Indirect UV40 (254 nm)	
Chloride, sulfate, fluoride, phosphate, carbonate and organic acids <sup>a</sup>	Bayer liquor	5.5–7.5 mmol/l sodium chromate, 3–5 mmol/l TTAB, 1–3 mmol/l DTAB, pH 9	Indirect UV (254 nm)	[35]

(continued on next page)

Table 4 (continued)

Anions	Sample	Electrolyte system	Detection	Reference
Chloride, nitrite, sulfate, nitrate, fluoride, bromate, phosphate, carbonate and organic acids <sup>a</sup>	Model mixture; Bayer liquor	5–6.5 mmol/l sodium chromate, 2.35–5 mmol/l TTAB, 1–2.65 mmol/l DTAB, pH 8.8 (potassium hydroxide)	Indirect UV (254 nm)	[36]
(a) Bromide, chloride, sulfate, nitrite, nitrate, fluoride, phosphate <sup>a</sup>	(a) Model mixture	(a) 5 mmol/l sodium chromate, Nice-Pak OFM Anion-BT, pH 8	Indirect UV (254 nm)	[6]
(b) Thiosulfate, chloride, sulfate, carbonate and organic acids <sup>a</sup>	(b) Kraft black liquor	(b) 5 mmol/l sodium chromate, Nice-Pak OFM Anion-BT, pH 10		
Chloride and organic acids <sup>a</sup>	Model mixture; nickel-plating baths	25 mmol/l phosphate, 0.5 mmol/l OFM-OH	Direct UV (185 nm)	[230]
Molybdate and tungstate	Al–W, Mo alloy		Direct UV (214 nm)	[234]
Chloride and sulfate <sup>a</sup>	Concrete digested with concentrated nitric acid	10 mmol/l lithium nitrate, 1 mmol/l sodium thiocyanate, 0.8% (v/v) 1-butanol, pH 6	Direct UV (214 nm)	[232]

<sup>a</sup>The anions are arranged according to their migration order under given electrolytic conditions.

separation of inorganic ions. The results from these tests indicate the promising potential of contactless conductivity detection in the CZE analysis of this group of analytes.

#### 4.3.2. Suppressed conductivity detection

Following the concept of suppressed conductivity detection, as known in ion chromatography, Dasgupta and Bao [85] and Avdalovic and coworkers [17,84] developed suppressed conductivity detectors for CZE. This approach to conductivity detection has inherent capabilities for enhanced detection sensitivity in comparison to the non-suppressed types, as discussed in Section 4.3.1, for the following reasons: (i) suppression of the conductivity of the carrier electrolyte by the ion-exchange process reduces the effective mobility of the carrier ion in the detection sensor. When this ion-exchange process does not influence the effective mobility of the analyte (or less than that of the carrier ion) it, in fact, enhances the molar response of the conductivity detector for the analyte according to Eq. (8). (ii) The use of the suppression process in the detector eliminates requirements concerning the differences in the effective mobilities of the analytes and the carrier ions (see above). This is due to the fact that the effective

mobility of the carrier ion in the detection cell differs significantly from that in the separation compartment, while those for the analytes remain constant within the separation and detection phases. Impressive LOD values (low ppb concentrations), as reported by the above authors, are certainly linked, at least in part, with these advantages. However, it is not yet clear how efficiently these advantages of suppressed conductivity detection in CZE can be exploited.

#### 4.4. Other detection techniques

Ion-selective electrodes are available for some inorganic anions and are currently used in their routine analysis [8]. Some types of potentiometric sensors may be designed as micro- or submicro devices and used in combination with CE techniques. Their use in the CZE analysis of inorganic anions is the subject of several papers [71,119–121]. Despite the fact that they have some drawbacks as far as their lifetimes and reproducibilities are concerned, these simple detection devices offer very high sensitivities in the detection of common inorganic anions when CZE separation is combined with sample electro-tacking [119]. Enhanced selectivities of ion-selective

Table 5  
CZE speciation of inorganic anions

Anions	Sample	Electrolyte system	Detection	Reference
<i>P-species</i>				
Phosphorous compounds		5 mmol/l EDTA, 0.15 mmol/l Anion-BT	Direct/ indirect UV (210 nm)	[258]
(a) Trimetaphosphate, monofluorophosphate, phosphonate, orthophosphate, phosphinate, hexametaphosphate, pyrophosphate and polyphosphonates <sup>a</sup> (b) Pyrophosphate, tripolyphosphate, tetrapolyphosphate and orthophosphate <sup>a</sup> Ortho-, pyro- and tripolyphosphate	(a) Model mixture, soap and toothpaste (b) Model mixture	(a) 100 mmol/l boric acid, 5 mmol/l disodium tetraborate, 2 mmol/l DETA, 5 mmol/l AMP, pH 6.8 (b) 100 mmol/l boric acid, 0.2 mmol/l DETA, 5 mmol/l AMP, 2 mmol/l magnesium(II), pH 7.1	Indirect UV (259 nm)	[60]
Pyro-, tripoly-, tetrapoly- and orthophosphate (polyphosphates with different chain lengths) <sup>a</sup>	Model mixture	Phthalate 2.25 mmol/l PMA, 1.6 mmol/l TEA, 0.75 mmol/l HMOH, 6.5 mmol/l sodium hydroxide, pH 7.7	Indirect UV (254 nm)	[62]
Trimetaphosphate tripolyphosphate, pyrophosphates, fluoride, monofluorophosphate and orthophosphate <sup>a</sup>	Model mixture; toothpaste	5 mmol/l ATP, 0.02 mmol/l CTAB, pH 3.6 (sodium hydroxide)	Indirect UV (260 nm)	[260]
Trimetaphosphate tripolyphosphate, pyrophosphate, tetrapolyphosphate and orthophosphate <sup>a</sup>	Polyphosphoric acid	(a) 5 mmol/l PMA, 20 mmol/l Tris, pH 7.2 (polyacrylamide-coated capillary) (b) 5 mmol/l PMA, 20 mmol/l Tris, 0.02 mmol/l CTAB, pH 7.2 (c) 5 mmol/l PMA, 20 mmol/l Tris, 1% methylcellulose, pH 7.2	Indirect UV (254 nm)	[261]
Tripolyphosphate pyrophosphate, orthophosphate and polycarboxylic acids <sup>a</sup>	Model mixture; detergent	(a) 5 mmol/l potassium chromate, 0.05 mmol/l CTAB, pH 3.5 (nitric acid) (b) 10 mmol/l ATP, 0.05 mmol/l CTAB	Indirect UV (260 nm)	[262]
<i>As-species</i>				
Arsenious dimethylarsinic, monophenylarsonic, monomethylarsonic and arsenic acids <sup>a</sup>		25 mmol/l sodium/disodium phosphate, pH 5.8–8	Direct UV (190 nm)	[238]
Arsenite, arsenate, monomethylarsonic and dimethylarsinic acids	Fish extract	10 mmol/l DTEADP, pH 8	Direct UV (190 nm)	[239]

(continued on next page)

Table 5 (continued)

Anions	Sample	Electrolyte system	Detection	Reference
As(III) and As(V)	Industrial waste		ICP/AES	[240]
Four arsenical species, selenate and selenite	Drinking water		ICP-MS	[124]
Arsenate	Model mixture;	20 mmol/l potassium	ICP-MS	[125]
monomethylarsonic acids, dimethylarsinic acid and arsenite <sup>a</sup>	drinking water	phthalate, 20 mmol/l boric acid, pH 9.03		
Arsenic anions			UV	[241]
Dimethylarsinic and monomethylarsonous acids			MAS	[242]
Arsenite, monomethylarsonic acid, arsanilic acid, dimethylarsinate and arsenate		Phosphate	Direct UV (191 nm)	[243]
Arsenocholine arsenate, monomethylarsonic acid, dimethylarsinic acid, arsenite and arsenobetaine <sup>a</sup>	Percolated water and leachate of waste	2.5 mmol/l sodium/disodium phosphate, phosphoric acid, 2% OFM-OH, pH 10	Direct UV (185 nm)	[244]
<i>S-species</i>				
Thiosulfate sulfide and sulfite <sup>a</sup>	Model mixture	Tris, hydrochloric acid, pH 8.75	Direct UV (200 nm)	[267]
Thiosulfate sulfite and sulfide <sup>a</sup>	Model mixture; corroding stainless steel crevice	(a) 25 mmol/l sodium chloride, 4 mmol/l OFM BT-OH, pH 10.8 (b) 1.5 mmol/l sodium sulfate, 2 mmol/l OFM BT, pH 10.5	Direct UV (214 nm)	[234]
Thiosulfate chloride, sulfate, nitrate, sulfide, sulfite, carbonate and organic acids <sup>a</sup>	Model mixture; soft drink, vinegar and wine	6 mmol/l potassium chromate, 3 mmol/l boric acid, 23–30 µmol/l CTAB, pH 8.75	Indirect UV (372 nm)	[143]
Thiosulfate chloride, sulfate and sulfide; tetrathionate separately (precipitation) <sup>a</sup>	Natural clayey water	10 mmol/l Tris, 1.5 mmol/l PMA, 0.5 mmol/l DETA, pH 8	Indirect UV (214 nm)	[58]
(a) Hydroxide, thiosulfate, chloride, sulfate, sulfite, carbonate and organic acids <sup>a</sup> (b) Hydroxide, thiosulfate, chloride, sulfate, sulfide and carbonate <sup>a</sup>	Model mixture; Kraft liquor	5 mmol/l sodium chromate, 0.5 mmol/l Nice-Pak OFM Anion-BT, pH 10.6–11 (sodium hydroxide)	(a) Indirect UV (254 nm) (b) Direct/indirect UV (214 nm)	[235]
Iodide thiosulfate, thiocyanate, sulfate, dithionate and tetrathionate	Model mixture	100 mmol/l boric acid, 5 mmol/l disodium tetraborate, 2 mmol/l DETA, 3 mmol/l NTS, pH 8	Indirect UV (284 nm)	[21]
<i>Se-species</i>				
Selenate, selenite, selenocystine and selenomethionine		TTAB, pH 8.5		[248]

Table 5 (continued)

Anions	Sample	Electrolyte system	Detection	Reference
Se(IV), Se(VI), selenomethionine and selenocysteine				[249]
Inorganic and organic (amino acids) selenium anions	Bacterial cell extract and synthetic sea water		ICP–AES	[284]
Four arsenical species, selenate and selenite	Drinking water		ICP–MS	[124]
Selenate and selenite	Bacterial suspensions	20 mmol/l sodium borate, 1.0 mmol/l TTAB, pH 9.5	Direct UV (200 nm)	[250]
<i>Halogen species</i>				
Chloride, sulfate, nitrate, chlorate, perchlorate and chlorite <sup>a</sup>	Model mixture; bleaching preparation, tap and swimming pool water	4.6 mmol/l sodium chromate, 0.46 mmol/l CIA-PAK OFM Anion BT, pH 8	Indirect UV (254 nm)	[266]
Periodate and iodate <sup>a</sup>	Model mixture; chromatographic support	500 mmol/l sodium acetate, pH 4	Direct UV (222 nm)	[263]
Periodate and iodate <sup>a</sup>	Model mixture; carbohydrates	100 mmol/l sodium acetate, pH 4.5 (sodium hydroxide)	Direct UV (222 nm)	[264]
Bromide, chloride, chlorate, bromate, perchlorate, chlorite and iodate <sup>a</sup>	Model mixture	100 mmol/l boric acid, 5 mmol/l disodium tetraborate, 2 mmol/l DETA, 3 mmol/l NTS, pH 8	Indirect UV (284 nm)	[21]
Chloride, chlorate, perchlorate, nitrite, nitrate, bromide and bromate		Potassium chromate, OFM	Indirect UV	[265]
<i>Cr-species</i>				
Chromium(VI) and chromium(III)		100 mmol/l chloroacetic acid, sodium chloroacetate, Mo(VI), pH 2–3	Direct UV (256 nm)	[252]
Chromium(III) (as a chromic acid–EDTA complex), chromium (VI) and nitrate		10 mmol/l phosphate, 0.5 mmol/l CTAB	Direct UV (254 nm)	[253]
Chromium(III) as a chromic acid–CDTA complex and chromium (VI)		Formate	Direct UV	[254]
Cr(III) and Cr(VI)	Water		Direct UV	[255]

<sup>a</sup>The anions are arranged according to their migration order under the given electrolytic conditions.

detection electrodes for some of these anionic constituents (iodide, nitrite, nitrate, thiocyanate) may be of interest for specific samples.

The data summarized in Table 5 show that CZE is a technique that is suitable to speciations of some elements present in different anionic constituents. Here, significant advantages can be expected by coupling CZE with inductively coupled plasma mass

spectrometry (ICP-MS), as already shown in several papers [122–125]. CZE can be interfaced with ICP-MS via nebulization [122,123] and the LOD values are linked with the efficiency of the nebulizer. However, in this instance, the carrier electrolyte constituents can cause build-up on the sampling interface, influencing the long-term stability of the detection system [125]. Recent works by Magnuson

et al. [124,125] implemented into the CZE–ICP-MS combination in the conversion of arsenic constituents into arsenic trihydride followed by diffusive hydride transfer into the ICP-MS system via a PTFE membrane. In this combination, the CZE separation was performed in a hydrodynamically modified electroosmotic flow of the carrier electrolyte solution. For a group of anionic arsenic constituents (arsenite, arsenate, monomethylarsonate and dimethylarsinite), LOD values in the range of 6–50 ppt were reported for this CZE–ICP-MS combination [125]. The electropherogram in Fig. 5 illustrates the use of this detection technique.

Mass spectrometry (MS) using an ion spray atmospheric pressure ionization source was coupled with co-electroosmotic CZE to detect inorganic anions [73]. Depending on the ion-adduct declustering and molecular fragmentation in the MS interface, the system could operate as an elemental analyzer or as a molecular detector for the determination of the oxidation state. The EOF modifiers in the carrier electrolyte solution were eliminated by using a capillary tube coated with a cationic polymer. Such CZE working conditions improved the background

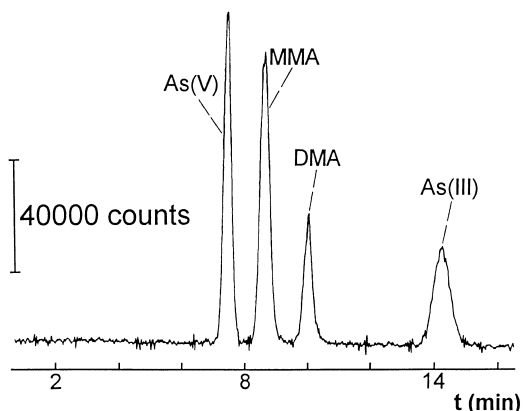


Fig. 5. CZE separation of arsenic species with ICP-MS detection. Peaks: As(V)=arsenate; MMA=monomethylarsonate; DMA=dimethylarsinate; As(III)=arsenite (each of the analytes at a concentration of 1 ppb). Capillary, 85 cm $\times$ 75  $\mu$ m I.D. fused silica; sample injection, electrokinetic (2 min with a superimposed hydrodynamic flow); carrier electrolyte, 20 mmol/l potassium hydrogen phthalate and 20 mmol/l boric acid (pH 9.03). For further details on experimental conditions, see ref. [125]. Adapted from ref. [125] with permission.

noise of the detector and reduced the complexities of mass spectra.

Recently, Vogt et al. [126] described an on-column detector based on proton-induced X-ray emission (PIXE). This introductory work showed its potential in terms of the detection selectivity relevant to CZE speciation of some elements.

## 5. Sample pretreatment techniques in the CE analysis of inorganic anions

Although sample preparation procedures in the determination of inorganic anions by CE techniques can include only simple operations [e.g. filtration, extraction of the analyte(s), sample dilution, pH adjustment, protein precipitation], this is not a general situation in the analysis of many practical samples. Very low concentrations of anions in samples, high concentrations of sample matrix anions relative to the analytes, multicomponent sample matrices, and matrix constituents that disturb the CZE separation are general problems that may be encountered in the analysis of practical samples.

### 5.1. Pre-column sample pretreatment

#### 5.1.1. Off-line pre-column sample pretreatment

Some of the sample pretreatment procedures, as elaborated for the determination of inorganic anions by other analytical techniques, are potentially applicable in CE. A recent overview of the sample pretreatment procedures used in the determination of inorganic anions in various matrices and by various analytical techniques can be found in the guidebook by Crompton [8]. Also, sample preparation techniques and procedures, as developed for ion chromatography [127,128], should be mentioned in this respect.

Fukushi and Hiiro [129,130] showed that coprecipitation enrichment is a convenient sample pretreatment technique in the ITP determination of fluoride and phosphate in sea water. Yoshida and Hida [131] used ion-pair extraction for the isolation of phosphate in a form of molybdophosphate complex from aqueous samples in a combination with the ITP determination. Here, the ITP separation in a dimethylformamide electrolyte system was favour-

able, as a chloroform extract (containing the phosphate complex) could be injected directly into the ITP analyzer. Taga et al. [132] employed ion-pair extraction in the ITP trace determination of phosphate. In this sample pretreatment procedure, considerable concentration of the analyte was achieved by trapping the molybdophosphate complex on a regenerated cellulose membrane. In a subsequent step, the membrane was dissolved in dimethylformamide and the resulting solution could be analyzed directly by ITP.

Cation exchangers in the silver form may be used to precipitate chloride in samples containing this anion in a large excess relative to the other anions (biological material, food products). This sample preparation procedure was used, e.g., in a combination with the ITP determination of sulfate, nitrate and phosphate in vegetable juices [133]. A PTFE membrane impregnated with a high purity cation-exchange resin was shown to effectively remove carbonate or hydroxide anions (cation exchanger in the hydrogen form), chloride or other halides (silver form) or sulfate (barium form) from samples before the CZE determination of inorganic anions [134].

Gas diffusion may be considered as a very selective sample pretreatment technique that is applicable to the isolation of some microconstituents from complex ionic matrices, in combination with CE separation techniques. The determination of bromide [135], carbon dioxide [136] and sulfide [286] in sea water samples may be given as examples of the off-line combination of this technique with CE. Its routine use may be very practical when sample pretreatment is automated, as described in Section 5.1.2.

#### 5.1.2. Coupling capillary zone electrophoresis with flow-injection systems

Flow-injection (FI) systems offer modules that are suitable for the automation of sample handling and/or sample pretreatment operations in CZE [137]. In this way, various sample pretreatment methodologies that are transferable into the FI format (e.g., solid-phase extraction, filtration, dialysis, gas diffusion, liquid–liquid extraction, precipitation reactions) can be used in combination with CE.

At present, FI modules are combined with laboratory-made CE instruments. A technical solution has

been described [20] that couples commercial CE equipment with FI systems via an interface, introducing the pretreated samples into the sample vials of the CE equipment. This approach was used in the CZE analysis of water samples, in combination with an ion-exchange sample pretreatment step [20] and in the determination of chloride, sulfate, nitrate and nitrite in soil samples [138]. The pretreatment of soil samples included extraction of the analytes and filtration of the resulting aqueous soil suspensions.

In the FI–CE tandem, as proposed by Kuban et al. [139], the sample that had been pretreated in the FI system was injected into a stream of the carrier electrolyte solution via a valve. This stream served as a source of the sample for its electrokinetic injection into the CZE system. Dialysis (inorganic and organic anions in milk and juice samples), gas diffusion (sulfite in wine, sulfite and acetate in vinegar), extraction on supported liquid membranes (cyanide and metallo-cyanides) are sample pretreatment techniques that have already been used in this FI–CE combination [140–143].

### 5.2. In-column sample pretreatment

#### 5.2.1. Electrostacking in capillary zone electrophoresis

In some situations, CZE itself concentrates the analytes present in the injected samples. This is due to the fact that the CZE separation of the analytes is accompanied by their concentration adaptations [104,105]. From the point of view of the concentration of the analytes, it is important that this adaptation process (electrostacking) becomes practical when the concentration of the carrier ion is significantly higher than the total concentration of the constituents present in the injected sample [144]. From this, it is clear that electrostacking can be exploited in a straightforward way for low-ionic-strength samples. In such instances, sample volumes loadable onto the column may be very high, as compression of the sample volume in the column in the initial phase of the separation eliminates band broadening [145]. These features of electrostacking are of interest, e.g., in the determination of trace inorganic anions present in non-ionic matrices [46].

Concentration of the ionized forms of some sample matrix constituents (weak acids and weak bases)

can be minimized by proper pH adjustment of the sample. When this pH adjustment is followed by the CZE separation carried out at a pH leading to (very) low effective mobilities of the matrix ion(s), very high sample loads can be applied, as the electrostacking process will concentrate selectively only ionized analytes. The CZE determination of trace inorganic anions present in boric acid [146,147] may serve as an example illustrating this approach. However, in this context, it should be noted that the use of a carrier electrolyte with a low pH-buffering capacity may require the use of a more complex separation protocol [147]. A recent work by Doble et al. [148] dealing with pH buffering in currently used chromate electrolyte systems may be instructive in this respect.

When electrostacking is applied in the trace analysis of inorganic anions, the purity of the carrier electrolyte solution becomes essential. For example, the work by Wojtusik and Harrold [66] showed that inorganic anionic impurities, present in the carrier electrolyte solution at concentrations as low as 10 ppb, are clearly detectable. The analytical impact of this on the detection and/or quantitation of trace constituents is obvious.

Electrostacking is not restricted to low-ionic-strength samples. For example, it is also effective in the CZE determination of nitrate and nitrite in biological matrices when highly concentrated carrier electrolyte solutions are used [24,149–151]. However, in these particular instances, high concentrations of less mobile anions present in the samples can introduce parallel ITP stacking (see below).

### 5.2.2. Transient isotachopheresis stacking in capillary zone electrophoresis

Observed for the first time in the CZE separation of organic acids present in serum samples [152], transient ITP stacking is currently used as a tool for the improving detectability by CZE of microconstituents in samples containing highly mobile macroconstituents (see also Fig. 6). A theoretical description and basic electrolyte requirements for transient ITP stacking in CZE can be found in the literature [153–155].

As shown by Jandik and Jones [3], transient ITP stacking led to a more than 100-fold increase in sensitivity in the determination of trace inorganic

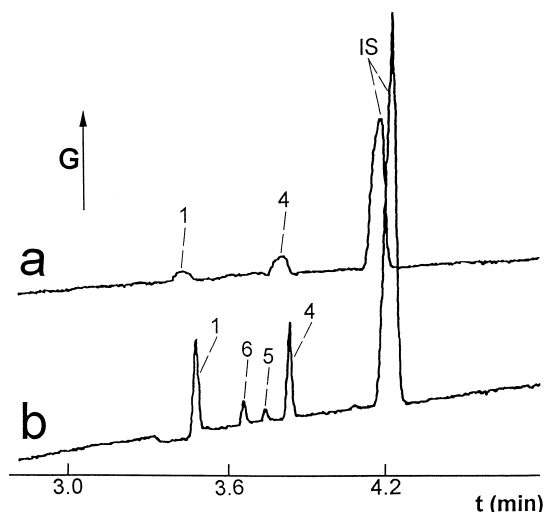


Fig. 6. CZE separation of trace inorganic anions with different types of electrokinetic injection. Peaks: 1=chloride (1 ppb), 4=sulfate (1 ppb), 5=nitrate (trace), 6=nitrite (trace), IS=tungstate (30 ppb). a=electrokinetic injection (5 kV for 24 s); b=electrokinetic injection with transient ITP stacking [preinjection of the leading electrolyte (10 mmol/l LiOH) at 40 mbar for 18 s; sample, 5 kV for 24 s]. Contact conductivity detection. Adapted from ref. [108] with permission.

anions. In the quoted work, octanesulfonate added to the sample served as a terminating anion in the transient ITP stage. The same authors [100] determined chloride and sulfate in citrate using the major sample constituent as a terminating anion. Recently, a group of inorganic anions was determined at low- to sub-ppb concentration levels in a conductive sample matrix (2 ppm ammonia and 50 ppb hydrazine) using transient ITP stacking [108].

### 5.2.3. Isotachopheretic concentration of the analytes present in low-ionic-strength samples

Concentration adaptations of the analytes is characteristic for ITP [28,96]. In the analysis of low ionic strength samples, this ITP capability may be conveniently utilized in the determination of trace constituents. For example, trace inorganic anions present in glycerol samples with varying degrees of chemical purity, at  $2.5\text{--}9.5 \cdot 10^{-6}$  % concentrations [156], were determined by ITP, as sample volumes as large as 300  $\mu\text{l}$  could be loaded onto the column (Fig. 7). In this instance, the sample load capacity of the separation system was still far from being



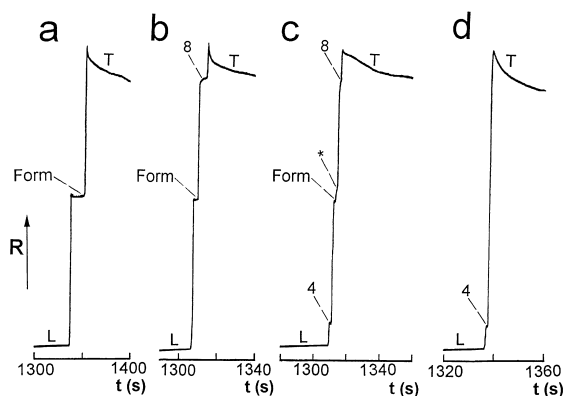


Fig. 7. Isotachopherograms from the analyses of different batches of glycerol. a=87% extrapure (formate,  $3.1 \cdot 10^{-4}\%$ ); b=100% extrapure (formate,  $5.9 \cdot 10^{-5}\%$ ; phosphate (8),  $6.3 \cdot 10^{-6}\%$ ); c=87% pro analysis (sulfate,  $4.8 \cdot 10^{-6}\%$ ; formate,  $7.8 \cdot 10^{-6}\%$ ; \*, unidentified); d=100% pro analysis (sulfate, below  $4.1 \cdot 10^{-6}\%$ ). The samples of glycerol were injected with the aid of a PTFE-lined sample injection valve with a 300- $\mu$ l internal sample loop. Leading electrolyte (L), 5 mmol/l HCl, 2 mmol/l BTP, pH adjusted with  $\beta$ -alanine to 3.6; EOF suppressor, 0.1% MHEC (w/v) in the leading electrolyte; terminating electrolyte (T), 5 mmol/l citric acid. The driving current was 32  $\mu$ A. Adapted from ref. [156] with permission.

completely exploited and, therefore, such a sample injection volume cannot be considered as an upper limit.

A reduction in the effective concentration of acetate anion in a sample (a low pH of the sample) followed by ITP separation at a low pH (to minimize the effective mobility of acetate) was effective in the determination of trace inorganic anions present in acetic acid [98]. Under these working conditions, sample volumes as large as 300  $\mu$ l could be injected for the separation and impressive concentration LOD values were achieved (trace inorganic anions present in acetic acid at  $0.32\text{--}1 \cdot 10^{-3}\%$  concentrations could be determined within 20 min).

### 5.3. On-line combinations of separation techniques

#### 5.3.1. On-line combination of isotachopheresis–capillary zone electrophoresis in a column-coupling separation system

Although it is possible to determine very low concentrations of inorganic anions by CZE in low-ionic-strength samples, problems occur when the

concentrations of the samples' constituents differ considerably. In these instances, electrostacking and transient ITP stacking are less effective, as the determination of microconstituents may require overloading the CZE column with sample. An on-line combination of ITP with CZE in the column-coupling configuration of the separation system offers very promising potential in such situations (see Fig. 8). Originally developed for the ITP separation of complex ionic mixtures [157,158], this configuration of the separation system was shown to be effective for an on-line combination of CZE with ITP sample pretreatment [159]. Concentration of the analytes, accompanied by well-defined in-column and post-column sample clean-up [160], is probably the main benefit of using ITP for sample pretreatment in this CE combination. This is because ITP sample pre-

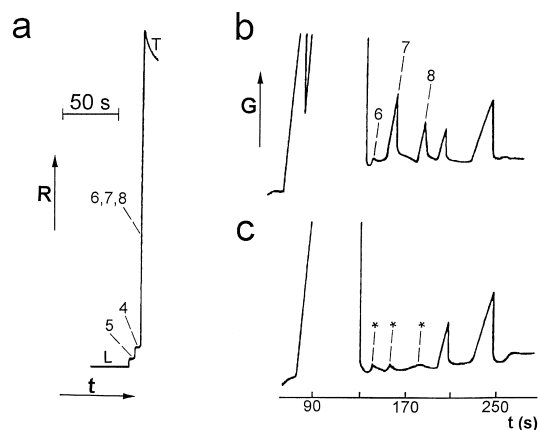


Fig. 8. ITP and CZE determination of macro- and microconstituents in a river water sample (Yamaska River, Quebec, Canada). The sample was injected directly into the column-coupling CE analyzer and was found by ITP to contain: chloride (L), 15 ppm (R.S.D.=2.6%); nitrate (5), 7.3 ppm (R.S.D.=0.5%); sulfate (4), 5.9 ppm (R.S.D.=0.9%). In the CZE stage the following were determined: fluoride (7), 13.1 ppb (R.S.D.=0.9%); phosphate (8), 60.9 ppb (R.S.D.=3.4%). Nitrite (6) was below the LOD (200 ppt). Asterisks in (c) indicate the migration positions of the microconstituents in the blank run. Leading electrolyte (L), 8 mmol/l HCl, 3 mmol/l BTP, pH adjusted with  $\beta$ -alanine to 3.4; EOF suppressor, 0.2% (w/v) MHEC in the leading electrolyte; terminating electrolyte (T), 4 mmol/l aspartic acid. The carrier electrolyte in the CZE stage, 10 mmol/l aspartic acid, pH adjusted with  $\beta$ -alanine to 3.4; EOF suppressor, 0.2% (w/v) MHEC in the carrier electrolyte. The driving currents were 250 and 75  $\mu$ A in the ITP and CZE modes, respectively. Adapted from ref. [161] with permission.

treatment considerably reduces the sample matrix load onto the CZE column while the concentrated analyte(s) is (are) transferred for a final CZE separation in a 'clean' sample fraction. Some of these advantages of the ITP–CZE tandem have already been illustrated in the analysis of common inorganic anions [161]. Here, sub-ppb LODs were achieved for nitrite, fluoride and phosphate, and these anions could be determined by CZE with a contact conductivity detector in samples with  $10^5$ – $10^6$ -fold higher concentrations of chloride, sulfate and nitrate. It was also shown that this configuration of the CE separation system allows the simultaneous ITP determination of chloride, nitrate and sulfate with the CZE determination of nitrite, fluoride and phosphate (see Fig. 9). For obvious reasons, this combination requires the use of chemicals of adequate purity (for details, see [161]).

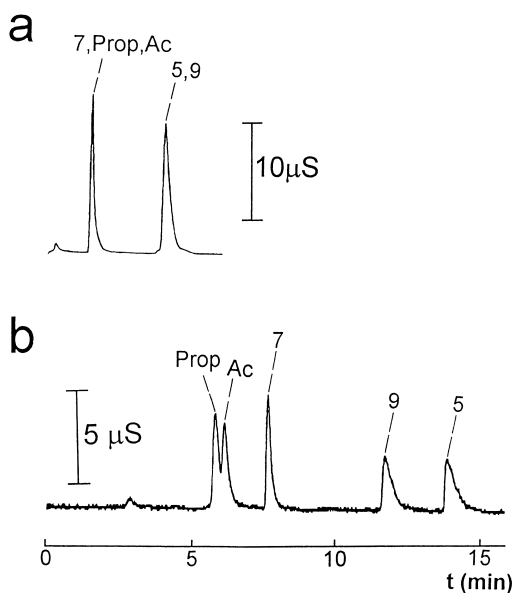


Fig. 9. Typical two-dimensional IC–CE separation of a mixture of anions using a valveless continuous interface. A = IC output from a mixture containing 100 ppm of propionate (prop), acetate (ac), nitrate (5), chlorate (9) and 20 ppm of fluoride (7). CZE output showing a complete separation by continuously introducing a portion of the IC effluent into the CZE system (50 cm capillary with a driving voltage of 15 kV). For further details on the experimental conditions, see ref. [107]. Adapted from ref. [107] with permission.

### 5.3.2. On-line coupling ion chromatography–capillary zone electrophoresis

Two approaches in coupling IC to CZE were described recently by Kar and Dasgupta [107]. In one of these IC–CZE combinations, a valve was used to transfer the desired fraction from the IC column effluent into the CZE column for final separation, with detection of the analytes by a suppressed conductivity detector. In the other approach, the IC column effluent was continuously transferred into the CZE column via a splitter. The ionic strength of the IC column effluent directed to the CZE column was modified by a suitable electrolyte (the carrier electrolyte at the CZE stage) at the CZE column inlet. In both instances, the use of suppressed IC was a significant advantage for the CZE separation, as CZE could handle low ionic strength samples. In addition, these IC–CZE combinations formed separation systems that exhibited some two-dimensional features (see Fig. 9).

## 6. Applications of CE techniques

In investigations aimed at finding suitable CE separating conditions for various groups of inorganic anions, different separation mechanisms and/or their combinations were studied. In this way, useful data related, especially, to the separation of inorganic anions by CZE were obtained. These are compiled in Tables 4 and 5 and, for a particular combination of the anions present either in a model mixture or in a practical sample, they provide the composition of the electrolyte systems and the detection conditions. The anions in the mixtures marked with asterisks are arranged in order of their increasing migration times, as shown in the electropherograms in the original papers. These data provide possibilities for the rapid assessment of various CZE separation alternatives relevant to a given mixture of anions.

### 6.1. Analysis of water, atmospheric aerosols and soil

The use of CE techniques for the analysis of inorganic anions present in water samples was studied by many authors. Some of the works related to this subject are given in Table 4. In the de-

termination of inorganic anions present in drinking [2,22,24,32,140,142,162–169], ground [63,163], mineral [16,165,170], surface [20,22,23,61,63,164,171–173], sea [174], rain [22,27,64,106,162,164,175,176] and waste [163,164,169,177–180] water samples by CZE, the use of chromate carrier electrolyte with indirect photometric detection was preferred. While the determination of macroconstituents (chloride, nitrate and sulfate) caused no problems (from the works quoted), it is apparent that the concentrations of typical inorganic anionic microconstituents (e.g., nitrite, fluoride, phosphate) in water were usually too low to be detected under these working conditions. The low sample load capacities of the columns (low I.D.s of the capillary tubes) and low concentrations of the carrier (visualization) anions probably explain the limitations of this, generally favoured, approach to the CZE determination of inorganic anions.

The use of sample pretreatment procedures as reviewed in the previous section may serve as a solution to the problems encountered in the determination of microconstituents. However, CE techniques themselves offer several alternatives for improving the detectability of microconstituents. Probably the simplest alternative is the use of electrokinetic injection, as suggested for estuarine water samples by Jackson and Haddad [171]. This sample injection technique provides discriminative concentrations of the separated constituents in the injection phase and, therefore, appropriate measures must be taken in the quantitation (e.g., the use of the standard addition technique [171]).

As discussed above, concentrated (high ionic strength) carrier electrolyte solutions are effective in enhancing sample loadability in CZE via electrostacking or transient ITP stacking of the sample constituents (see Section 5.2.1 Section 5.2.2.). These approaches were employed by several authors in the CZE determination of anionic microconstituents (nitrite, nitrate, bromide, thiocyanate, sulfide) present in water samples, in combination with direct photometric detection [23,24,32,165,171,173,174,181,182]. Although applicable to the determination of other inorganic anions (see Section 6.3 and the absorptivity data in Table 1), the limitations of these approaches are apparently linked with the limited applicability of direct photometric detection.

Conductivity detection offers a universal detection alternative (see Section 4.3) in the CZE analysis of inorganic anions. So far, however, it was used only in a limited number of works dealing with the CZE determination of inorganic anions in water [2,22,106,161]. Nevertheless, concentration LODs attainable for anions with conductivity detectors [22,56,84,85,108,161] and a comparison with indirect photometric detection [56] show that it is potentially a very powerful detection technique for inorganic ions, in general. Inorganic anions present in various water samples were separated by CZE in a 300- $\mu$ m I.D. capillary column with contact conductivity detection of the analytes [22]. Samples (200–400 nl) of moderate ionic strength could be injected into the column of such an enhanced sample loadability and, consequently, microconstituents (nitrite, fluoride and phosphate) could be determined from the response of the conductivity detector. CZE with conductivity detection on-line coupled with ITP separation (for details see Section 5.3.1) provides an integrated CE system that is suitable for the determination of inorganic anionic microconstituents in water samples in instances when the concentration ratio of macro- to microconstituents is very high.

A series of papers deals with the CZE determination of inorganic anions in atmospheric aerosols [183–187]. In an evaluation of a group of carrier electrolytes, pyromellitate was found to be an optimum carrier (visualization) anion for the most mobile (inorganic) anions, while 2,6-naphthalenedicarboxylate gave the best results for less mobile (organic) anions [184]. Under the CZE working conditions employed in the analysis of aerosol extracts, concentration LODs for the inorganic anions ranged from 170 to 220 ppb [184]. Good agreements of the results from the CZE determinations with those obtained by ion chromatography (deviations generally better than 20% at concentrations larger than 1 ppm) were reported [185].

Several authors studied the use of CZE for the determination of inorganic anions present in soil [138,171,188–190]. In the quoted works, attention was paid to the determination of chloride, sulfate and nitrate in aqueous soil extracts and soil solutions. Westergaard and Hansen [190] developed a complementary CZE method that was suitable for the

determination of low-molecular-mass organic acids. These authors showed that favourable CZE working conditions for both inorganic and organic anions require the use of two different electrolyte systems (a need for a match of the effective mobilities of the analytes with the carrier anion; see Section 4.2). The LODs for the inorganic anions under typical CZE working conditions, as reported by various authors [188,190], were in the range of 0.3–1.5 ppm for indirect photometric detection. Such detectabilities were sufficient for the determination of the anions in various types of soil samples. The use of electrokinetic injection offers improvements in the detectability of these samples, and also in instances when the anions are extracted from soil with buffer solutions [171]. Inorganic anions in soil extracts and soil solutions are accompanied by dissolved organic material. This material was reported to cause no problems in CZE analysis and this fact was noted as a practical advantage of CZE procedures in comparison to current procedures using mostly IC [190].

### 6.2. Analysis of food, plant materials, drugs and cosmetics

A rapid CZE procedure suitable for the simultaneous determination of inorganic and organic anions in wine and juice was developed by Arellano et al. [57,191]. Using pyromellitate as a carrier (visualization) anion, these authors achieved surprisingly low LODs for some inorganic anions with the aid of indirect photometric detection [the LOD values spanned from 14 ppb (sulfate) to 655 ppb (nitrate)].

Inorganic anions present in a cola drink (chloride, sulfate and phosphate) were separated in about 6 min using CZE with conductivity detection [56]. Soga et al. [192,193] described a rapid CZE method for the determination of inorganic (chloride, sulfate and phosphate) and organic acids in beer and wort. These anions were separated and quantified in less than 7 min using a very simple sample preparation technique (degassing and sample dilution). Reproducible results obtained in the determination of the anions agreed well with those provided by conventional methods [193].

A CZE procedure that was suitable for the determination of some inorganic anions (chloride, sulfate, phosphate) in milk was described by Schmitt

et al. [194] to monitor modifications of the ionic equilibria in milk under the influence of temperature changes. A simple sample preparation technique (ultrafiltration and dilution of the ultrafiltrate) and a short analysis time made CZE very convenient in these ionic equilibria studies. The use of ITP in the determination of inorganic and organic acids during milk fermentation (milk souring) was described by Stránský et al. [195]. These authors showed that this CE technique provided very reproducible results in the determination of the major anions (R.S.D. values 1% or less) and they used it to monitor the kinetics of culture fermentation.

CE techniques were proved to be suitable for the determination of sulfite in food products and beverages [142,143,196]. Sulfite oxidized to sulfate using a Monier-Williams distillation was determined via the latter anion in one of the proposed CZE procedures [196]. An interesting approach was described by Kuban and Karlberg [142,143] using CZE with a FI sample pretreatment procedure (see Section 5.1.2). Gas diffusion sample pretreatment, which was used at the FI stage, provided the possibility of resolving the free and total contents of sulfite or related sulfur dioxide. The high selectivity and reproducibility of this pretreatment method were demonstrated using wine and vinegar samples [142,143].

The use of CZE for the determination of inorganic (bromide, chloride, nitrate, nitrite, sulfate and phosphate) and organic (formate, citrate, oxalate) anions in vegetables was studied in detail by Jimidar et al. [34]. In this work, special attention was paid to the quantitation of nitrite and nitrate. These anions were determined in various vegetable samples in two CZE runs that differed only in the sample injection technique. Nitrate (anionic macroconstituent in the samples) could be determined in the sample injected hydrodynamically, while, for nitrite, concentrating electrokinetic sample injection was needed. The results obtained by CZE agreed well with those obtained in comparative analyses performed by a reference method.

CZE with direct photometric detection (210 nm) was found to be suitable for the determination of nitrite and nitrate in various food products (cheese, cabbage puree, fruit juice, meat) [181]. Levels of nitrate and nitrite in leaves of plants were determined

by CZE in the work by Kawamura et al. [197]. The microanalytical features of CZE were found to be useful in the determination of inorganic anions present in cell sap samples obtained from plant tissues [198].

The use of ITP for the determination of nitrate [199], and nitrate and sulfate [200] in vegetables was also studied and this CE technique provided rapid and reproducible procedures that required no sample preparation. Its evaluation within an International Plant–Analytical Exchange testing setup [200] revealed its very good performance in terms of accuracy and reproducibility of the determination of nitrate and sulfate in plant materials. In another report, ITP was shown to be suitable for the determination of fluoride in feed [201].

CZE is a useful analytical technique for inorganic anion screening in bulk pharmaceuticals and their intermediates, as demonstrated by Nair and Izo [202]. Using a current chromate buffer, these authors achieved (under optimized working conditions) LODs that were low enough (0.5 ppm) to detect some of the anions in pharmaceuticals. Similar possibilities of CZE are discussed in the work by Williams et al. [203]. Lurie [204] developed a CZE methodology that was suitable for the determination of inorganic anions, acetate, citrate and tartrate present in illicit drugs (heroin).

A CZE procedure for the separation of inorganic anions present in various brands of toothpaste, with emphasis on the determination of monofluorophosphate and fluoride, was described by Wang et al. [205]. Sample preparation before the CZE determination included removal of organic contaminants by SPE on a reversed-phase sorbent and filtration of the cleaned eluate. This sample preparation procedure gave good recoveries for both analytes and the results of the CZE determinations were in good agreement with those obtained by IC. The determination of fluoride in toothpaste by CZE is also described in the work by Harakuwe and Haddad [206].

### 6.3. Analysis of biological and biomedical samples

Nitrite and nitrate represent the products of the final pathway of nitric oxide metabolism. Therefore, these anions are analyzed in serum, urine, cere-

brospinal fluid and tissue homogenates. There is a series of CZE works that are linked either directly or indirectly with this problem [7,24,149–151,207–212]. Typically, in the CZE determination of nitrite and nitrate, direct photometric detection is preferred as it is fully compatible with (highly) concentrated carrier electrolyte solutions (see, e.g., [24,207,208,149,151]). An interesting detection scheme based on chemiluminescence in combination with CZE, which was suitable for the detection of nitrite and nitrate in biological fluids, was described recently [150].

For reasons discussed above (Section 5.2.1) the use of concentrated carrier electrolytes is favourable as it increases sample load capacities of the CZE columns for high-ionic-strength biological samples and, consequently, improves LODs for nitrate and nitrite. The determination of these anions in biological fluids can be further enhanced by the presence of acetonitrile in the samples (used in the precipitation of proteins [149]). LODs achieved for nitrate and nitrite in plasma and urine ultrafiltrates were 25 ppb [207] and, under these conditions, both anions were detected in rat brain ultrafiltrate. On the other hand, only nitrate was detected in the serum and urine ultrafiltrates. This fact was ascribed to oxidation of nitrite by oxidants present in plasma and urine [207]. The results obtained by Friedberg et al. [149] indicate that this need not be the general case.

The formation of S-nitroso compounds from nitroprusside, nitric oxide or nitrite and reduced thiols has a relevance to investigations of the biological roles of nitric oxide. ITP was found to be useful in monitoring the reactions involved in this process [213].

CZE with indirect photometric detection was used in the determination of sulfate in plasma in a study of abnormal sulfate metabolism in vitamin D-deficient rats [214]. MEKC, using alkyltrimethylammonium surfactants, was shown to be a promising technique for the determination of thiocyanate, iodide and nitrate in serum, in combination with ion-exchange sample pretreatment [87].

The submicroanalytical capabilities of CZE were effectively used in the determination of inorganic ions present in lung airway surface fluid [166,268]. Here, 100 nl samples collected from the surface via an injection capillary were immediately analyzed by

CZE with conductivity detection. Chloride, sulfate, nitrite, nitrate and phosphate could be determined in such ultrasmall sample volumes. CZE was adapted to the determination of nitrite and nitrate in single identified buccal neurons and ganglia in the opisthobranch mollusc *Pleurobranchaea californica* (a model system for the study of the chemistry of neuron function) [208]. Neurons were injected into the capillary and, after the separation, nitrate and nitrite were detected by direct photometric detection with LODs lower than 4  $\mu\text{mol/l}$ . These anions were present at mmol/l concentrations in NADPH-diaphorase-positive neurons and they were not detected in NADPH-diaphorase-negative neurons.

CE techniques may be conveniently used in monitoring the formation or depletion of inorganic anions in microbiological processes. ITP determination of thiosulfate produced from cystine by the keratinolytic prokaryote *Streptomyces fradiae* [215] and a bacterial-facilitated depletion of cyanide monitored by CZE [216] may serve as examples illustrating the potential of CE in this area.

#### 6.4. Technical material and industrial applications

Determination of inorganic anions present in various materials used in the production of advanced electronic components represent analytical problems in which CE techniques may find wide applicability. A series of CZE works dealt with analytical problems from this field [65,146,147,217–223]. The analysis of high purity water for inorganic (ultra)trace contaminants is one of these problems where the concentrating capabilities of CZE itself [146] or the use of CZE in combination with transient ITP stacking [3,56,108] can be beneficial in reaching sub ppb LODs for inorganic anions. The electropherograms shown in Fig. 6 clearly indicate the potential of the latter alternative in high purity water analysis applications.

The destructive analysis of borophosphosilicate thin film (routinely used as interlevel dielectrics in semiconductor very large scale integrated fabrication) by CZE in combination with its vapour-phase decomposition was described by Carpio et al. [218]. Here, CZE was shown to be an effective technique in the determination of boron (tetrafluoroborate) and phosphorus (phosphate and phosphite). Boden et al.

[217] described a CE procedure that was suitable for the determination of inorganic anions linked with low anionic contamination on as-polished silicon wafers. This procedure included transient ITP stacking in the initial phase of the separation followed by CZE destacking and separation. Bromide, chloride, sulfate, nitrite, nitrate, chlorate and oxalate were determined in this way. Verhelst et al. [65] investigated the use of CZE in the determination of inorganic ions in water extracts from dielectric silicone gels and from silicone protective coatings used in the production of electronic devices. Using electrokinetic sample injection (to concentrate the ions in the injection phase), they were able to determine chloride and sulfate in the extracts with LODs of about 10 ppb. Anions present at low level concentrations in water extracts from hard disk drive heads can be determined by CZE, as shown by Oehrlé [220]. Also, in this instance, the determination of the anions (chloride, sulfate, nitrate, fluoride, phosphate, oxalate) required the use of electrokinetic sample injection to reach sub ppb LODs. CZE can be useful in the analysis of chemicals used in the semiconductor and electronic industry. The CZE determination of chloride, sulfate, nitrate and phosphate in *N*-methyl-2-pyrrolidone and  $\alpha$ -butyrolactone (important solvents in the production of electronic components) should also be mentioned in this context [219].

The CZE determination of trace inorganic anions present in some inorganic chemicals, such as boric acid, ammonia and hydrazine, is possible [46,108,146,147]. Favourable working conditions are achieved when the major constituent is not ionized (see Section 5.2.1). In such situations, large sample volumes can be injected into the CZE column and, consequently, low LODs can be achieved. As shown by Bondoux et al. [146], the addition of a suitable terminating anion (e.g., octanesulfonate) to the sample may be essential for detecting (ultra)trace anions. Here, a transient ITP in the initial stage of the separation may also reduce losses of anions due to adsorption on the wall of the injection vial. These capabilities of CZE are favourable, e.g., for the determination of anions in ultrapure water used for steam generation in fossil and nuclear power plants [46,108,146,224,225]. For such sample types, ITP itself was shown to have advantages linked with the

very large sample volumes that it can accommodate (for details, see Section 5.2.3).

CE techniques were shown to provide convenient analytical alternatives for the determination of inorganic anions in various technical materials. Examples related to these applications include: the CZE determination of sulfate in detergent products [226], purity testing of sulfonic acids [227], determination of inorganic anions in inks by CZE [228,229], CZE analysis of nickel- [230] and chromium- [91] plating baths, ITP determination of chloride, chromate and sulfate in fresh concrete [231], CZE determination of chloride and sulfate in concrete digested with concentrated nitric acid [232], CZE determination of inorganic anions in water-miscible cooling lubricants [233], and the CZE determination of Cr(VI), Mo(VI) and (V) in steel [269].

In corrosion studies, the anionic constituents of interest may be present in the samples from the monitored sites at  $10^3$  times lower concentrations in comparison with the major constituents (typically chloride). Such concentration ratios of the sample constituents prevented the use of CZE electrolyte systems that are currently combined with indirect photometric detection in monitoring the corrosion processes of stainless steel [234]. In the quoted work, this problem was solved by using the major anionic constituent present in the sample as the carrier anion in the electrolyte system, in combination with direct photometric detection at 214 nm. This mobility match made the CZE separation of the inorganic anions of interest (thiosulfate, sulfide, sulfite, nitrite and nitrate) possible, when these were present in the samples containing chloride in about 100-fold excess and in the analysis of solutions from corroding stainless steel crevices.

Several of the CE applications have relevance to some industrial processes. Of these, studies by Haddad et al. [35] and Harakuwe et al. [36], aimed at the CZE separation of anions present in Bayer liquors (by-products of alumina and aluminium metal production), should be mentioned. The full resolution of chloride, sulfate, fluoride, carbonate, phosphate, oxalate, formate and malonate in Bayer liquor was possible under the separating conditions developed by these authors.

One of the first works dealing with the CZE separation of inorganic anions [6] showed that CZE

can be useful in the analysis of kraft black liquor (a complex ionic mixture originating from the processes in the pulp and paper industry). Here, it was shown that a simple sample clean-up procedure using SPE on octadecyl-modified silica is sufficient when the determination of major components (thiosulfate, chloride, sulfate, oxalate, formate, carbonate, acetate, propionate, butyrate) is of interest. A detailed investigation by Salomon and Romano [235] extended the number of anionic constituents detectable in the process fluids and provides a detail overview of the possibilities of CZE in the determination of inorganic and organic anions in the white, black and green liquors from kraft mills. Recently, other works dealing with the CZE determination of anions present in kraft black liquors were published [236,237].

#### 6.5. Speciation of inorganic anions

At present, CE techniques contribute to the speciation of the elements present in two or more ionic constituents (for a review of this subject, see, e.g. refs. [12–15]). From the works dealing with the CE speciation of elements present in anionic constituents, we can deduce that these separation techniques are applicable to speciations, mainly, in following instances: (i) when an element, in different oxidation states, is present in stable anionic constituents with different migration properties; (ii) when an element in a given oxidation state forms stable anionic constituents with different migration properties. This classification includes the CE separation of samples containing nitrate and nitrite as nitrogen speciations. However, these are not considered in this section and the separation of the two was not included in Table 5. This table summarizes some examples of the CZE speciation of anions of As, Se, Cr, P, S and halogen elements.

A series of works has been published that deals with the CZE separation of arsenite, arsenate and organoarsenic anions [122–125,238–246]. An example of the use of CZE for the separation of thio- and oxothioarsenates is also given [247]. From these works, it is apparent that separations in the co-electroosmotic mode are preferred, with detection of arsenic constituents often being by direct UV photometric detection (190 nm). Indirect detection was used only rarely [245] and a conductivity detector

was shown to provide detectabilities for arsenic anions that did not deviate significantly from those obtained by direct photometric detection [246]. ICP-MS, employed as a post-column detection technique in CZE, enhanced both the sensitivity and selectivity of the detection of arsenic anions [122–125]. Here, a FI arrangement of the CZE separation (hydrodynamic flow of the carrier electrolyte solution superimposed on its electroosmotic transport) with a post-column conversion of the arsenic anions to hydride was shown to be especially sensitive. Low ppt LODs were claimed for this CZE-ICP-MS combination [125] (see also Fig. 5).

The CZE separation of selenium anions is the subject of several papers [122–124,248–251]. In the separation of these anions, the co-electroosmotic mode of separation with direct photometric detection is preferred. The light absorptivity of selenite is significantly higher than that of selenate at a detection wavelength of 200 nm and, consequently, the LOD values for selenate and selenite linked with the electrokinetic injection were 2 and 0.4 ppm, respectively (in the injection of a bacterial suspension [250]). Indirect photometric detection, which was used by Gilon and Potin-Gautier [251] for the separation of selenate, selenite, selenocystine and selenomethionine, in combination with concentrating electrokinetic injection, provided LOD values at low ppb concentrations for the inorganic Se anions. This detection technique was found to be sensitive enough for the detection of selenate (61 ppb) in thermal water containing inorganic anionic macroconstituents in large excesses. The migration times of the analytes present in the thermal water sample, compared to those obtained for the anions present in a model sample, clearly indicate that, in this instance, a transient ITP process was effective (see Section 5.2.2).

The CZE speciation of Cr(VI) and Cr(III) requires that Cr(III) is complexed (derivatized) into an anionically migrating ionic form [252–255]. 1,2-Cyclohexanediaminetetraacetic acid (CDTA) [254] and EDTA [253] were found to be suitable complexing agents for this purpose. In the former instance, direct photometric detection at a detection wavelength of 214 nm gave 19 and 59 ppb LOD values for Cr(VI) and Cr(III), respectively. About tenfold lower values of the LODs are reported for both Cr constituents in the latter instance, when photometric

detection at 254 nm was used. Himeno et al. [252] developed a derivatization procedure in which Cr(III) rapidly formed a stable heteropolyanion with molybdate. This derivatization reaction was shown to require milder reaction conditions (the reaction was performed at room temperature) than CDTA and EDTA. The work by Olesik et al. [123], describing the coupling of CZE with ICP-atomic emission spectroscopy (AES) and ICP-MS, indicates that very low LOD values for the Cr constituents should be attainable by these hyphenated techniques.

Oxoanions containing phosphorus in different oxidation states are easily separable by CE techniques, as shown in an early ITP work by Boček et al. [256]. In the past, ITP was used by several authors to separate the anionic constituents of phosphorus, and relevant works in this area were reviewed [1,28,257]. A detail study by Shamsi and Danielson [60] showed that CZE is a powerful technique for separating the various anionic constituents of phosphorus. Using ribonucleotide electrolytes with 2 mmol/l DETA (to suppress EOF), they separated mixtures of 12 polyphosphates and 12 polyphosphonates. They found that the complexation of polyphosphates with  $Mg^{2+}$  influenced their effective mobilities in a differentiating way. In this respect, the effect of a multiple positively charged DETA, used in combination with the complexing cation, should be mentioned. The LOD values achieved for the phosphorus anions under these CZE working conditions with indirect photometric detection were close to those achieved by the same authors in the ion chromatographic separation of these constituents. The determination of phosphates and phosphonates in soap, toothpaste and a pesticide formulation illustrate the practical applicability of the proposed CZE procedure. A group of 18 phosphorus anions was separated by Lee et al. [258] using EDTA as a carrier anion with direct and indirect photometric detection of the anions at a detection wavelength of 210 nm. Stover and Keffer [62,259] separated groups of polyphosphates by CZE. In one of the quoted works [62], Stover resolved polyphosphates with various average chain lengths (from 5.6 to 44) in 20 min using a carrier electrolyte consisting of pyromellitic acid, hexamethonium hydroxide and triethanolamine. Differences in the effective mobilities of the polyanions were ascribed to their interactions (ion-pairing) with a double



charged hexamethonium. Based on the results obtained with different EOF modifiers (DETA, DTA<sup>+</sup>), the author stressed a significant role of the nature of the modifier on the separation of polyphosphates. In a series of works, Wang and Li [260–262] dealt with the CZE separation of polyphosphates. These authors [261] showed that a linear polyacrylamide gel, in combination with pyromellitate as a carrier anion, gave favourable separating and detecting conditions for polyphosphoric acid. Here, the sieving effect of the gel was assumed to be responsible for the resolution of the polyanions.

The CZE separation of halides and oxoanions of halogen elements in various oxidation states are reported in several papers [21,263–266]. As these are mostly anions of strong acids, their separation in aqueous solutions is usually based on the differences in the actual mobilities (see Section 2.1). Using this separation mechanism, a group of seven anions was separated [21]. The same separation mechanism was effective in the separation of chloride, chlorate, perchlorate and chlorite in the presence of other inorganic anions in tap water [266]. For some of these anions, differences in the effective mobilities could be enhanced by host–guest complexations [30] or via selective interactions with PVP [38].

Sulfur forms a variety of anionic constituents and some of them were shown to be separable by CE techniques [1,21,28,58,143,234,235,267]. Sulfur-containing anionic constituents differ significantly in their migration and detection properties and probably all of separation mechanisms outlined in Section 2 may be applied to their separation. A detailed investigation aimed at the speciation of sulfur anions was carried out recently by Motellier et al. [58]. This work focused on the choice of a carrier electrolyte solution that would be suitable for both the separation and the indirect photometric detection of sulfur anions at pH 8 (corresponding to the natural pH of water samples in which the anions were determined). The separation and detection conditions used in other works dealing with the separation of sulfur anions can be found in Table 5.

### 6.6. List of abbreviations

BTP	1,3-bis[tris(hydroxymethyl)methylamino]-propane; bis–tris propane
CDTA	1,2-cyclohexanediaminetetraacetic acid

CE	capillary electrophoresis
CHES	2-( <i>N</i> -cyclohexylamino)ethanesulfonic acid
CIA-Pak OFM Anion-BT	a proprietary solution of EOF modifier
CTA	hexadecyltrimethylammonium (cetyltrimethylammonium)
CZE	capillary zone electrophoresis
CZE–ICP–MS	capillary zone electrophoresis–inductively coupled plasma mass spectrometry
DETA	diethylenetriamine
DMBr	decamethonium bromide
DMFA	dimethylformamide
DMMAPS	3-( <i>N,N</i> -dimethylmyristylammonio)-propanesulfonate
DMOH	decamethonium hydroxide
DTA	dodecyltrimethylammonium
DTEADP	dodecyltriethylammonium dihydrogenphosphate
EC	electrochromatography
EOF	electroosmotic flow
EDA	ethylenediamine
FD	fluorescence detection
FI	flow-injection
FI–CE	flow-injection–capillary electrophoresis
HM	hexamethonium [1,6-bis(trimethyl)ammonium]
IC	ion chromatography
IC–CZE	ion chromatography–capillary zone electrophoresis
ICP–AES	inductively coupled plasma atomic emission spectroscopy
ICP–MS	inductively coupled plasma mass spectrometry
IS–MS	ionspray mass spectrometry
ISE	ion-selective electrode
ITP	capillary isotachopheresis
ITP–CZE	capillary isotachopheresis–capillary zone electrophoresis
LIF	laser-induced fluorescence
LOD	limit of detection
MAS	molecular absorption spectrometry
MEKC	micellar electrokinetic chromatography
MHEC	methylhydroxyethylcellulose
MS	mass spectrometry
NDS	naphthalenedisulfonate
Nice-Pak OFM Anion-BT	a proprietary solution of EOF modifier
Nitroso-R salt	sodium salt of 1-nitroso-2-naphthol-3,6-disulfonic acid
126NNS	sodium salt of 1-nitroso-2-naphthol-6-disulfonic acid
NTS	naphthalenetrisulfonate
PAR	4-(2-pyridylazo)resorcinol

PDC	pyridinedicarboxylic acid
PDDPi	poly(1,1-dimethyl-3,5-dimethylenepiperidinium)
PDMA	poly(diallyldimethylammonium)
PEG	poly(ethylene glycol)
PMA	pyrometallitic acid
PTFE	polytetrafluoroethylene
PVP	polyvinylpyrrolidone
SPE	solid-phase extraction
TBA	tetrabutylammonium
TEA	tetraethylammonium
TETA	triethylenetetraamine
TMA	trimellitic acid
Tris	Tris(hydroxymethyl)aminoethane
TTA	tetradecyltrimethylammonium

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