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## Review

# Prospects for detection and sensitivity enhancement of inorganic ions in capillary electrophoresis

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### Abstract

While capillary electrophoresis (CE) is now a well established technique for the determination of inorganic ions, the current sensitivity limitations of the method are an evident obstacle to progress. The advances in CE methodology to compensate for these limitations are reviewed in this paper with particular attention paid to non-absorbance-based detection techniques. Recently developed detection modes for inorganic cationic and anionic species are compared in terms of applicability, effects on separation efficiency, costs and manufacturing concerns. A comprehensive survey of sensitivity enhancements based on on-capillary and pre-electrophoresis concentration techniques and on chemical derivatization is also presented along with the most typical application examples. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Reviews; Detection, electrophoresis; Metal cations; Metal complexes; Inorganic anions

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## 1. Introduction

Capillary electrophoresis (CE) continues to grow in significance as an analytical technique in a wide range of application areas for inorganic species [1–6]. Since the early reported spectacular separations of numerous inorganic ions [7–9], the advantageous separation performance of CE is attracting the interest of many separation scientists. However, after the first euphoria a feeling of discontent with the detection capabilities of the technique often comes up, especially as soon as real-world applications are concerned. The narrow-diameter capillaries used for CE separations limit the detection sensitivity due to mass loading limitations. In addition, the concentration sensitivity of common on-column UV detection is restricted in so far as the capillary diameter limits the optical pathlength. Obviously, direct UV detection is hardly a universal detection technique in inorganic ion analysis since metal ions are generally non-absorbing and only a few inorganic anions like nitrite, nitrate, iodide, thiocyanate, sulfide and some others exhibit sufficiently high molar absorptivities. The alternative is indirect UV–Vis detection which is presently the preferred detection mode for inorganic ions, but detection limits are often only at ppm levels (unless on- and pre-capillary pre-concentration techniques are applied). Conductivity detection as another universal detection method has until recently been restrained in application by non-availability of commercial designs.

Improvements in detection have therefore remained one of the main trends in the development of CE over the last years. A growing understanding that without substantial gains in sensitivity, CE could face serious problems on the way to be refined and accepted for routine use, is one of the motives. The progress in the development of detection methodologies made so far for inorganic ions has been facilitated by the experience accumulated from ion chromatography (IC) [10]. As a result, a diversity of approaches has been reported for enhancement of detection sensitivity in CE.

In the present review, the recent advances in detection concerning both cationic and anionic inorganic analytes are discussed, with special emphasis given to non-absorbance-based detection methods and on-capillary concentration techniques inherent in

CE. This review also includes a presentation of developments involving a combination of pre-capillary derivatization and direct UV–visible detection as well as at pre-electrophoresis enrichment schemes. The use of indirect photometric detection is not considered here, and readers interested to assess its current status in cation and anion detection are recommended to consult two recent studies [11,12].

## 2. Advances in detection of inorganic ions

### 2.1. Mass spectrometry

For the most efficient solution to the problem of enhanced detection for metal ions and metal-containing inorganic species, one must first look to inductively coupled plasma mass spectrometry (ICP-MS). The interfacing of CE to ICP-MS for the aim of trace inorganic analysis was explored by several groups [13–17]. These studies revealed that the major challenges in CE–ICP-MS coupling [18,19] such as the low flow-rate of CE separations limiting the choice of a nebuliser, a post-capillary detector design with accompanying problems in applying a high voltage across the capillary and keeping the electrode grounded, and separation buffer incompatibilities with the ionization process have been basically overcome. In particular, Olesik et al. [13] have developed an interface to generate a fine aerosol that can be delivered from the end of the capillary to ICP with a good transport efficiency and minimal dead volume. As a result, limits of detection as low as  $1 \cdot 10^{-8} M$  Sr(II) were attained. However, a laminar flow induced in the capillary by a pneumatic nebuliser interface and generating a parabolic shaped velocity profile was found out as a factor limiting detectability. A further paper [20] reports an examination of the nebulisers construction and operating parameters that can be varied to control and eliminate the laminar flow. Liu et al. [14] demonstrated the feasibility of using a commercially available direct injection nebuliser system ensuring 100% sample introduction to ICP-MS. With this interface, no suction and no significant band broadening were observed. Detection limits were one- to two-orders of magnitude lower than those obtained by the group of Olesik. Instead of a nebulizer, a CE interface

incorporating a hydride generation system may be used for species like arsenic compounds [21], so that nebulization-based problems can be circumvented.

Due to the element-specific nature of MS detection, there is in principle no need to electrophoretically separate the target species of different elements from each other (and from any other interfering matrix components). By taking this advantage, the electrophoretic resolution can be sacrificed in order to reduce analysis time. The selectivity of a mass spectrometer has also a valuable practical merit by solving the task of identification for unknowns and/or co-migrating species by means of recording full-scan spectra and comparison of mass and characteristic isotopic distribution patterns.

The most interesting progress already made in applications of CE-ICP-MS includes speciation analysis [13–18,20–25] and the characterization of

metal ion interactions with biological and naturally occurring macromolecules [26–29]. Due to both the advantageous sensitivity of ICP-MS and the minor effect of a CE system on the distribution of chemical species, this combination holds great promise in element speciation studies. As an example, Fig. 1 shows an electropherogram for arsenic speciation in a real-world sample in the range of 50 to 200  $\mu\text{g/l}$ . However, investment and running costs are necessarily to be lowered and instrumentation simplified for better user convenience.

A survey of examples on the determination and speciation of inorganic ions reported so far is given in Table 1.

Whereas ICP-MS detection yields an element-specific signal, electrospray MS detection (including ion spray-MS detection, which can be regarded as a pneumatically assisted version of electrospray) can

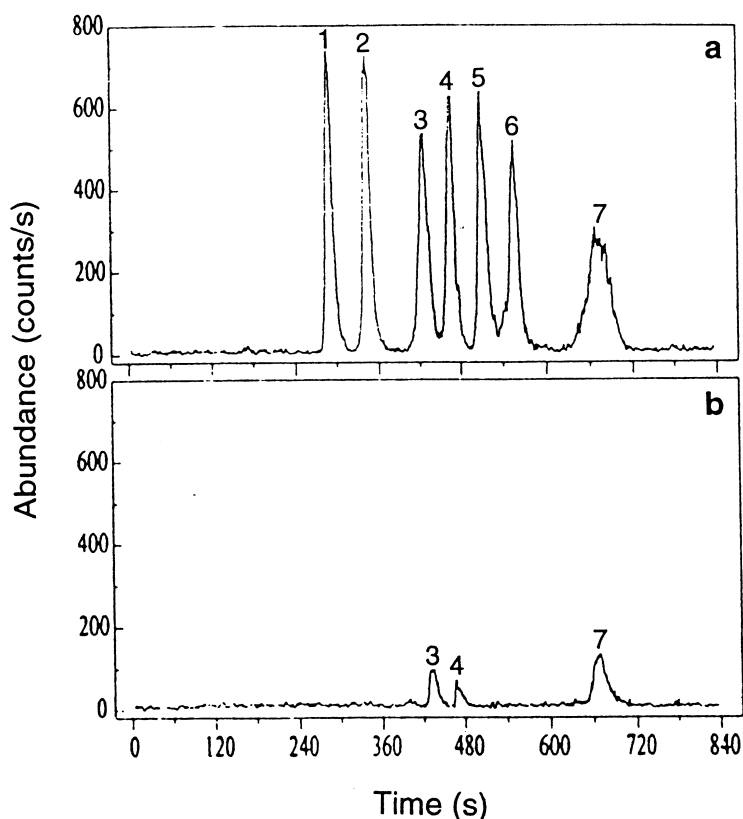


Fig. 1. Arsenic speciation by CE-ICP-MS (detection at  $m/z$  75). (a) Standard; (b) plant extract containing arsenic species in the range of 50–200  $\mu\text{g/l}$  As. Peaks: 1=Arsenocholine; 2=arsenobetaine; 3=dimethylarsinic acid; 4=As(III), 5=monomethylarsonic acid; 6=monophenylarsonic acid and 7=As(V). Reproduced from Ref. [16] with permission.

Table 1  
Examples for ICP-MS detection in CE of inorganic ions

Analytes	Approximate concentration detection limits ( $\mu\text{g/l}$ )	Sample type	Ref.
As(III), As(V), Co(II), Cr(III), Cr(VI), Fe(III), Li(I), Sr(II), Sn(II), Sn(IV)	0.06–2	Standards	[13]
As(III), As(V), K(I), Li(I), Se(IV), Se(VI), Sr(II), Cd(II), Co(II), Mn(II), Pb(II), Tl(I)	0.007–1	Standards	[14]
Pt(IV)	1	Soil extracts	[23]
As(III), As(V)	0.006–0.058	Drinking water	[21]
As(III), As(V)	10	Plant material	[16]
Se(IV), Se(VI)	10–50	Standards, body fluids	[24,25]

lead to structure-selective information including the molecular mass of an analyte. The benefits of the electrospray interface has been demonstrated in initial studies by Huggins and Henion [30] and Corr and Anacleto [31]. Both groups detected a representative set of metal ions and inorganic anions. One should be aware of the fact that electrospray mass spectra of inorganic cations can contain high degrees of ion-solvent clustering, which complicate the spectra. On the other hand, spectra showing only singly-charged bare elements can be obtained by using a sufficiently high declustering potential between the sampling orifice (where the ions from the electrospray are pushed into the low pressure region of the source) and the skimmers at the entrance into the high-vacuum mass analyser. For inorganic anions, even at low declustering potentials ion-adduct clusters are rarely observed.

## 2.2. Electrochemical detection

Electrochemical principles suitable for detection in CE of inorganic cations and anions include conductivity, amperometry and potentiometry. In all cases, the high voltage applied to the separation capillary can lead to serious interferences with the electrochemical detection signal. For this reason, on-capillary detection is rarely used for electrochemical detection techniques. Instead, the detection electrode can be positioned at the outlet of the separation capillary, especially when capillaries with an inner diameter of 25  $\mu\text{m}$  or less are used (end-

capillary detection). In this arrangement, the high electric field strength is confined to the inside of the separation capillary, whereas outside and at the position of the detection electrode the electric field strength is low and does not significantly interfere with the detection signal. Alternatively, the high electric field can be completely decoupled from the detection electrode by connecting the end of the separation capillary with a short transfer capillary by means of a porous coupling piece surrounded by carrier electrolyte with the high voltage electrode; the current passes the porous coupling piece, whereas the electroosmotic flow (EOF) generated in the separation capillary carries the analytes through the transfer capillary to the detection electrode (off-capillary detection).

Conductivity detection has recently reached the stage of commercial availability; amperometric and potentiometric detection techniques have up to now only been realized in laboratory-built instrumentation.

### 2.2.1. Conductivity detectors

A real breakthrough in the development of end-capillary conductivity detection was a consequence of the work of Jones et al. [32]. The design of the cell, where the conductivity sensor and the end of the capillary are permanently encapsulated in two coupling connectors, permits fast and easy interchangeability of sensors and capillaries, while maintaining a precisely defined detection volume.

Due to the fact that an analyte ion displaces a

carrier electrolyte co-ion during the migration process, the conductivity signal depends – among other parameters – on the differences in ionic mobilities of these two ions. Therefore, carrier electrolytes with a low-mobility anion are preferred for the analysis of inorganic anions which exhibit a relatively high ionic mobility. Similarly, carrier electrolytes with a low-mobility cation are suited for detection of alkali and alkaline-earth cations. For sensitive detection of larger cations with lower ionic mobilities, an indirect mode with acidic electrolytes is appropriate. Obviously, this situation is in contradiction to the general rule that the mobilities of analyte ions and carrier electrolyte co-ions should be similar in order to minimize electromigrative dispersion. Such problems can be partly overcome by increasing the concentration of the carrier electrolyte. Detection limits in combination with pressure injection are in the range of 20 to 50  $\mu\text{g/l}$  and can be decreased to the sub-ppb level when isotachophoretic stacking procedures (see Section 4.2) are applied [33]. Typical carrier electrolytes for inorganic anions and cations compatible with conductivity detection as well as several applications reported so far are summarized in Table 2.

Conductivity detection can be used in series with indirect UV detection when a UV-absorbing carrier electrolyte co-ion is used; for detection of anions, a carrier electrolyte containing 4-aminobenzoate can

be used. In this case, highest sensitivity is achieved by conductivity detection for fast migrating analytes, whereas slower migrating analytes give a better response in the indirect UV detection mode. In so far, the simultaneous use of both detection modes allows low detection limits for all analytes within a wide range of mobilities [38,39]. A typical application of this approach is shown in Fig. 2.

In conductivity detection, a further increase in sensitivity is possible when using an approach well known from ion chromatography, namely suppressed conductivity detection. It was introduced into CE by Dasgupta and co-workers [40,41]. The detector is based on a tubular cation-exchange membrane suppressor, housed in a reservoir of dilute acid regenerant solution, attached to the end of the separation capillary; the conductivity detection electrodes are positioned in a capillary following the suppressor; the electrode for the high-voltage applied to the separation capillary is placed into the regenerant solution. By this arrangement, the detector is decoupled from the electric field and the EOF generated in the separation capillary forces the carrier electrolyte and the analytes through the suppressor to the detector. Carrier electrolytes which are compatible with conductivity suppression and at the same time match the mobilities of inorganic anions include sodium tetraborate, sodium glycinate, sodium tauri-

Table 2  
Applications of conductivity detection of inorganic ions in CE

Sample	Carrier electrolyte	Ref.
Inorganic anions in soft drinks or rain water	50–100 mM CHES, 20–40 mM LiOH (pH 9.2)	[32,34]
Inorganic and organic arsenic and selenium species in water samples	50 mM CHES, 20 mM LiOH	[35]
Inorganic anions in lung airway surface fluid	100 mM CHES, 40 mM LiOH, 2% 2-propanol, 80 $\mu\text{M}$ spermine	[36]
Inorganic and organic anions in electrodeposition coatings	50 mM CHES, 30 mM arginine (pH 9)	[37]
Inorganic and organic anions in beer	7.5 mM 4-aminobenzoic acid adjusted to pH 5.75 with histidine, 0.12 mM TTAB	[38]
Inorganic and organic anions in wine	7.5 mM 4-aminobenzoic acid and 10.5 mM Bis-Tris adjusted to pH 7 with LiOH, 0.1 mM TTAB	[39]
Cations in saliva	30 mM MES, 30 mM histidine, 3 mM 18-crown-6	[32]

CHES=2-(*N*-Cyclohexylamino)ethanesulfonic acid; MES=2-(*N*-morpholino)ethanesulfonic acid; TTAB=Tetradecyltrimethylammonium bromide.

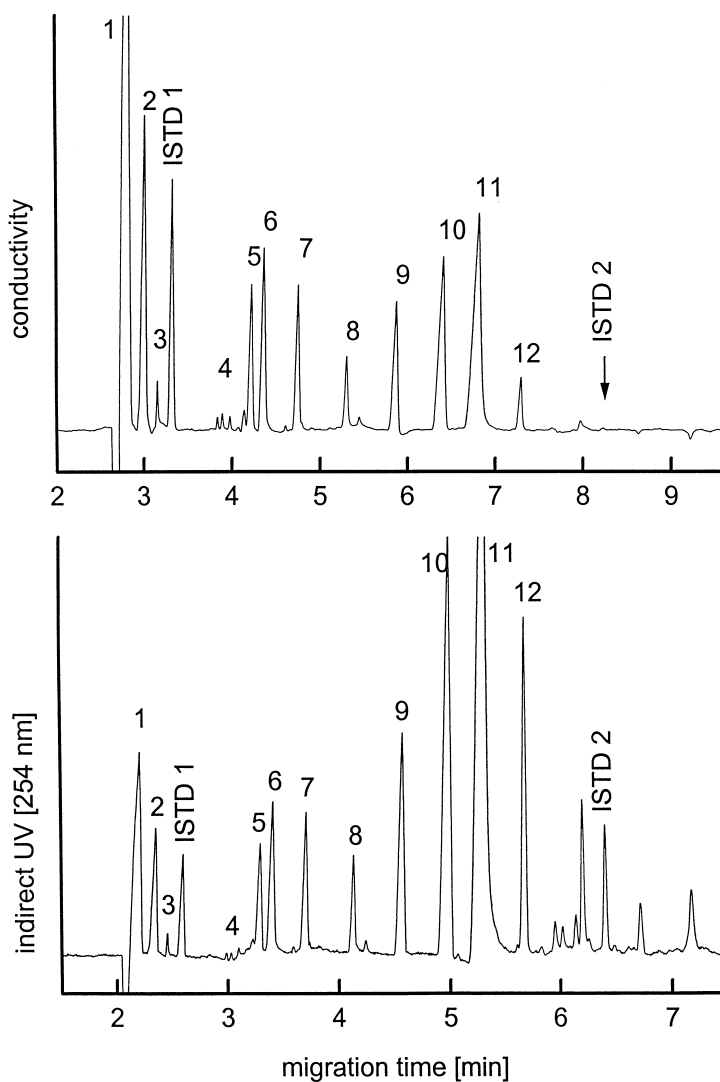


Fig. 2. Separation of inorganic anions and carboxylic acids in a beer sample using simultaneous conductivity and indirect UV detection. Carrier electrolyte: 7.5 mM 4-aminobenzoic acid, 0.12 mM tetradecyltrimethylammonium bromide (pH 5.75 adjusted with histidine). Peaks: 1=Chloride, 2=sulfate, 3=oxalate, 4=formate, 5=malate, 6=citrate, 7=succinate, 8=pyruvate, 9=acetate, 10=lactate, 11=phosphate, 12=pyroglutamate, ISTD 1=chlorate (internal standard 1), ISTD 2=1-chlorovaleric acid (internal standard 2).

nate, sodium carbonate, sodium phenate or sodium cyanide [42,43]. Detection limits at the level of 1  $\mu\text{g/l}$  have been reported.

The design of conductivity cells compatible with the small inner diameters of the separation capillaries is not simple and any dead volumes must strictly be avoided. In so far, a contactless conductivity detection with the electrodes situated at the outside of the capillaries might have considerable advantages.

Zemann et al. [44] have reported a contactless capacitively coupled conductivity detector suitable for detection of both inorganic cations and anions. It consists of two electrodes which are placed cylindrically around the outer surface of the separation capillary with a detection gap of 2 mm. Each of the two electrodes serves as a cylindrical capacitor with the liquid inside the capillary being the corresponding internal wire. The gap between the elec-

trodes acts as resistor depending on the conductivity of the migrating zone. In combination with an oscillator, contactless conductivity measurements are viable resulting in detection limits of approximately 200  $\mu\text{g}/\text{l}$  for inorganic anions and cations. Some improvements are still required to compete with other conductivity detector designs.

### 2.2.2. Amperometric detection

Even the first amperometric end-column detectors introduced by Cassidy and coworkers [45,46] for detection of metal ions separated by CE offered significant sensitivity enhancement in comparison with absorbance techniques. Detection limits down to  $10^{-7}$  M have been reported. In an attempt to improve the reproducibility, Wen and Cassidy [47] conducted a comprehensive evaluation of the potential of a pulsed-amperometric detection system with particular focus on parameters affecting the analytical signal and its stability. The pulse waveform had a simple bipolar shape. Detection of metal ions could be carried out either during the negative pulse by reduction of metal ions or during the positive pulse by reoxidation of the reduced metals. Superior performance characteristics in comparison with the constant-voltage mode are advantages that might make the pulsed detection system attractive for implementation into commercial instruments. An electropherogram for the determination of traces of Zn(II) in snow is shown in Fig. 3. In continuation of this detection concept, Cassidy et al. [48] have also used fast cyclic-voltammetry waveforms as well as multiple-step waveforms for metal ion analysis; detection limit improvements down to  $10^{-8}$  M were possible.

Constant-potential amperometric detection at gold electrodes has been used in a reductive mode for the analysis of inorganic mercury and organomercury cations [49]; anions like nitrite and sulfite have been detected in a constant-potential oxidative mode and applications have been reported for rain water samples [50].

### 2.2.3. Potentiometric detection

Microelectrodes compatible with the small dimensions encountered in CE may have specific advantages in an potentiometric detection mode, since the signal will be independent on the size of the elec-

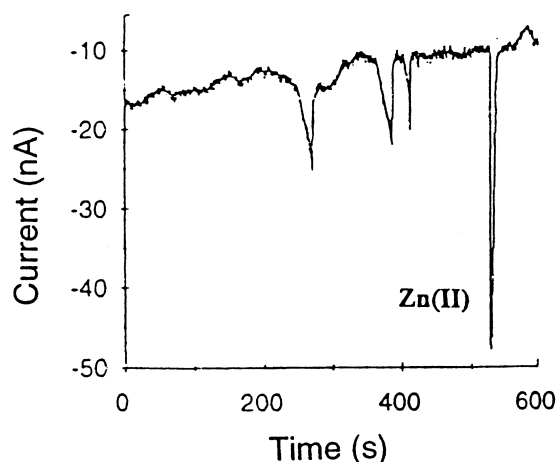


Fig. 3. Determination of zinc in a snow sample with pulsed-amperometric detection at  $-800$  mV and  $100$  mV (vs. saturated calomel electrode). Sample concentration:  $8.4 \cdot 10^{-7}$  M. Reproduced from Ref. [47] with permission.

trode (provided that the response is fully Nernstian) so that microelectrodes can be used without sacrificing sensitivity. Simon and co-workers [51–53] have introduced ion-selective microelectrodes based on liquid membranes containing ion carriers with relatively low selectivity for detection of alkali and alkaline earth metal ions. Later, this approach has also been used for detection of inorganic anions [54,55]. A typical example is given in Fig. 4.

### 2.3. Fluorescence

Most inorganic anions and cations do not exhibit analytically useful fluorescence properties. Nevertheless, fluorescence detection appears to be well suitable to sensitively detect metal ions complexed with chelating reagents, e.g., 8-hydroxyquinoline-5-sulfonic acid (HQS) [56] or lumogallion [57], that render them fluorescent properties. In an important paper by Sepaniak et al. [58], CE in conjunction with laser-induced fluorescence detection has been miniaturized and implemented in the design of an integrated fiber-optic sensor. As can be seen in Fig. 5, the sensor is configured as a single-vial CE system interfaced to a fiber-optic that monitors the outlet of the capillary. The latter is filled with the carrier electrolyte prior to measurement, while the sample acts as the injection-side reservoir. The performance

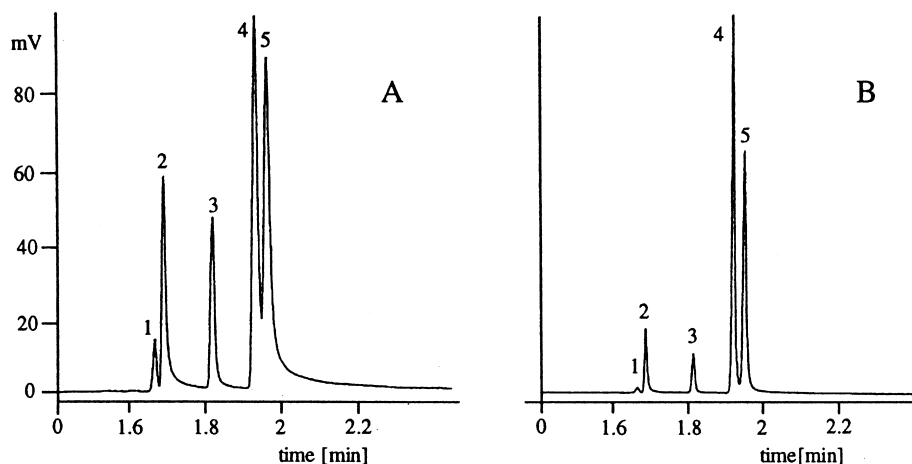


Fig. 4. Separation of anions by CE with potentiometric detection using a liquid membrane ion selective electrode containing 10% tridodecylmethylammonium chloride in 2-nitrophenyl octyl ether. Carrier electrolyte: 20 mM sodium sulfate adjusted to pH 2.5 with sulfuric acid. (A) Signal recorded by the detector; (B) delogarithmized form. Peaks: 1=Bromide, 2=iodide, 3=nitrate, 4=perchlorate, 5=thiocyanate, 6=salicylate; concentrations between 0.1 and 0.5 mM. Reproduced from Ref. [54] with permission.

of this CE-based sensor has been evaluated by taking as an example separations of Ca(II) and Mg(II) using in situ complexation with HQS and a frontal mode of operation, and the preliminary results have demonstrated sensor's potential utility for remote analysis.

Alternatively, fluorescence detection can be performed in an indirect format, in which the carrier electrolyte contains a fluorescent additive to provide a fluorescent background signal. Possible additives for cationic species are quinine sulfate [59], 6-aminoquinoline [60,61], 2-aminopyridine [62] or cerium(III) [63], for anionic species the sodium salt of fluorescein [64,65] or 2,5-dihydroxybenzoate [66,67]. However, sensitivities are worse than those that can be obtained in the direct detection mode.

Overall, fluorescence detection does not yet receive wide acceptance in CE of inorganic ions, though its gains in sensitivity (typically one- to three-orders of magnitude) and selectivity over photometric detection are significant and it is already commercially available.

#### 2.4. Miscellaneous

The combination of CE with chemiluminescence (CL)-based post-capillary reactions catalyzed by metal ions, such as the luminol/hydrogen peroxide

reaction, is promising when extremely high sensitivity is required [68,69]. For Co(II) the detection limit reaches  $5 \cdot 10^{-13}$  mol/l [70], which means an improvement over other detection techniques by several orders of magnitude. Evidently, CL detection is still an evolving technique, and advances should therefore focus on the development of new, instrumentally simpler detector designs.

Time-resolved on-column luminescence detection can be used to yield submicromolar detection limits for europium(III) chelates [71]. However, the application possibilities of this detector to real samples are not yet fully exploited.

Along with ICP-MS, atomic emission spectroscopy (AES) based on an ICP-source is seemingly a viable detection technique for CE of metal species. Olesik et al. [13] used the separation capillary inserted into a pneumatic nebuliser sample introduction system for coupling CE to ICP-AES and achieved limits of detection for Sr(II) and Cr(III) in the range of  $10^{-6}$ – $10^{-7}$  M. The shortcoming of the ten- to hundred-fold loss in sensitivity as compared to ICP-MS, however, would limit the applicability of CE-ICP-AES. For the same reason of moderate sensitivity, microwave-induced plasma AES has not attracted much interest as CE detector since the first report by Liu and Lopez-Avila [72].

Other detector designs feasible for selected inor-



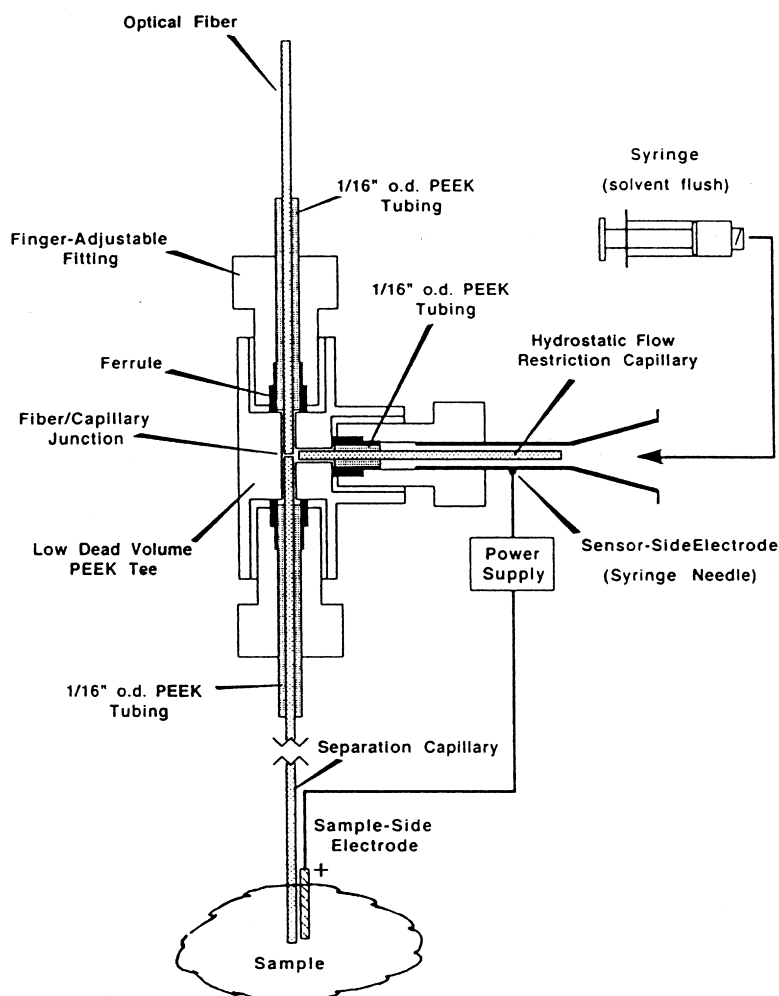


Fig. 5. Schematic diagram of an integrated fiber-optic fluorescence sensor in combination with CE separations. PEEK=Polyether ether ketone; 1/16"= 1/16 in. (1 in.=2.54 cm). Reproduced from Ref. [58] with permission.

ganic ions include refractive index, radioactivity and X-ray detection. Generally, they are less versatile, less likely to be refined for routine purposes and consequently have so far undergone limited development. None of them is yet brought down to practical applications. In particular, refractive index detection based on a laser diode and holographic optical elements [73], though providing acceptable sensitivity, suffers from interfering Joule heat effects when the high voltage is applied. Application of radioactivity detection [74] has been reported for the separation of metal ions characteristically associated with nuclear fission. On-capillary proton-induced X-

ray emission (PIXE) detection [75,76], while furnishing metal-specific information, features moderate sensitivity and bulky, complicated instrumentation. Besides, there are certain methodological problems to be overcome to accomplish the PIXE measurements in a real on-line mode and to record more than one data point per peak.

### 3. Chemical derivatization for direct absorbance detection

Pre-capillary derivatisation leading to UV-Vis

absorbing species is hardly useful for inorganic anions, whereas it presents a powerful strategy for detection of metal ions when complexation reactions are exploited (for a detailed discussion see Refs. [1,3,77]). An analysis of literature data shows that the performance of a given detection system regarding sensitivity is especially encouraging with light-absorbing chelating reagents, i.e., metallochromic reagents, capable to form stable complexes with high molar absorptivity ( $\epsilon \sim 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ ) in the visible spectral region. Table 3 lists a variety of reagents that allow detection limits at a level of  $10^{-7} \text{ M}$  for metal ions. An important practical consideration is that many of those reagents shown in Table 3 are commercially available.

Often the excess of complexing reagent present in the sample mixture is electrophoretically well separated from the metal ion complexes. In such cases, the signal-to-noise ratio may sometimes be better in the UV range even for colored metal complexes due to a greater molar absorptivity and higher light output of the deuterium lamp. For instance, Xu et al. [92] reported an eight-fold increase in detectability for the Fe(II)–1,10-phenanthroline complex when the absorbance was measured at 270 nm instead of at 508 nm. Obviously, such an approach is not feasible when the reagent must be included in the carrier electrolyte to suppress dissociation of the complex.

In a recent paper by Butler et al. [94], an optical detector based on a high intensity visible light

Table 3

Summary of metallochromic organic reagents for detection of metal ions in CE (detection limits are at a level of  $10^{-7} \text{ M}$ )

Complexing reagent	Analytes	Detection wavelength (nm)	Ref.
4-(2-Pyridylazo)resorcinol	Cr(III), Ni(II), Co(II,III), Cu(II), Fe(II,III), Zn(II)	500	[78–81]
2,2'-Dihydroxyazobenzene-5,5'-disulfonic acid	Al(III), Co(III), Fe(III)	490	[82]
2-(5-Nitro-2-pyridylazo)-5-( <i>N</i> -propyl- <i>N</i> -sulfopropylamino)-phenol	Fe(II), Co(II), Ni(II)	560	[83]
2-(5-Bromo-2-pyridylazo)-5-( <i>N</i> -propyl- <i>N</i> -sulfopropyl-amino)phenol	Co(II), Fe(II), Cu(II), Pb(II), V(IV), Zn(II)	550	[84]
2-(5'-Bromo-2'-pyridylazo)-5-diethylaminophenol	Co(II)	587	[85]
1-(2,4-Dihydroxy-1-phenylazo)-8-hydroxy-3,6-naphthalenesulfonic acid	Al(III)	450	[86]
3,6-Bis(2-sulfophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid	Ba(II), Sr(II)	654	[87]
Arsenazo III	U(VI)	650	[88]
	La(III), lanthanides	654	[89]
2-Nitroso-1-naphthol-4-sulfonic acid	Co(II), Cu(II), Ni(II)	520	[90]
$\alpha,\beta,\gamma,\delta$ -Tetrakis(4-carboxyphenyl)porphyrine	Zn(II)	422	[91]
1,10-Phenanthroline	Fe(II)	270	[92]
4,7-Dimethyl-1,10-phenanthroline	Cu(II)	220	[93]

emitting diode (LED) as radiation source was described and evaluated for CE of metal–4-(2-pyridylazo)resorcinol (PAR) complexes. The most common LEDs cover the approximate wavelength range of 440–660 nm that makes them exceptionally suitable for the detection of metal complexes of metallochromic dyes. The sensitivity performance of the device was claimed to be comparable to that of a commercial detector, but its unprecedented simplicity, in particular the absence of any focusing optical elements, and the modular nature are the advantages. According to a study by Macka et al. [95], the LED-based detectors applied to metal–arsenazo I complexes exhibit lower noise compared to tungsten and mercury lamps.

#### 4. Pre-concentration techniques

On-capillary sample stacking is one of the simplest ways to improve detectability in CE of inorganic ions. Sample stacking may take place when the conductivity of the sample is smaller than that of the carrier electrolyte (field-amplified sample stacking) or when a transient isotachopheresis (ITP) takes place at the interface between the sample zone and the carrier electrolyte (isotachophoretic sample stacking).

Pre-concentration is also viable in a capillary-coupling configuration, where the first capillary is used in an ITP mode to focus the analytes and the second capillary is operated in a zone electrophoretic mode to separate the analytes of interest.

Finally, various pre-electrophoresis enrichment procedures are feasible such as solid-phase extraction (SPE) or extraction by supported liquid membranes; these procedures are similar to those known from IC.

##### 4.1. On-capillary pre-concentration by field-amplified sample stacking

The standard approach to realize field-amplified sample stacking consists in the injection of a very large volume of the sample solution, which must be of considerably lower ionic strength than the carrier electrolyte. After applying a high voltage, analyte ions first experience a higher electric field in the sample region and move rapidly toward the interface

between the lower and higher conductivity zones. Upon reaching the interface, they are slowed down and focused as a narrow band, thereby increasing the concentration in this sample band. In such a way concentration detection limits can be lowered by one- to two-orders of magnitude due to the increased injection volume.

Field-amplified sample stacking is inherent to all applications with samples of lower conductivity than the carrier electrolyte. In so far, it seems unnecessary for the present review to include specific examples for inorganic ions. Attention should be paid to the fact that problems may arise during the injection of very large volumes as a consequence of the mismatch in EOFs within the sample zone and the carrier electrolyte zone. Therefore, the water plug should be removed during or after the stacking process. In the case of medium- to low-mobility anions, the stacking takes place with a negative polarity at the injection side; while the analytes are focused at the interface between sample and carrier electrolyte, the EOF moves the water plug out of the capillary at the injection side. When most of the water plug has been removed, the polarity is switched and the analytes separated in a counterelectroosmotic mode. This approach has been used for inorganic selenium and arsenic species with detection limits at the  $\mu\text{g/l}$  level [96,97]. For anions with mobilities high enough to overcome the EOF, no polarity switching would be necessary; in this way, Colburn et al. [88] achieved the stacking of U(VI) as its anionic arsenazo III complex. In the case of medium- to low-mobility cations, the EOF must be permanently reversed; stacking takes place with a positive polarity at the injection side; after removing most of the water plug, the polarity is switched and the analytes separated. An applications of this mechanism has been demonstrated for the stacking of cobalt as its cationic chelate with 2-(5-bromo-2-pyridylazo)-5-(diethylamino)-phenol [98].

A modification of the field-amplified sample stacking procedure inside the capillary is head-column field-amplified sample stacking (sometimes called field-amplified sample injection). In this case, first a short zone of low conductivity is injected at the capillary inlet, so that the electric field within this zone is much higher than in the carrier electrolyte. Afterwards, analyte ions are injected by means of

electromigration and are stacked at the interface between the low conductivity zone and the carrier electrolyte. Thereby, only little sample solvent is introduced into the capillary.

For metal ion analysis after complexation, the prerequisite of low ionic strength in the sample to achieve efficient focusing may be in contradiction to the necessity of a sufficiently high ligand concentration. This is especially true for metal complexes prone to dissociation or when an appropriate reagent concentration is necessary for assuring fast complexation kinetics.

Common stacking methods can be combined with on-capillary complexation of metal ion analytes, as has been reported by Regan et al. [81]. This procedure included the injection of PAR, followed by the injection of the sample and finally a certain period of reaction time. Subsequently, the separation of the complexed analytes was started. Detection limits of  $1 \cdot 10^{-8}$  M for Co(II), Fe(II) and Zn(II) were possible. Fig. 6 demonstrates an application to a water sample.

#### 4.2. On-capillary pre-concentration by isotachophoretic sample stacking

Isotachophoretic sample stacking can be realized by injecting a certain volume of a leading electrolyte, the sample and finally a certain volume of a terminating electrolyte into the capillary. Isotachophoretic mechanisms can also be used for pre-concentration of analyte ions in the presence of a large excess of a matrix ion; depending on its mobility, the matrix ion can act as leading ion (or as terminating ion) and the carrier electrolyte co-ion as terminating ion (or leading ion). Analytes with mobilities between those of the matrix ion and the electrolyte ion will undergo isotachophoretic focusing. This technique has been used by Bächmann et al. [99] for determination of inorganic anions down to concentrations of  $3 \mu\text{M}$  in samples containing fluoride as major matrix ion with chromate as carrier electrolyte. The technique tolerated analyte-to-matrix-ratios up to  $1:6 \cdot 10^4$ . Similarly, inorganic anions in a hydroxide matrix can be focused when a salicylate carrier electrolyte is used [100]. Instead of establishing the isotachophoretic pre-concentration by the matrix ion and the electrolyte co-ion, the same

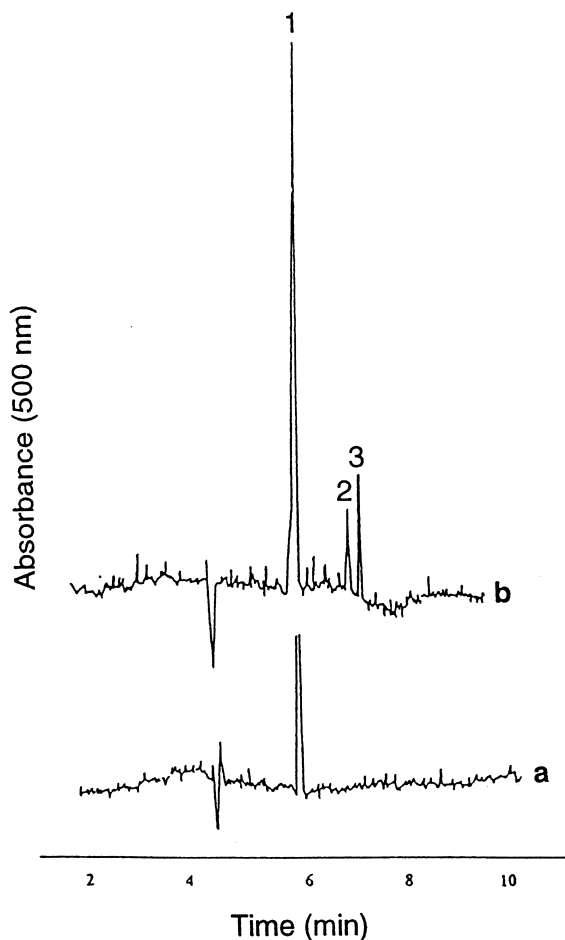


Fig. 6. Electropherograms of a pond water sample spiked with  $1 \cdot 10^{-7}$  M iron and zinc and analyzed by (a) pre-capillary complexation and (b) on-capillary complexation and peak stacking. Peaks: 1=Free PAR; 2=Fe(II) and 3=Zn(II). Reproduced from Ref. [81] with permission.

effect can be achieved by adding a second matrix ion with suitable mobility to the sample [100]; this approach yields a high degree of versatility during the optimization of the separation system.

Transient isotachopheresis can also play an important role during electromigrative injection. If for example inorganic anions are injected by electromigration into a high-mobility carrier electrolyte (such as chromate), a low-mobility matrix ion present in the sample (or added to the sample) can act as terminating ion and accomplish together with the

chromate as leading electrolyte the pre-concentration step. If the carrier electrolyte does not fulfil the mobility criterion for a leading electrolyte, the injection of a certain volume of a suitable leading electrolyte is appropriate before the electromigrative injection of the sample. This approach allowed detection limits of about 1  $\mu\text{g/l}$  and made possible the ultra trace determination of anions on silicon wafer surfaces [101].

#### 4.3. Pre-electrophoresis enrichment

Instead of on-capillary isotachophoretic pre-concentration, a two-capillary format can be used with the first capillary acting in the ITP mode (as a means of high sample load) and the second in the zone electrophoresis mode. In a capillary switching instrumentation, focused zones from the first capillary are transferred to the second capillary where the separation is accomplished. The advantages of this combination have been demonstrated by Kaniansky et al. [102] for inorganic anions and by Kennedler et al. [103] for trace determination of iron as its EDTA complex.

A range of pre-electrophoresis techniques in CE have been adapted from HPLC applications; in this context, it is quite obvious to use solid-phase extraction (SPE) procedures. Buchberger and Haddad [104] have demonstrated that metal cyanides can be collected efficiently on a  $\text{C}_{18}$  cartridge pre-conditioned with an ion-pairing reagent and then eluted by a small volume of an organic solvent.

In a similar way, a range of cationic organometallics have been concentrated before CE analysis using different instrumental design [105,106]. Specifically,  $\text{C}_{18}$  membrane disk SPE was shown to overcome several drawbacks encountered in cartridge SPE and allows enrichment factors up to 40 000 for organotin and organolead compounds [105].

In order to attain a high efficiency of SPE for inorganic ions on common reversed-phase materials, the analytes have to be transformed into hydrophobic derivatives. An attractive way to fulfil such requirements without the need to use organic solvents in the elution process is the use of carefully designed water-soluble chelating reagents. In preliminary experiments [107], the utility of bis(carboxymethyl)-

dithiocarbamate to complex and concentrate trace metal ions prior to CE was explored. At a pH of 3 when the ligand carboxyl groups are non-ionized, metal ion complexes have no apparent charge and are retained on a  $\text{C}_{18}$  cartridge. Application of the basic eluent, such as a borate buffer at pH 9 well compatible with the composition of electrolyte for subsequent CE separation, causes the complexes to be ionized and eluted rapidly and quantitatively. Thus concentration factors greater than 500-fold can be attained when large sample volumes are used.

Instead of reversed-phase materials, chelating resins like Chelex-100 are useful for SPE of metal ions. After pre-concentration, elution from the resin can be performed by a small volume of 2 *M* nitric acid. In the work by Arce et al. [108], an automated mechanical interface has been designed and validated for coupling SPE with capillary zone electrophoresis. This arrangement shown in Fig. 7 allows enrichment of heavy metals, e.g., Mn(II), Pb(II), Cd(II) and Al(III), down to regulatory limits established by legislation for drinking water.

Supported liquid membranes (SLMs) for pre-concentration of inorganic ions are based on an organic liquid phase that is held in the pores of a thin porous support and contains a complexing or ion-pairing reagent. The aqueous sample flows across one side of the membrane, whereas a small volume of an aqueous acceptor phase contacts the other side of the membrane. Enrichment factors up to 250 for copper(II) and 150 for zinc(II) were achieved with 8-hydroxyquinoline in di-*n*-butyl ether as liquid membrane and an acceptor phase containing 1,2-cyclohexanediaminetetraacetic acid [109]. Pre-concentration on SLMs has also been employed for different metallo-cyanide complexes prior to CZE separation [110]. Due to the presence of methyltriocetylammmonium chloride in the membrane phase, metallo-cyanides diffuse through the membrane by replacing chloride ions and thus forming a stronger ion pair with methyltriocetylammmonium ion. In the stripping step, the complexes are liberated and accumulate in the acceptor compartment of the membrane unit containing a perchlorate solution which was found suitable for direct injection into the CE instrument. An increase in sensitivity by a factor of 50 to 600 permits cyanide species to be detected below the limits stated for drinking water.

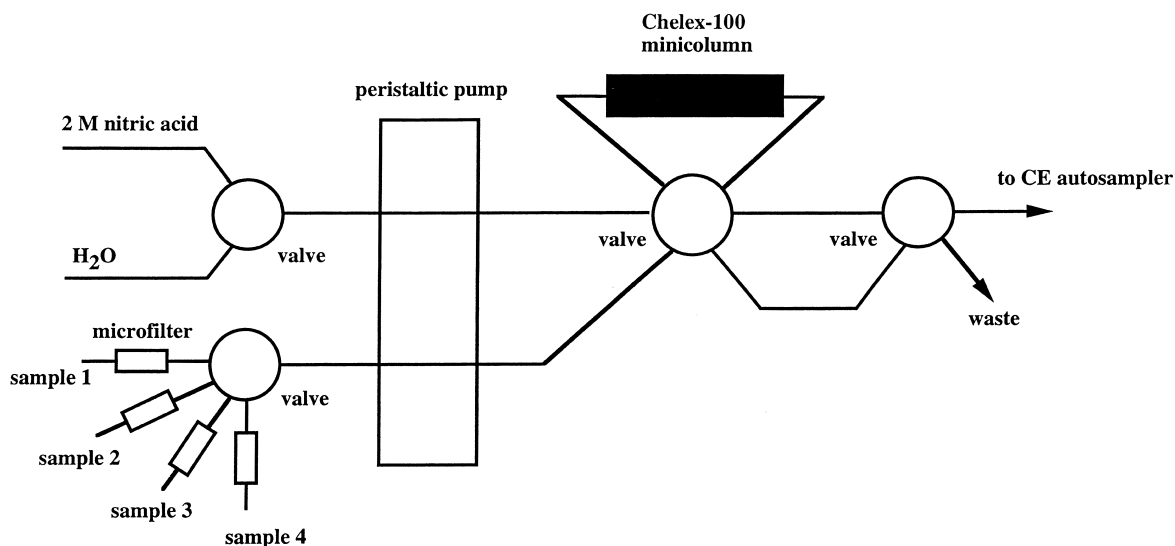


Fig. 7. Automated system for combination of sample preconcentration on a chelating resin with CE. Reproduced from Ref. [108] with permission.

## 5. Conclusions

In all likelihood, the attention of analytical chemists to CE as a standard tool for inorganic ion analysis will increase over the next few years. Among the reasons for this development is the fact that the performance of CE detectors has improved considerably and new detection techniques have reached the stage of practical applicability. One of the most powerful detection method for trace inorganic analysis seems to be mass spectrometry hyphenated to CE by an ICP interface. This combination is relatively new and there are still a lot of investigations necessary with respect to interface designs as well as cheaper and more user-friendly instrumentation. While there are just few things that cannot or could not be accomplished by ICP-MS detection, it is not going to replace other detection systems. A variety of less sophisticated detectors adequately serves many of the needs of inorganic ion CE analysis. The range of cost-effective detection techniques as well as their commercial availability from various manufacturers is still increasing.

Together with the improvements in detection techniques, progress in sample enrichment methodology using various on-capillary and pre-electrophoresis approaches has resulted in attractive de-

tection limits without superfluous investment and running costs. Advancements leading to further sensitivity improvements in the short-term future might include on-line pre-concentration by means of analyte concentrator cartridges or membrane devices coupled with the CE capillary. Finally, pre-capillary derivatization allows the development of procedures that are tailor-made for the trace analysis of selected analytes, especially in the field of metal ion analysis. Continued research focusing on advanced reagents is anticipated in the coming years. Generally, there is not just one specific approach to improve the detection limits. System optimization in CE is the art of choosing the most efficient tool from the broad range available nowadays.

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