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Review

Capillary electrophoresis of inorganic cations

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Abstract

The capillary electrophoresis (CE) methods of determination of inorganic cations are critically surveyed, with emphasis on the most recent works. The metal ion complexation is treated in detail, as well as the detection techniques. The advantages and drawbacks of CE compared to HPLC are briefly considered and typical examples of application to various matrices are given in a table.

Keywords: Reviews; Inorganic cations; Metal complexes

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1. Introduction

Capillary electrophoresis (CE) has recently been developing very rapidly. The first paper on the CE analysis of inorganic cations was published by Hjertén in 1967 (separation of Bi^{3+} and Cu^{2+} with lactic acid as the complexing agent) [1], but the real boom in CE started after 1990 in close connection with rapid development of the instrumentation. Since then the number of papers dealing with analysis of cations by CE has multiplied even if this is only a small part of the CE applications (see, e.g., book Refs. [2,3], the book chapters in Refs. [4,5] and a number of reviews [6–16]).

The traditional approach to the separations of inorganic ions, ion chromatography (IC), is partially being replaced by CE due to the following main advantages of the latter method [16,17] (i) a higher

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separation efficiency (a flat local velocity profile in CE running buffers compared to parabolic profiles in IC), (ii) a higher speed of analysis caused either by the absence of a partition process between the mobile and stationary phase in capillary zone electrophoresis (CZE) or by the fast mass transfer due to the dynamic structure of micelles in micellar electrokinetic chromatography (MEKC) (where the analytes are distributed between a pseudostationary phase and the electrolyte), (iii) a very small amount of sample required permits, e.g., an analysis of cations in a single small rat or mice eye lens [18] or analysis of the cations and anions present in a single rain drop [19,20], (iv) very low mass detection limits, (v) a low consumption of chemicals (low cost per analysis), (vi) a relatively simple instrumentation, easy automation, (vii) a good tolerance to sample matrix, e.g., to high pH values.

The disadvantages of CE compared to IC include: (i) a lower sensitivity and higher concentration detection limits, (ii) the migration times are less reproducible than the IC retention times due to instability of the electroosmotic flow (EOF); however, the reproducibility of the effective electrophoretic mobilities in CE is comparable to the reproducibility of the retention factors in IC, (iii) IC is more extensively developed; validated procedures and computer optimization approaches are available in IC, while routine applications of CE are still less common. However, a validation of the CE method for the determination of cations in solid natural products has been published [21], (iv) the selectivity range in CE is limited, as the selectivity can only be manipulated by the electrolyte composition.

CE and IC are complementary rather than competing techniques and exhibit different selectivities; CE is used for separation of those mixtures of cations that are difficult to separate by IC.

2. Theoretical considerations

The electrophoretic mobility of a cation, $\mu_{ep(ion)}$, can be related to the limiting ionic equivalent conductivity, λ_{ekv}, by Eq. (1),

$$\mu_{ep(ion)} = \lambda_{ekv}/F = q_i/6\pi\eta r_i \quad (1)$$

Table 1
Hydrated ionic radii r_i (in cm) of selected inorganic cations [7]

Cation	$10^8 r_i$	Cation	$10^8 r_i$	Cation	$10^8 r_i$
Ba^{2+}	2.572	Gd^{3+}	3.651	Ni^{2+}	3.244
Ca^{2+}	2.750	Ho^{3+}	3.706	Pb^{2+}	2.297
Cd^{2+}	3.039	K^{+}	1.114	Pr^{3+}	3.520
Ce^{3+}	3.530	La^{3+}	3.530	Rb^{+}	1.058
Co^{2+}	3.150	Li^{+}	2.117	Sm^{3+}	3.587
Cs^{+}	1.044	Mg^{2+}	3.088	Sr^{2+}	2.742
Cu^{2+}	3.000	Mn^{2+}	3.168	Tu^{3+}	3.757
Dy^{3+}	3.745	Na^{+}	1.624	Yb^{3+}	3.745
Er^{3+}	3.728	Nd^{3+}	3.540	Zn^{2+}	3.046
Eu^{3+}	3.624	NH_4^{+}	1.104		

where F is the Faraday constant ($F = 9.6487 \cdot 10^4$ A s mol^{-1}); λ_{ekv} (cm^2 mol^{-1} ohm^{-1}) is related, by the Stokes law, to the charge of the hydrated cation, q_i, to the dynamic viscosity of the electrolyte, η (g cm^2 s^{-1}), and to the radius of the hydrated cation, r_i (cm). The hydrated ion radii of selected inorganic cations, calculated from the limiting ionic equivalent conductivities, are listed in Table 1 [7].

The $\mu_{ep(ion)}$ values can be calculated from the experimental data, the apparent mobility of the cation, $\mu_{app(ion)}$, and the mobility of the electroosmotic flow, μ_{eo}, according to Eq. (2):

$$\mu_{ep(ion)} = \mu_{app(ion)} - \mu_{eo} = (1/t_{m(ion)} - 1/t_{m(eo)})(l_T \cdot L_d/V) \quad (2)$$

where $t_{m(ion)}$ is the migration time of the cation, $t_{m(eo)}$ is the migration time of an EOF marker (an uncharged solute), both in s, L_T and L_d are the overall capillary length and the length of the capillary to the detector (both in cm), respectively.

The experimental and calculated electrophoretic mobilities of some inorganic cations are compared in Table 2. The electrophoretic mobilities derived from the limiting ionic equivalent conductivity differ somewhat from the experimentally measured values that are dependent on the composition of the background electrolyte and its pH.

3. Direct CE analysis of cations

Inorganic cations are smaller and thus have higher charge densities (q_i/r_i ratios) than most organic ions;

Table 2
Comparison of experimental [22] and calculated (Eq. (1)) electrophoretic mobilities for the alkali and alkaline earth metal ions [7]

Cation	$\mu_{ep,exp}$ ($\cdot 10^{-4}$ cm^2/V s)	$\mu_{ep,calc}$ ($\cdot 10^{-4}$ cm^2/V s)
Cs^+	7.32	7.21
NH_4^+	6.75	6.84
K^+	6.75	6.75
Ba^{2+}	5.38	5.27
Sr^{2+}	4.88	4.96
Ca^{2+}	4.88	4.96
Na^+	4.62	4.67
Mg^{2+}	4.44	4.41
Li^+	3.66	3.62

Electrolyte: 0.5 m*M* $Ce(SO_4)_2$.

therefore, as follows from Eq. (1), their electrophoretic mobilities are higher. The problems connected with CE analysis of inorganic cations are due to small differences in their migration rates (see Table 2), and, similar to the CE analysis of inorganic anions [17], to their low absorption of UV radiation.

Only the alkali metal ions exhibit large differences in their mobilities and thus can be easily separated within a very short time (less than 2 min), if the EOF and the cations migrate in the same direction (toward the cathode). The exceptions are K^+ and NH_4^+ ions which are not separated at a slightly acidic pH (Table 2). Their separation can be attained in alkaline buffers as the ammonium ions are less protonated and their mobility is smaller while the K^+ ion mobility is not affected by the pH.

Bivalent and trivalent cations, such as those of the alkaline earth, rare earth and transition metals, cannot be separated in a simple electrolyte as their mobilities are very similar due to similar charge-to-size ratios (see, e.g., the pairs of Ca^{2+}/Sr^{2+}, Mn^{2+}/Mg^{2+} or Zn^{2+}/Mg^{2+}, Table 1). An exception is the Pb^{2+} ion with a higher mobility due to its smaller hydrated radius resulting from a lower degree of hydration. Complexation reactions of these cations must be employed to enhance the differences in their mobilities.

4. Metal ion complexation

Complexation of the cations to be separated with auxiliary ligands is used to change the selectivity of the separation and/or to facilitate the detection. In principle, two experimental approaches are used in the CE analysis of cations, an off-line preparation of complexes, prior to the CE analysis, and on-line complexation in the separation capillary. Their application depends on the stability of the complexes formed (e.g., ref. [13]).

4.1. On-line complexation

If weak complexes are rapidly formed, then on-capillary partial complexation can be used. A ligand is added to the running electrolyte and a rapid equilibrium between the free metal ions and their complexes is established, with most of the ions present in free form. Owing to different complexation degrees with various charges on the complexes, the ions have different migration rates. The CZE mode and indirect UV detection are usually employed in this case, as only a small fraction of the cations is complexed.

The effective mobility of cation M^{2+}, reacting with ligand L^- to consecutively form complexes with different numbers of the monovalent ligands L^- and different stabilities, can be described by Eq. (3),

$$\mu_{eff} = \alpha\mu_{eff}(M^{2+}) + \beta\mu_{eff}(ML^+) + \gamma\mu_{eff}(ML_2) + .. + \omega\mu_{eff}(ML_m^{(m-2)-}) + \mu_{eo} \quad (3)$$

where α, β, γ, $\ldots\omega$ are the mole fractions of the consecutive complexes. Metal ions which are complexed to a higher extent migrate more slowly.

The mobilities of the running buffer ions should be close to the analyte mobilities. The difference in the conductivities, Δk, that causes asymmetry of the peaks, is given by Eq. (4) [23],

$$\Delta k = c_B \mu_B (\mu_A - \mu_B)(\mu_R - \mu_B) \quad (4)$$

where μ_B, μ_A and μ_R are the ionic mobilities of the analyte cation, the electrolyte co-ion and the electrolyte counter-ion and c_B is the analyte concentration. It follows from Eq. (4) that the peak asymmetry increases with increasing concentration of the analyte cation in the sample and that both the co-ion and counter-ion mobilities affect the peak asymmetry. Recommended buffers are, e.g., borate, bicarbonate, glycine, taurine, nicotineamide, β-alanine. Poor peak shapes can also be connected with slow complexation equilibria in the capillary.

Fast equilibration is a prerequisite for on-capillary complexation. Various complexing agents have been recommended and compared. Stepwise complexation with α-hydroxyisobutyric acid (α-HIBA) is often used, similar to IC where it serves for the separation of the lanthanoids, and simultaneous separations of the alkali, alkaline earth and transition metals [24–26]. Very good separations have also been obtained with other complexing agents, e.g., lactic, succinic, malonic, tartaric and citric acid. An excellent separation of 27 cations of the alkali, alkaline earth, transition and rare earth metal ions has been obtained using an electrolyte consisting of 15 m*M* lactic acid as the complexing agent, 8 m*M* 4-methylbenzylamine as the UV absorbing compound and 5% methanol, pH 4.25 (Fig. 1) [27].

The equilibria of complexation reactions with weakly acidic or basic ligands is influenced by the pH of the running buffer and by the concentration of the complexing agent, c_{HL}, as follows from Eq. (5) [28],

$$\mu_{ep} = a + bc_{HL} + c\mathrm{pH}c_{HL} + dc_{HL}^2 \quad (5)$$

where *a*, *b*, *c* and *d* are empirical constants.

The effect of the pH and the type of the weak

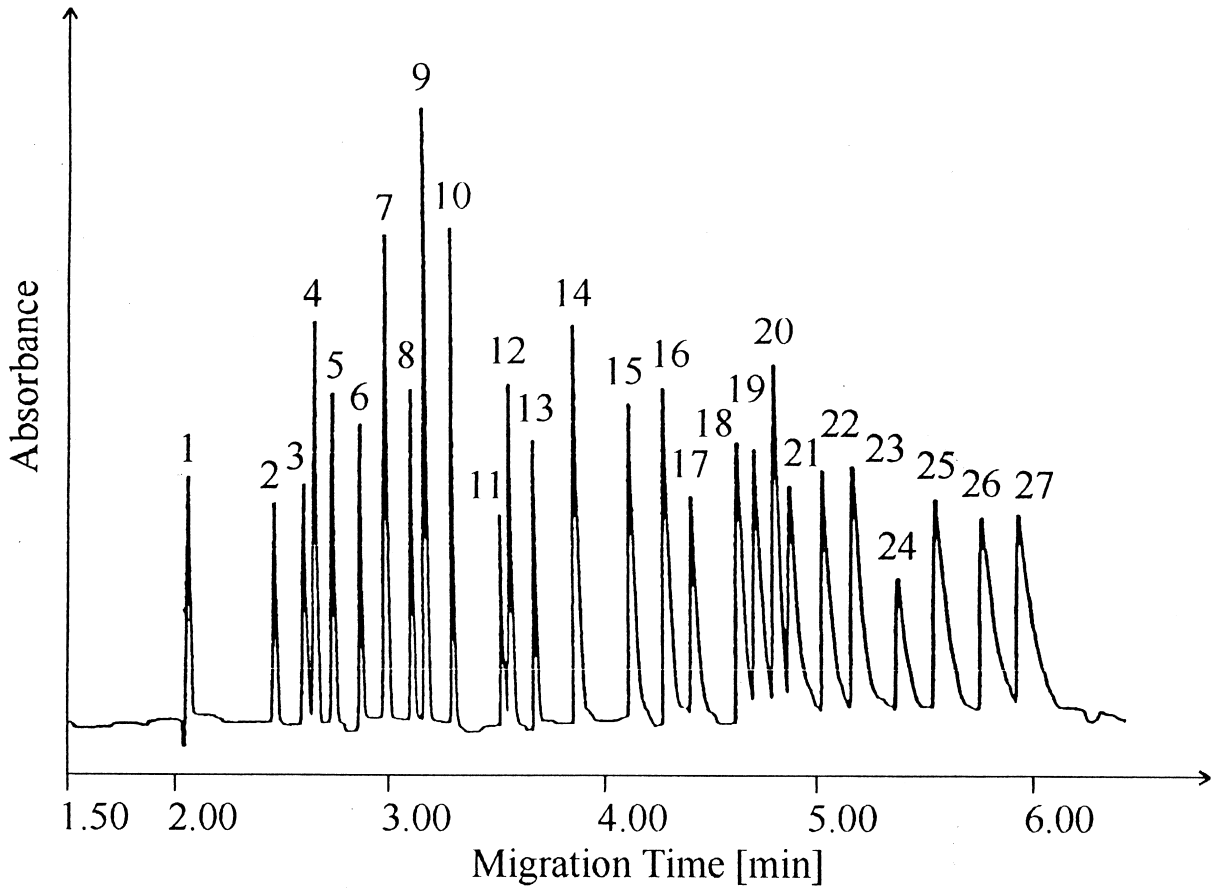

Fig. 1. Electropherogram of the separation of alkali, alkaline earth, transition metals and lanthanoids. Capillary, 60 cm×75 μm fused-silica; running electrolyte, 15 m*M* lactic acid, 8 m*M* 4-methylbenzylamine, 5% methanol, pH 4.25; separation voltage, 30 kV; temperature, 20°C; injection, hydrostatic for 6 s; detection, indirect UV at 214 nm. Peaks, 1=K^+, 2=Ba^{2+}, 3=Sr^{2+}, 4=Na^+, 5=Ca^{2+}, 6=Mg^{2+}, 7=Mn^{2+}, 8=Cd^{2+}, 9=Li^+, 10=Co^{2+}, 11=Pb^{2+}, 12=Ni^{2+}, 13=Zn^{2+}, 14=La^{3+}, 15=Ce^{3+}, 16=Pr^{3+}, 17=Nd^{3+}, 18=Sm^{3+}, 19=Gd^{3+}, 20=Cu^{2+}, 21=Tb^{3+}, 22=Dy^{3+}, 23=Ho^{3+}, 24=Er^{3+}, 25=Tm^{3+}, 26=Yb^{3+}, 27=Lu^{3+}. (Reproduced with permission from Ref. [27]).

complexing agent (acetic, glycolic, lactic, α-HIBA, oxalic, malonic, malic, tartaric, succinic and citric acids) on the separation of the alkali and alkaline earth metals have been studied [29]. An optimal pH for the separation was around the pK_a of the monoprotic acid. With di- and triprotic acids, the pH must lie between p$K_{a,1}$ and p$K_{a,2}$. At pH values above p$K_{a,2}$, the mobility and the efficiency decreases. Glycolic, lactic, succinic, α-HIBA and malonic acids at a pH around 4 yield comparably good results if the concentrations of the analytes are similar. If the concentration of one cation is much higher than those of other cations, oxalic acid at pH 4.0, or citric acid at pH 4.5, should be used.

The complexing agent must contain suitable binding groups (carboxyl, hydroxyl), its ionic groups should not interfere with the complexation equilibrium (they should be located far from the binding groups) and the agent should absorb at different wavelengths than the complex.

A mathematical model has been developed for prediction of the electrophoretic mobilities of cations, using α-HIBA as the complexing agent and imidazole as the UV absorbing compound for indirect UV detection [28]. The calculated mobilities of 14 cations [alkali, alkaline earth and transition metal (II) cations] were in a good agreement with the experimental results. A chemometric approach was used for optimization of the electrolyte pH, the concentration of the complexation agent and the concentration of the visualization agent in the separation of cations present at very low concentrations [30].

4.2. Off-line complexation

If the complexes of metals with ligands are sufficiently stable under the CE conditions, then off-capillary complexation is preferred. An excess of a strongly complexing agent is added to the sample prior to the CE analysis. On-column UV detection is possible as the fraction of complexed ions is large. If there is a danger of the complex dissociation during the CE analysis, the complexation agent is added to the running buffer in a low concentration. The number of ligands does not affect the separation but the buffer components or competing complexing ligands do. The calculations of the effective mobilities are more complicated than in the case of on-line complexation as all the equilibria must be included in the prediction of separation.

Cationic, anionic or neutral metal complexes can be formed off-line and separated by CE or MEKC, in dependence on their structure and charge [13]. In MEKC, metal complexes interact with micelles mainly through hydrophobic but also polar interactions and the migration times increase. If charged complexes are separated by MEKC, then both the ion charge-to-size ratio and the degree of partition into the micelles participate in the control of the migration rates.

An advantage of cationic complexes lies in rapid analyses in CZE due to the coelectroosmotic migration. However, the number of metals that can be separated in this mode is limited by a narrow migration window and/or by their similar mobilities. When using MEKC, the polarity can be reversed by an addition of a cationic surfactant to the electrolyte and thus the separation can be improved [31].

Anionic metal complexes, such as those with cyanide, move, during CZE in uncoated capillaries, to the anode against the EOF and are detected within an acceptable time due to their large charge-to-size ratio. Large ligands move very slowly or not at all. It is then necessary to suppress or reverse the EOF by adding a cationic surfactant or by a suitable coating of the capillary (e.g., Refs. [32–35]).

Neutral complexes used in analyses of metal ions include, e.g., α,β,γ,δ-tetrakis(4-carboxyphenyl)porphine chelates [36], bis(2-hydroxyethyl)dithiocarbamate complexes [37] or acetylacetone complexes [38]. They can be separated by MEKC. It has been demonstrated that the migration times can be predicted from the dodecane–water partition data if the distribution of the complexes between the running buffer and the micelles is the predominating process [38]. MEKC is a technique complementary to the high-performance liquid chromatography (HPLC) of metal ions, due to its high separation efficiency and different selectivity.

Several conditions must be satisfied in off-line complexation. The ligand should react with a large number of metal cations and should suppress the original properties of the metals. The complexes should have a high UV absorbance, high solubility and a low electronegativity to prevent adsorption on

the capillary wall [13]. The complex must be sufficiently separated from the free complexing agent.

The ligand purity plays an important role in separations of cations [39]. The ligand and the other reagents should be free of metal ions and other substances that could possibly form more stable complexes with the analytes.

The complexes of Cu^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+}, Fe^{2+} and Fe^{3+} metal ions with weak, medium and strong complexing agents, α-HIBA, 8-hydroxyquinoline-5-sulfonic acid (HSQ) and ethylenediaminetetraacetic acid (EDTA) were compared (Table 3) and the average number of ligands was calculated [40]. With the monovalent ligand α-HIBA, the metal ions migrate mainly as a mixture of the free metal ions M^{2+} and the ML^{+} complexes. The optimal concentration of α-HIBA in the running buffer has been found to be 15 m*M*; at concentrations higher than 50 m*M*, the migration times are too long. The migration order and resolution can be calculated. In the presence of HSQ, the metal ions are almost fully complexed, predominantly in the ML_2^{2-} complexes. The migration behaviour of cations in the presence of HSQ is complicated and depends on the differences in the cation-HSQ complex structures, on their kinetic behaviour and on the differences in their stability constants. EDTA is a very popular complexing agent in analytical determinations of various metals as it forms strong chelates with monovalent, divalent, trivalent and also tetravalent metals.

4.3. Crown ether additives

Separation of cations can be influenced by their interaction with crown ethers, e.g., Refs. [41–43], which depends on the sizes of the cation and the crown ether cavity. The concentration of a crown ether in the running buffer also plays a role. The best results have been obtained with 18-crown-6-ether where the selectivity changes were largest. The use of crown ethers makes it possible to separate potassium from ammonium.

5. Detection

UV–Vis detection is most common in capillary electrophoresis, as it is simple and reliable, and is discussed in detail, e.g., in Refs. [2,3]. The problems connected with the detection in the CE analysis of inorganic cations are due to their low absorption in the UV region. Similar to the CE analysis of anions, an indirect UV or fluorescence detection have been introduced, based on charge displacement of an absorbing co-ion. The main advantage of indirect UV detection is universal application and thus it is most commonly used in inorganic ion analysis. The problems of indirect detection are discussed in detail in, e.g., Refs. [44–52]. The UV visualization agents (probes) involve, e.g., Cu(II) salts [53], chromate, aromatic amines and heterocyclic compounds, e.g., benzylamine, 4-methylbenzylamine (UV-Cat 1), dimethylbenzylamine, imidazole, *p*-toluidine, pyridine, (e.g., [51,54]), creatinine [55], ephedrine [56] or anionic chromophores such as benzoate and anisate [57]. Examples of analyses of cations in tap water and in Mattoni mineral water with indirect UV detection using $CuSO_4$ as the visualization agent are shown in Fig. 2A and B [132].

To achieve a high sensitivity in indirect detection, the cation peak width should be minimized. Interactions of the cations and visualization agent with the capillary wall should be suppressed. The visualization agent should exhibit a mobility close to that of

Table 3
Consecutive stability constants [40]

Cation	Weak α-HIBA			Medium HSQ		Strong EDTA
	Log β_1	Log β_2	Log β_3	Log β_1	Log β_2	Log β_1
Cu^{2+}	2.73	4.34	4.38	12.50	23.10	18.80
Zn^{2+}	1.72	3.01	3.40	8.40	15.10	16.50
Ni^{2+}	1.67	2.80	2.84	10.00	18.10	18.62
Pb^{2+}	–	–	–	8.53	16.13	18.04
Fe^{2+}	–	–	–	8.40	15.10	14.32
Fe^{3+}	–	–	–	11.6	22.8	25.10

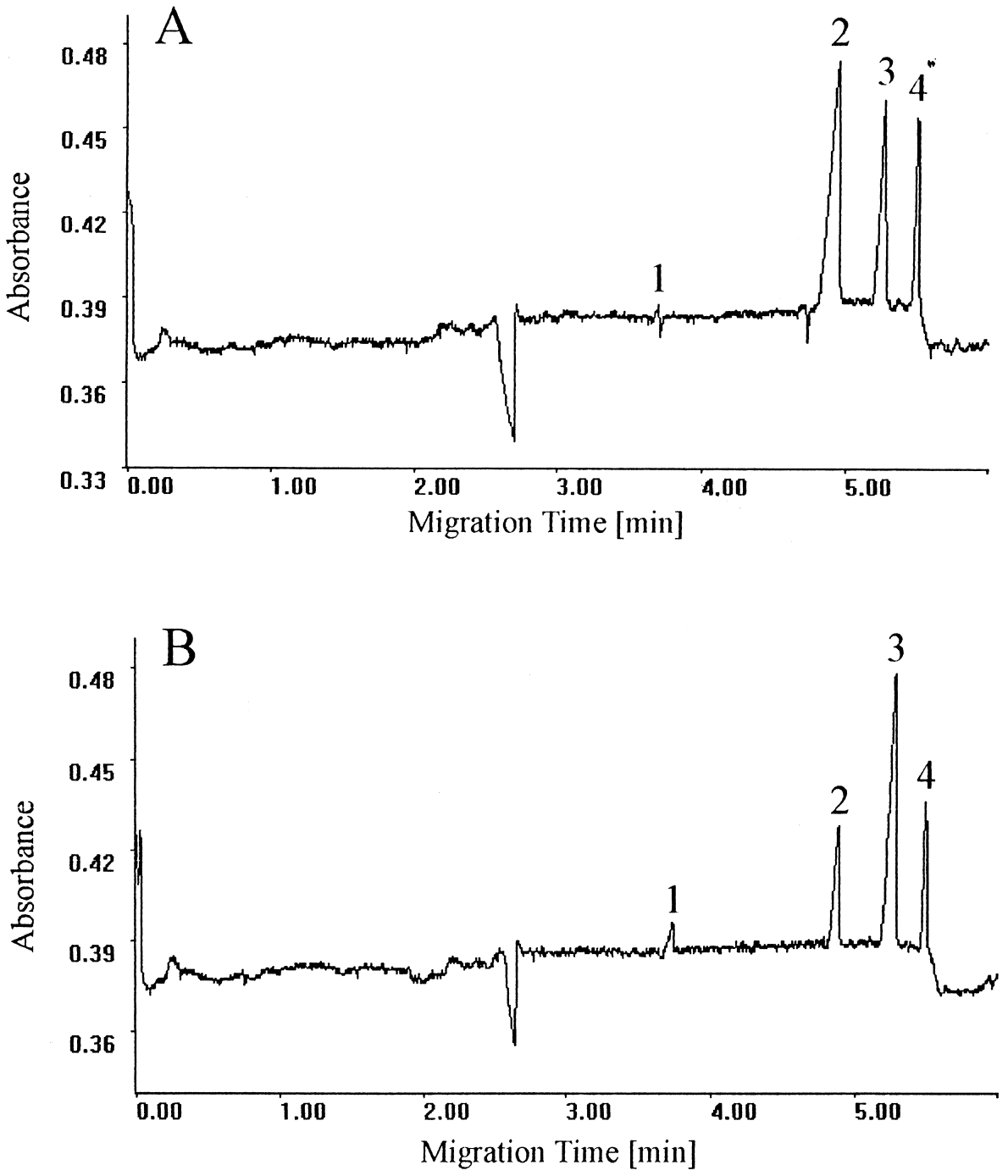

Fig. 2. Electropherograms of the analysis of cations in tap water (A) and Mattoni mineral water (B). Capillary, 73 cm (60 cm effective length)×72 μm fused-silica; running electrolyte, 4 m*M* $CuSO_4$, 4 m*M* HCOOH, pH 3.0; separation voltage, 20 kV; temperature, 20°C; injection, hydrodynamic, 10 mbar for 6 s; detection, indirect UV at 215 nm. Peaks, 1=K^+, 2=Na^+, 3=Ca^{2+}, 4=Mg^{2+} [132].

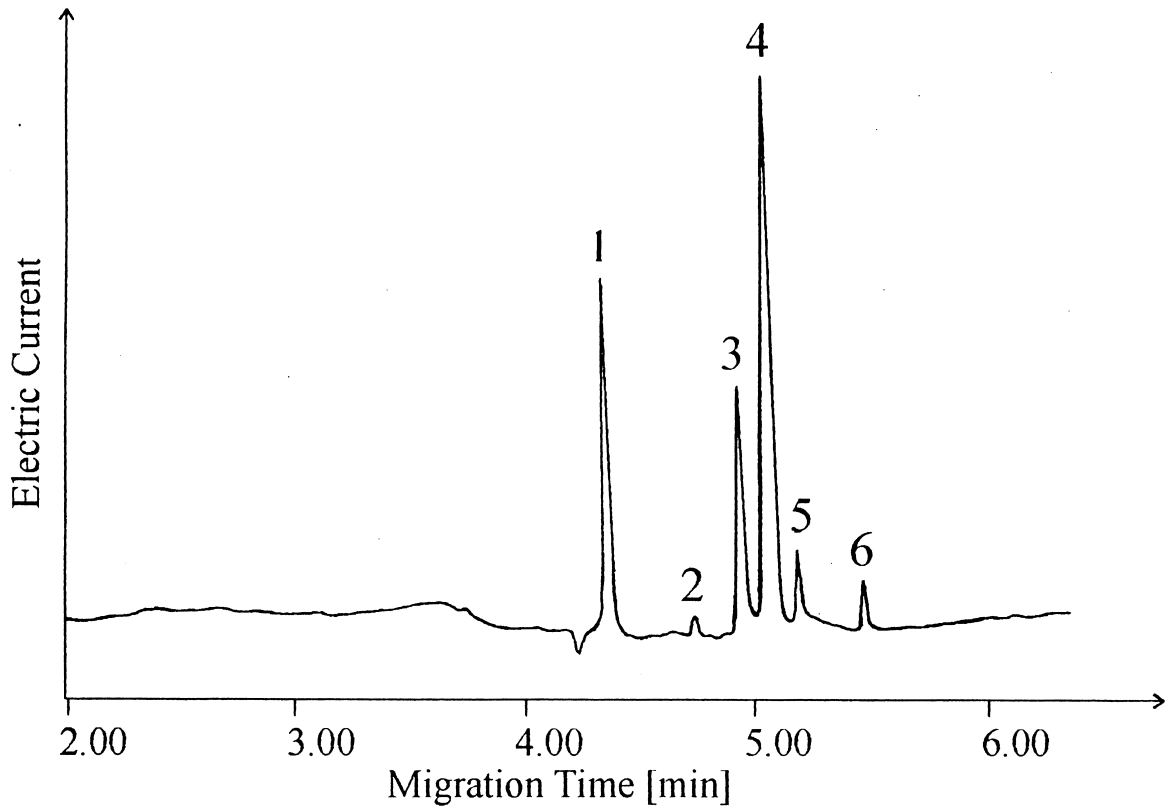

Fig. 3. Electropherogram of the analysis of cationic impurities in the drug Carbetocin with conductivity detector. Capillary, 70.0 cm×50 μm fused-silica; running electrolyte, 30 m*M* histidine, 30 m*M* 2-morpholinoethanesulfonic acid, pH 6.0; separation voltage, 30 kV; temperature, 20°C; injection, hydrodynamic, 20 mbar for 6 s; detection, conductometric. Peaks, 1=K^+, 2=Ba^{2+}, 3=Ca^{2+}, 4=Mg^{2+}, 5=Na^+, 6=Li^+. (Kindly provided by Dr. I. Jelínek from our Department).

the cations (see Eq. (4)), its UV absorbance should be as high and the detector noise as small as possible [14]. Only the visualization agent should be displaced by the analytes.

Indirect fluorescence detection has further been used in the analysis of cations [58–60]. Indirect laser-induced fluorescence has also been tested for detection of cations, using quinine sulfate as the fluorescence agent, but the sensitivity obtained with this expensive detection mode has so far not been superior to indirect UV detection [60].

Direct UV–Vis or fluorescence detection is possible if the ligand used for the analyte complexation reaction contains a chromophore or a fluorophore (e.g., ref. [61]). Several metal ions, e.g., Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, form complexes with cyanide [62,63]. Analogously, Fe^{2+} and Fe^{3+} form complexes with *o*-phenanthroline in the presence of EDTA [64] and Au^{3+} with chloride [65] that can be detected spectrophotometrically. 8-Hydroxyquinoline-5-sulfonic acid (HAS) forms complexes with metals that fluoresce [32,61,66]. Dithizone sulfonate complexes were used in determination of traces of inorganic mercury [67]. PAR forms colour complexes with Cu^{2+}, Pb^{2+}, Ni^{2+}, Cd^{2+}, Fe^{2+} and Fe^{3+} [33,34], arsenoazo I forms complexes with Ba^{2+}, Sr^{2+}, Ca^{2+} and Mg^{2+} [39], arsenoazo III was recommended for the separation of lanthanoids and U^{6+} [68], sulfonoazo III for the determination of Ba^{2+} and Sr^{2+} [35]. Detection limits of 10^{-7} *M* have been attained, using PAR complexes with the transition metals [33].

Similar to CE analysis of anions, on- or end-column conductivity detection (CD) can be used for

cations. CD is a nearly universal bulk property detection mode for small ions. Inorganic or organic buffers with low conductivities, e.g., borate or MES–histidine, and higher ionic strengths are used when employing conductivity detection. A ten-times higher sensitivity compared to indirect UV detection was claimed [69]. Fig. 3 depicts a determination of cationic impurities (K^+, Ba^{2+}, Ca^{2+}, Mg^{2+}, Na^+ and Li^+ ions) in the drug Carbetocin using a MES–histidine buffer with conductivity detection. High-frequency (contactless conductivity) detection has been suggested for analysis of Rb^+, K^+, Na^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Cd^{2+} and Li^+ cations, with a detection limit of about $1\cdot10^{-4}$ *M* [70].

A selective amperometric detector with a mercury film microelectrode was tested for metal ions, yielding limits of detection in the one tenth of ppb region [71,72]. A pulse amperometric mode improved the stability of the baseline compared to the constant voltage mode [73]. Electrochemical detection has also been used in the CE analysis of Tl^+, Pb^{2+}, Cd^{2+} and Cu^{2+} [71].

CE–MS was used in the analysis of cations as a method simultaneously providing positive identification and quantification [74,75]. However, the sensitivity of the measurement was not considerably improved over indirect UV detection due to a high noise.

ICP-MS, ICP-OES or ICP-AES detection techniques have been discussed in several papers [76–82]. Problems in interfacing the ICP-MS detection to CE are associated with low flow-rates and small samples analyzed in CE [77]. Detection limits between 6 to 58 ppt were attained for four arsenic species, using post-capillary hybridization prior to ICP-MS [77], and $1\cdot10^{-3}$ *M* for As^{3+} and As^{5+} using ICP-AES [78]. ICP–MS detection was further used in the analysis of Se^{4+} and Se^{6+} [79,80] with detection limits of 1 to $3\cdot10^{-7}$ *M*, Pt^{2+} and Pt^{4+} [81] with detection limits of 2 to $4\cdot10^{-6}$ *M* and for determination of Mn^{2+}, Ni^{2+}, Co^{2+} and La^{3+} with detection limits of $3\cdot10^{-4}$ to $1\cdot10^{-4}$ *M* [82].

6. Applications

A number of applications can be found in the literature. A very good selection is given in the reviews [11,14]. Some important applications of CE in the analysis of cations are summarized in Table 4. The table is subdivided into sections according to the analytes: (A) alkali and alkali earth metals, (B) transition metals, (C) lanthanoids and uranium. In each section, various detection modes are distinguished, i.e., a direct and indirect visible and UV, an indirect fluorescence, a conductivity, an electrochemical, an ICP-MS and an ICP-AES detection.

7. Conclusion

As can be seen above, CE techniques constitute a very attractive alternative to more common methods of determining inorganic cations (spectroscopy, chromatography), primarily because of a high resolution and possibility of multicomponent separation using simple and rapid procedures. On the other hand, the limits of detection and quantitation often compare unfavourably with those attained in spectroscopy and chromatography [83].

8. List of abbreviations

AES	Atomic emission spectrometry
Arsenazo I	2-(4,5-Dihydroxy-2,7-disulfo-3-naphthylazo)phenylarsonic acid
Arsenazo III	2,2′-(1,8-Dihydroxy-3,6-disulfonaphthylene-2,7-bisazo)-bisbenzenearsonic acid
5-Br-PADAP	2-(-5′-Bromo-2′-pyridylazo)-5-diethylaminophenol
5-Br-PAPS	2-(-5′-Bromo-2′-pyridylazo)-5-(*N*-propyl-*N*-sulfopropylamino)phenol
CDTA	Cyclohexane-1,2-diaminetetraacetic acid
CTAB	Cetyltrimethylammoniumbromide
DBA	*N*,*N*-Dimethylbenzylamine
DDP	Dimethylphenylphosphonium hydroxide
DEA	*N*,*N*-Diethylaniline
DHBP	1,1′-Di-*n*-heptyl-4,4′-bipyridinium
DTPA	Diethylenetriaminepentaacetic acid
EDTA	Ethylenediaminetetraacetic acid
HEC	Hydroxyethylcellulose

Table 4
Examples of typical applications

Analyte	Conditions (running electrolyte, pH, capillary length, length to the detector, inner diameter, voltage)	Detection, concentration range and sample type	Ref.
(A) Alkali and alkali earth metals			
Ba^{2+}, Sr^{2+}	20 m*M* MES, 10 m*M* Tris, 0.30 m*M* sulfonazo III, pH 6.2 60 cm (52 cm)×75 μm, 30 kV	Vis at 654 nm $3\cdot10^{-7}$–$5\cdot10^{-7}$ *M*	[35]
Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}	1 m*M* citric acid, 17 m*M* acetic acid, DEA, 1.0 m*M* arsenazo I, pH 9.5 60 cm (52 cm)×75 μm, 30 kV	Vis at 568 nm $1\cdot10^{-6}$–$1\cdot10^{-4}$ *M*	[39]
Ca^{2+}	20 m*M* $Na_2B_4O_7$, 2 m*M* EDTA, pH 9.2 72 cm (25 cm)×50 μm, 20 kV	UV at 200 nm $1\cdot10^{-4}$–$5\cdot10^{-4}$ *M* vegetables	[84]
K^+, Ca^{2+}, Na^+, Mg^{2+}, Cu^{2+}	5 m*M* UV Cat-1, 6.5 m*M* HIBA, pH 4.4 60 cm (52 cm)×75 μm, 20 kV	Indirect UV at 214 or 185 nm, $1\cdot10^{-5}$–$5\cdot10^{-4}$ *M* tap water, juice	[25]
Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Cs^{2+}	5 m*M* UV Cat-1, 6.5–40 m*M* HIBA, pH 4.4 60 cm (–)×75 μm, 20 kV	Indirect UV at 214 nm $4\cdot10^{-5}$–$2\cdot10^{-2}$ *M*	[26]
K^+, Na^+, Ca^{2+}, Mg^{2+}	12 m*M* HIBA, 6 m*M* imidazole, pH 3.95 62 cm (50 cm)×50 μm, 25 kV	Indirect UV at 214 nm tap water	[28]
K^+, Na^+, Ca^{2+}, Mg^{2+}	4 m*M* tartaric acid, 6 m*M* imidazole, pH 4.00 62 cm (50 cm)×50 μm, 25 kV	Indirect UV at 214 nm tap water	[28]
Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}	5 m*M* imidazole, 4.0 m*M* malonic acid, pH 4.0 42 cm (35 cm)×50 μm, 25 kV	Indirect UV at 215 nm $4\cdot10^{-4}$ *M*	[29]
NH_4^+, K^+, Ca^{2+}, Na^+, Mg^{2+}, Li^+	10 m*M* imidazole, 2.5 m*M* 18-crown-6, pH 4.5 57 cm (50 cm)×75 μm, 25 kV	Indirect UV at 214 nm $4\cdot10^{-7}$ *M*	[41]
NH_4^+, K^+, Ba^{2+}, Ca^{2+}, Na^+, Mg^{2+}, Li^+	1 m*M* UV Cat-2, 30 m*M* tropolone, 3.5 m*M* 18-crown-6, – 60 cm (–)×75 μm, 20 kV	Indirect UV at 185 nm $3\cdot10^{-4}$–$4\cdot10^{-2}$ *M*	[42]
NH_4^+, K^+, Na^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, Li^+, Ba^{2+}	4 m*M* $CuSO_4$, 4 m*M* 18-crown-6, 4 m*M* formic acid, pH 3.1 66 cm (58.5 cm)×75 μm, 20 kV	Indirect UV at 215 nm $1\cdot10^{-4}$–$3\cdot10^{-3}$ *M*	[43]
K^+, Na^+, Ba^{2+}, Ca^{2+}, Mg^{2+}, Li^+	5 m*M* imidazole, H_2SO_4, pH 4.5 63 cm (55 cm)×75 μm, 25 kV	Indirect UV at 214 nm $2\cdot10^{-6}$–$4\cdot10^{-6}$ *M*	[51]
NH_4^+, K^+, Na^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, Li^+, Ba^{2+}	4.0 m*M* $CuSO_4$, 4.0 m*M* HCOOH, 4.0 m*M* 18-crown-6, pH 3.0 50 cm (–)×50 μm, 20 kV	Indirect UV at 215 nm $3\cdot10^{-5}$–$1\cdot10^{-3}$ *M* Drinking water	[53]
K^+, Na^+, Mg^{2+}, Li^+, lanthanoids	0.03 *M* creatinine, 4 m*M* HIBA, acetic acid, pH 4.8 20 cm (–)×25 μm, 12 kV	Indirect UV at 220 nm $5\cdot10^{-4}$–10^{-3} *M*	[55]
K^+, Ba^{2+}, Na^+, Li^+	10 m*M* *p*-anisic acid, Tris, pH 8.24 72 cm (50 cm)×50 μm, 7.5 kV	Indirect UV at 270 nm $5\cdot10^{-4}$–$1\cdot10^{-3}$ *M*	[57]
K^+, Ca^{2+}, Na^+, Mg^{2+}, Li^+	0.38 m*M* quinine sulfate, 0.58 m*M* H_2SO_4, pH 3.7 82.3 cm (70.7 cm)×18 μm, 40 kV	Indirect fluorescence $1\cdot10^{-5}$–$4\cdot10^{-5}$ *M*	[58]
K^+, Ba^{2+}, Sr^{2+}, Ca^{2+}, Na^+, Mg^{2+}, Li^+	5 m*M* UV Cat-2, 6.5 m*M* tropolone, pH 4.4 60 cm (52 cm)×75 μm, 20 kV	Indirect UV at 185 nm $1\cdot10^{-5}$–$1\cdot10^{-4}$ *M*	[85]
K^+, Ca^{2+}, Sr^{2+}, Mg^{2+},	8 m*M* nicotinamide, 0.6 m*M* 18-crown-6,	Indirect UV at 214	[86]

Table 4 (*continued*)

Analyte	Conditions (running electrolyte, pH, capillary length, length to the detector, inner diameter, voltage)	Detection, concentration range and sample type	Ref.
Na^+, Al^{3+}, Cu^{2+},	formic acid, pH 3.2	or 254 nm	
Ba^{2+}, Li^+, VO^{2+}	60 cm (52.5 cm)×75 μm, 25 kV	$1\cdot10^{-5}$–$1\cdot10^{-4}$ *M*	
NH_4^+, K^+, Ca^{2+}, Na^+,	8 m*M* nicotinamide, 0.95 m*M* 18-crown-6,	Indirect UV at 214	[86]
Mg^{2+}, Sr^{2+}, Al^{3+},	12% CH_3OH, formic acid, pH 3.2	or 254 nm	
Ba^{2+}, Li^+	60 cm (52.5 cm)×75 μm, 25 kV	$1\cdot10^{-5}$–$5\cdot10^{-5}$ *M*	
Cs^+, K^+, Ca^{2+}, Mg^{2+},	0.1 m*M* methyl green, 1 m*M* Tris,	Indirect Vis at 630 nm	[87]
Na^+, Li^+	acetic acid, pH 6.5	$5\cdot10^{-4}$ *M*	
	65 cm (50 cm)×100 μm, 10 kV		
Cs^+, NH_4^+, K^+, Ca^{2+},	500 μ*M* $Ce(SO_4)_2$, 2.5 m*M* 18-crown-6, –	Indirect fluorescence	[88]
Na^+, Mg^{2+}, Sr^{2+},	55 cm (–)×75 μm, 30 kV	$1\cdot10^{-7}$–$3\cdot10^{-6}$ *M*	
Ba^{2+}, Li^+		rain water, soft drink	
K^+, Ca^{2+}, Na^+, Mg^{2+}	5 m*M* UV Cat-1, 6.5 m*M* HIBA, pH 4.4	Indirect UV at 214 nm	[89]
	60 cm (–)×75 μm, 20 kV	milk	
K^+, Ba^{2+}, Sn^{2+}, Li^+,	5 m*M* benzimidazole, 40 m*M* 18-crown-6,	Indirect UV at 254 nm	[90]
Ca^{2+}, Mg^{2+}, Na^+, Rb^+,	0.1% HEC, 0.1% mHEC,	10^{-5}–$2\cdot10^{-2}$ *M*	
NH_4^+, Cs^+	tartaric acid, pH 5.2	drinking and rain water,	
	25 cm (–)×300 μm,	mineral water	
	copolymer inside, 75 μA		
K^+, Na^+, Ca^{2+}, Mg^{2+}	4 m*M* $CuSO_4$, 4 m*M* formic acid,	Indirect UV 215 nm	[91]
	H_2SO_4, pH 3	human tears	
	52 cm (47 cm)×75 μm, 20 kV		
Na^+, K^+, Mg^{2+}, Ca^{2+},	5 m*M* UV Cat-1, 6.5 m*M* HIBA,	Indirect UV at 185 or	[92]
Sr^{2+}, Ba^{2+}	6.2 m*M* 18-crown-6, 25% CH_3OH, –	254 nm, $4\cdot10^{-4}$–$3\cdot10^{-3}$ *M*	
	60 cm (52 cm)×75 μm, 20 kV	seawater and formation water	
K^+, Na^+, Ca^{2+}, Mg^{2+}	10 m*M* imidazole, 6 m*M* HIBA,	Indirect UV at 220 nm	[93]
	5 m*M* 18-crown-6, acetic acid, pH 3.91	$4\cdot10^{-4}$ *M*	
	55 cm (–)×75 μm, 30 kV	seawater	
NH_4^+, Ca^{2+}, Na^+,	5.05 m*M* UV Cat-1, 3.78 m*M* 18-crown-6,	Indirect UV at 185, 254	[94]
Mg^{2+}, K^+	13.06 m*M* HIBA, pH 3.6	or 214 nm, $2\cdot10^{-4}$–$7\cdot10^{-4}$ *M*	
	60 cm (–)×75 μm, 20 kV	atmospheric aerosol	
Cs^+, NH_4^+, K^+, Na^+,	4 m*M* METOL, 2 m*M* 18-crown-6, –	Indirect UV at 220 nm	[95]
Ca^{2+}, Mg^{2+}, Sr^{2+},	80 cm (65 cm)×75 μm, 30 kV	$1\cdot10^{-4}$ *M*	
Ba^{2+}, Li^+			
NH_4^+, K^+, Ca^{2+}, Na^+,	5 m*M* DDP, 2 m*M*, 18-crown-6,	Indirect UV at 210 nm	[96]
Mg^{2+}, Li^+	6 m*M* HIBA, –	$4\cdot10^{-5}$ *M*	
	50 cm (–)×50 μm, 20 kV	silicone products	
NH_4^+, Na^+	5 m*M* UV Cat-1, 6.5 m*M* HIBA,	Indirect UV at 214 nm	[97]
	2 m*M* 18-crown-6, –	$2\cdot10^{-4}$ *M*	
	60 cm (–)×75 μm, 20 kV	trace explosives	
K^+, Ca^{2+}, Na^+,	2.6 m*M* HIBA, 2 m*M* UV Cat-1,	Indirect UV at 214 nm	[98]
Ba^{2+}, Li^+	0.8 m*M* 18-crown-6, –	$1\cdot10^{-2}$ *M*	
	60 cm (–)×75 μm, 20 kV	human vitreous humor	
K^+, NH_4^+, Ca^{2+},	2.5 m*M* $Cu(NO_3)_2$, 5 m*M* ethylenediamine,	Indirect UV at 214 nm	[99]
Na^+, Mg^{2+}	1 m*M* fumaric acid, TEAOH, pH 8.5	$1\cdot10^{-4}$–$3\cdot10^{-4}$ *M*	
	50 cm (22 cm)×75 μm, 25 kV	cations and anions in a single run	
Cs^+, K^+, NH_4^+, Na^+,	6 m*M* 4-aminopyridine, 2.7 m*M* H_2CrO_4,	Indirect UV at 262 nm	[100]
Ca^{2+}, Mg^{2+}, Li^+	30 μ*M* CTAB, pH 8	tap water, rain water, milk	
	50 cm (20 cm)×50 μm, 20 kV	cations and anions in a single run	
K^+, Na^+, Li^+	5 m*M* MES, 3–100 m*M* HIS, pH 6.0	End-column conductivity	[101]
	35.8 cm (–)×75 μm, 15 kV	$1\cdot10^{-4}$ *M*	

(*continued on next page*)

Table 4 (*continued*)

Analyte	Conditions (running electrolyte, pH, capillary length, length to the detector, inner diameter, voltage)	Detection, concentration range and sample type	Ref.
Rb^+, K^+, Na^+, Li^+	20 m*M* MES, HIS, pH 6 60 cm (–)×75 μm, 15 kV	On-column conductivity $2\cdot10^{-5}$ *M*, human serum	[102]
K^+, Na^+, Li^+	20 m*M* MES, HIS, pH 6.1 70 cm (–)×75 μm, 25 kV	On-column conductivity $1\cdot10^{-3}$ *M*, human serum	[103]
K^+	20 m*M* $Na_2B_4O_7$, – 25 cm (–)×75 μm, 8 kV	Conductometric $1\cdot10^{-3}$ *M*	[104]
(B) Transition metals (eventually with alkali and alkali earth metals)			
Co^{2+}, Cr^{3+}, Fe^{3+}, Ni^{2+}	50 m*M* NaH_2PO_4, 12.5 m*M* $Na_2B_4O_7$, 0.02 m*M* SDS, 0.1 m*M* PAR 85 cm (70 cm)×50 μm, 16.5 kV	UV at 500 nm $1\cdot10^{-3}$ *M*	[13]
Mo^{6+}, Sc^{3+}, Fe^{3+}, Zn^{2+}, Cd^{2+}, Zr^{4+}, Co^{2+}, Y^{6+}, Cu^{2+}, Sn^{4+}, Ta^{5+}, Hg^{2+}	10 m*M* $Na_2B_4O_7$, 75 m*M* TTAB, 10 m*M* sodium *n*-octanesulfonate, pH 9.0 50 cm (–)×75 μm, 15 kV	UV at 254 nm $4\cdot10^{-5}$–$2\cdot10^{-4}$ *M*	[13]
Cd^{2+}, Pb^{2+}, Pt^{2+}, Co^{2+}, Ni^{2+}, Bi^{3+}, Cr^{3+}, Cu^{2+}, Hg^{2+}	60 m*M* MOPS, 30 m*M* Tris, 10 m*M* SDS, 0.1 m*M* HEDTC, pH 7.2 60 cm (52 cm)×75 μm, 20 kV	UV at 254 nm $3\cdot10^{-5}$ *M*	[13]
Mn^{2+}, Cu^{2+}, Al^{3+}, Cd^{2+}, Fe^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}	10 m*M* $Na_2B_4O_7$, 0.1 m*M* HQS, pH 9.0 42 cm (35 cm)×75 μm, 15 kV	UV at 254 nm $6\cdot10^{-5}$–$1\cdot10^{-4}$ *M*	[32]
Cr^{3+}, Ca^{2+}, Cu^{2+}, Pb^{2+}, Ni^{2+}, Fe^{2+}, Zn^{2+}, Fe^{3+}, Cd^{2+}	10 m*M* $(NH_4)_3PO_4$, 75 m*M* SDS, 0.1 m*M* PAR, pH 8 50 cm (42 cm)×75 μm, 15 kV	UV at 254 nm $6\cdot10^{-5}$–$2\cdot10^{-4}$ *M*	[34]
Fe^{2+}, Fe^{3+}, Cr^{3+}, Co^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}	10 m*M* phosphate, 75 m*M* SDS, 10^{-4} *M* PAR, pH 8 50 cm (–)×75 μm, 15 kV	UV at 254 nm $7\cdot10^{-5}$–$5\cdot10^{-4}$ *M*	[34]
Cu^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, Fe^{3+}	10 m*M* Na_2HPO_4, 6 m*M* $Na_2B_4O_7$, pH 8.0 0.1 m*M* HQS, 0.1 m*M* polyethylene glycol 57 cm (50 cm)×75 μm, 25 kV	UV at 254 nm $2\cdot10^{-5}$ *M*	[40]
Pb^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+}	7.5 m*M* salicylic acid, 0.1 m*M* EDTA, 0.02 m*M* HTAB, pH 4.01 57 cm (50 cm)×50 μm, −12 kV	UV at 200 nm $1\cdot10^{-4}$–$2\cdot10^{-4}$ *M*	[40]
Fe^{3+}, Fe^{2+}	7.5 m*M* salicylic acid, 0.5 m*M* EDTA, 0.02 m*M* HTAB, pH 4.01 57 cm (50 cm)×50 μm, −20 kV	UV at 200 nm $2\cdot10^{-4}$ *M*	[40]
Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Fe^{2+}, Cu^{2+}	10 m*M* $Na_2B_4O_7$, 0.1 m*M* HQS, pH 9.0 35 cm (–)×75 μm, 15 kV	UV at 254 nm $1\cdot10^{-4}$–$2\cdot10^{-4}$ *M*	[61]
Cu^{2+}, Ni^{2+}, Fe^{2+}, Au^+, Ag^+	20 m*M* Na_2HPO_4, 36 m*M* NaCl, 1 m*M* NaCN, 10 μ*M* TTAB, pH 11 58 cm (32 cm)×50 μm, −12 kV	UV at 204 nm $9\cdot10^{-8}$–$3\cdot10^{-6}$ *M* minerals, sand	[63]
Pd^{2+}, Pt^{4+}, Au^{3+}	0.1 *M* HCl, 0.4 *M* NaCl 70 cm (50 cm)×50 μm, −7 kV	UV at 220 nm $4\cdot10^{-8}$–$1\cdot10^{-7}$ *M*	[65]
Hg^{2+}	10 m*M* CH_3COONa, 5 mg/l dithizone sulfonate, pH 5.0 65 cm (60 cm)×100 μm, −25 kV	Vis at 480 nm $5\cdot10^{-8}$ *M*	[67]
Co^{2+}, Ni^{2+}, Zn^{2+}, Hg^{2+}	50 m*M* CH_3COONa, 2 m*M* CTAB, 0.1 m*M* 5-Br-PADAP, pH 6.0 67 cm (58 cm)×75 μm, −20 kV	UV–Vis fast-scanning $1\cdot10^{-5}$–$1\cdot10^{-4}$ *M* hair sample	[83]

Table 4 (*continued*)

Analyte	Conditions (running electrolyte, pH, capillary length, length to the detector, inner diameter, voltage)	Detection, concentration range and sample type	Ref.
Fe^{2+}, Fe^{3+}, Cu^{2+}, Ni^{2+}, Cr^{3+}, Hg^{2+}, Pd^{2+}, Ag^{+}, Co^{2+}	20 m*M* Na_2HPO_4, KH_2PO_4, 2 m*M* NaCN, pH 9.4 35 cm×75 μm, 4.5 kV or 7 kV	UV at 214 nm $4\cdot10^{-7}$–$5\cdot10^{-6}$ *M*	[105]
Co^{3+}, Bi^{3+}, Fe^{3+}, Cr^{3+}, V^{4+}, Pb^{2+}, Hg^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}	20 m*M* NaH_2PO_4, 5 m*M* DTPA, pH 8.5 57 cm (50 cm)×75 μm, 25 kV	UV at 214 nm $2\cdot10^{-6}$–$8\cdot10^{-6}$ *M*	[106]
Fe^{2+}, Cu^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+}	20 m*M* Na_2HPO_4, 100 m*M* NaCl, 3 m*M* NaCN, 1.2 m*M* TBAB, 40 μ*M* TTAB, pH 11 80 cm (60 cm)×50 μm, −15 kV	UV at 208 nm $5\cdot10^{-6}$–$7\cdot10^{-3}$ *M* catalytic converters	[107]
Fe^{2+}, Pd^{2+}, Co^{2+}, Pt^{2+}, Fe^{3+}, Cr^{3+}, Au^{+}, Ag^{+}	5 m*M* phosphate/triethanolamine, 0.8 m*M* HMB, pH 8.5 60 cm (–)×75 μm, 20 kV	UV at 214 nm	[108]
Fe^{3+}, Cr^{3+}, Mn^{2+}, Zn^{2+}, Cu^{2+}	10 m*M* $Na_2B_4O_7$, 1 m*M* CDTA, pH 9.0 50 cm (42 cm)×75 μm, 15 kV	UV at 214 nm $6\cdot10^{-4}$–$5\cdot10^{-3}$ *M*	[109]
Cr^{6+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Co^{3+}	10 m*M* HCOOH, 1 m*M* CDTA, NaOH, pH 3.8 50 cm (42 cm)×75 μm, 20 kV	UV at 214 nm $3\cdot10^{-3}$–1 *M*	[109]
Cd^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}	24 m*M* acetate buffer, 0.08 m*M* 5-Br-PAPS, pH 4.9 70 cm (50 cm)×50 μm, 30 kV	UV at 550 nm $5\cdot10^{-8}$–$1\cdot10^{-6}$ *M*	[110]
Cr^{3+}, Fe^{3+}, Cu^{2+}, Pb^{2+}	0.1 m*M* acetate buffer, 0.1 m*M* TTAB, pH 5.5 80 cm (60 cm)×50 μm, −30 kV	UV at 225 nm $6\cdot10^{-6}$–$3\cdot10^{-5}$ *M*	[111]
Al^{3+}, Bi^{3+}, Cr^{3+}, Cu^{2+}, Pd^{2+}, Ag^{+}, Tl^{+}, Sb^{3+}, Sn^{4+}, U^{5+}, V^{4+}, Zr^{4+}	20 m*M* $Na_2B_4O_7$, 1 m*M* CDTA, 5% ethylene glycol, pH 9.0 50 cm (42.5 cm)×75 μm, 12.5 kV	UV at 214 nm $1\cdot10^{-6}$ *M*	[112]
Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Pd^{2+}, Pt^{4+}, Cu^{2+}, Cr^{3+}, Au^{+}, Ag^{+}	5 m*M* Na_2HPO_4, 5 m*M* triethanolamine, 0.8 m*M* hexamethonium bromide, – 60 cm (–)×75 μm, −25 kV	UV at 214 nm $6\cdot10^{-9}$–$3\cdot10^{-7}$ *M*	[113]
Hg^{2+}, Pb^{2+}, Hg^{+}, Se^{4+}	40 m*M* NaH_2PO_4, $Na_2B_4O_7$, 40 m*M* SDS, 5.0 m*M* NTA, pH 7.0 63 cm (50 cm)×50 μm, 20 kV	UV at 200 nm $7\cdot10^{-5}$–$2\cdot10^{-4}$ *M*	[114]
Cu^{+}, Fe^{2+}, Fe^{3+}	50 m*M* CH_3COONH_4, CH_3COOH, 2 m*M* 1,10-phenanthroline, pH 4.5 80 cm (40 cm)×75 μm, 15 kV	Thermal lensing tap water, rain water	[115]
K^{+}, Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Cd^{2+}, Co^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, lanthanoids	15 m*M* lactic acid, 10 m*M* UV Cat-1, pH 4.3 60 cm (–)×75 μm, 30 kV	Indirect UV at 214 nm	[16]
K^{+}, Na^{+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, H^{+}, NH_4^{+}	5 m*M* imidazole, 6.5 m*M* HIBA, 0.55 m*M* 18-crown-6, 20% CH_3OH, pH 4.5 60 cm (–)×75 μm, 20 kV	Indirect UV at 214 nm $9\cdot10^{-6}$–$3\cdot10^{-5}$ *M* oyster tissue, tea	[21]
K^{+}, Ba^{2+}, Sr^{2+}, Ca^{2+}, Na^{+}, Mg^{2+}, Mn^{2+}, Cd^{2+}, Fe^{2+}, Co^{2+}, Pb^{2+}, Ni^{2+}, Li^{+}, Zn^{2+}, Cu^{2+}	6.5 m*M* HIBA, 5 m*M* UV Cat-1, acetic acid, pH 4.4 52 cm (–)×75 μm, 20 kV	Indirect UV at 214 nm $3\cdot10^{-6}$–$3\cdot10^{-5}$ *M*	[24]

(*continued on next page*)

Table 4 (*continued*)

Analyte	Conditions (running electrolyte, pH, capillary length, length to the detector, inner diameter, voltage)	Detection, concentration range and sample type	Ref.
K^+, Na^+, Pb^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}	2 m*M* phthalic acid, m*M* UV Cat-1, 20% CH_3OH, pH 3.3 60 cm (–)×75 μm, 15 kV	Indirect UV at 214 nm	[27]
K^+, Na^+, Li^+, Mg^{2+}, Ba^{2+}, Sr^{2+}, Mn^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}	2.5 m*M* tartaric acid, 6 m*M* *p*-toluidine, 20% CH_3OH, pH 4.8 60 cm (–)×75 μm, 30 kV	Indirect UV at 214 nm $3\cdot10^{-6}$–$2\cdot10^{-5}$ *M*	[27]
K^+, Ba^{2+}, Sr^{2+}, Na^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Cd^{2+}, Li^+, Co^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, lanthanoids	15 m*M* lactic acid, 8 m*M* UV Cat-1, 5% CH_3OH, pH 4.25 60 cm (–)×75 μm, 30 kV	Indirect UV at 214 nm $1\cdot10^{-5}$–$8\cdot10^{-5}$ *M*	[27]
K^+, Ba^{2+}, Sr^{2+}, Ca^{2+}, Na^+, Mg^{2+}, Mn^{2+}, Cd^{2+}, Fe^{2+}, Co^{2+}, Li^+, Ni^{2+}, Zn^{2+}, Cu^{2+}	12 m*M* HIBA, 6 m*M* imidazole, pH 3.95 62 cm (50 cm)×50 μm, 25 kV	Indirect UV at 214 nm prediction, optimization $1\cdot10^{-4}$ *M*	[28]
Cu^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, Fe^{2+}	15 m*M* HIBA, 5 m*M* creatinine, pH 3.45 57 cm (50 cm)×50 μm, 8 kV	Indirect UV at 200 nm $5\cdot10^{-5}$–$1\cdot10^{-4}$ *M*	[40]
Li^+, K^+, Ca^{2+}, Cr^{3+}, Zn^{2+}, Al^{3+}, Cu^{2+}	5.2 m*M* ephedrine, 4.7 m*M* HIBA, pH 2.8 50 cm (–)×50 μm, 15 kV	Indirect UV at 204 nm $3\cdot10^{-6}$ *M*	[56]
Rb^+, K^+, Na^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Cd^{2+}, Li^+	10 m*M* lactic acid, 8 m*M* UV Cat-1, 15% CH_3OH, pH 4.9 60 cm (52.5 cm)×50 μm, 20 kV	Indirect UV at 214 nm $1\cdot10^{-4}$ *M*	[70]
Rb^+, Cs^+, K^+, Ba^{2+}, Sr^{2+}, Ca^{2+}, Mn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Cu^{2+}, lanthanoids	10 m*M* creatinine, 5 m*M* HIBA, 20% CH_3OH, pH 4.5 90 cm (75 cm)×50 μm, 30 kV	Indirect UV and MS $5\cdot10^{-4}$ *M*	[75]
K^+, Ba^{2+}, Sr^{2+}, Ca^{2+}, Na^+, Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Pb^{2+}, Li^+	6.5 m*M* HIBA, 5 m*M* UV Cat-1, pH 4.4 60 cm (52 cm)×75 μm, 20 kV	Indirect UV at 185 nm $3\cdot10^{-6}$–$3\cdot10^{-5}$ *M*	[85]
NH_4^+, K^+, Na^+, Ca^{2+}, Sr^{2+}, Mg^{2+}, Mn^{2+}, Ba^{2+}, Cd^{2+}, Fe^{2+}, Li^+, Co^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+}	11 m*M* lactic acid, 2.6 m*M* 18-crown-6, 7.5 m*M* UV Cat-1, 8% CH_3OH, pH 4.3 60 cm (52.5 cm)×75 μm, 30 kV	Indirect UV at 214 or 254 nm $1\cdot10^{-5}$–$8\cdot10^{-5}$ *M*	[86]
K^+, Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, Na^+, Al^{3+}, Cu^{2+}, Li^+, VO^{2+}	8 m*M* nicotinamide, formic acid, pH 3.2 60 cm (52.5 cm)×75 μm, 25 kV	Indirect UV at 214 or 254 nm $3\cdot10^{-3}$–$3\cdot10^{-5}$ *M*	[86]
Cs^+, NH_4^+, Na^+, Li^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, Al^{3+}, Ce^{3+}	4 m*M* METOL, 20% acetone, – 74 cm (57 cm)×50 μm, 30 kV	Indirect UV at 220 nm $1\cdot10^{-4}$ *M* Baltic seawater	[95]
NH_4^+, K^+, Ca^{2+}, Na^+, Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Cd^{2+}, Ni^{2+}, Zn^{2+}, Li^+	10 m*M* imidazole, 5 m*M* lactic acid, 0.5 m*M* 18-crown-6, pH 4.5 57 cm (50 cm)×75 μm, 20 kV	Indirect UV at 214 nm optimization $1\cdot10^{-6}$–$2\cdot10^{-5}$ *M*	[116]
Mn^{2+}, Pb^{2+}, Cd^{2+},	4 m*M* HCOOH, 4 m*M* $CuSO_4$,	Indirect UV at 214 nm	[117]

Table 4 (*continued*)

Analyte	Conditions (running electrolyte, pH, capillary length, length to the detector, inner diameter, voltage)	Detection, concentration range and sample type	Ref.
Al^{3+}, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}, Fe^{2+}	3 m*M* 18-crown-6, pH 4.5 67 cm (–)×75 μm, 20 kV	$1\cdot10^{-7}$–$2\cdot10^{-6}$ *M*	
K^{+}, Ba^{2+}, Ca^{2+}, Na^{+}, Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Li^{+}, lanthanoids	6 m*M* DBA, 4.2 m*M* HIBA, acetic acid, pH 5.0, 0.2 m*M* TX-100 60 cm (–)×75 μm, 30 kV	Indirect UV at 214 nm $1\cdot10^{-5}$–$4\cdot10^{-4}$ *M*	[118]
Ca^{2+}, Na^{+}, Fe^{2+}, Zn^{2+}	6.5 m*M* HIBA, 5 m*M* UV Cat-1, pH 4.4 60 cm (–)×75 μm, 20 kV	Indirect UV at 185 nm $8\cdot10^{-6}$–$1\cdot10^{-4}$ *M*	[119]
Li^{+}, Na^{+}, K^{+}, Cs^{+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}	13 m*M* glycolic acid, 10 m*M* imidazole, pH 4.0 90 cm (83 cm)×75 μm, 25 kV	Indirect UV at 210 nm $1\cdot10^{-6}$ *M*	[120]
Li^{+}, Na^{+}, K^{+}, Cs^{+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}	12 m*M* glycolic acid, 10 m*M* pyridine, pH 4.0 90 cm (83 cm)×75 μm, 25 kV	Indirect UV at 254 nm $1\cdot10^{-9}$–$4\cdot10^{-6}$ *M*	[120]
Li^{+}, Na^{+}, K^{+}, Cs^{+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cr^{3+},Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}	16 m*M* glycolic acid, 10 m*M* benzylamine, pH 4.0 90 cm (83 cm)×75 μm, 25 kV	Indirect UV at 210 nm $1\cdot10^{-6}$ *M*	[120]
Li^{+}, Na^{+}, K^{+}, Cs^{+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}	12.2 m*M* glycolic acid, 5 m*M* imidazole, 5 m*M* ephedrine, pH 4.0 90 cm (83 cm)×75 μm, 25 kV	Indirect UV at 210 nm $1\cdot10^{-6}$ *M*	[120]
Li^{+}, Na^{+}, K^{+}, Cs^{+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}	6.75 m*M* HIBA, 5 m*M* imidazole, pH 4.0 90 cm (83 cm)×75 μm, 25 kV	Indirect UV at 210 nm $1\cdot10^{-6}$ *M*	[120]
Cs^{+}, K^{+}, Ag^{+}, Na^{+}, Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, Li^{+}, Al^{3+}	5 m*M* pyridine, H_2SO_4, pH 3.2 90 cm (83 cm)×75 μm, 25 kV	Indirect UV at 254 nm $1\cdot10^{-6}$ *M*	[120]
NH_4^{+}, K^{+}, Na^{+}, Li^{+}, Mg^{2+}, Ca^{2+}, Cr^{3+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}	6.5 m*M* HIBA, 5 m*M* imidazole, 0.53 m*M* 18-crown-6, 20% CH_3OH, pH 4.5 60 cm (–)×75 μm, 20 kV	Indirect UV at 214 nm $3\cdot10^{-5}$–$9\cdot10^{-5}$ *M* tea infusion	[121]
As^{3+}, As^{5+}, Se^{4+}, Se^{6+}	5 m*M* K_2CrO_4, 0.25 m*M* CTAB, pH 10 57 cm (50 cm)×75 μm, −15 kV	Indirect UV at 254 nm 10^{-4} *M*	[122]
Na^{+}, Al^{3+}, AlF^{2+}, AlF_2^{+}, $Al(oxalate)^{+}$	5 m*M* imidazole, 1 m*M* H_2SO_4, pH 3.5 45 cm (–)×75 μm, 15 kV	Indirect UV at 214 nm $2\cdot10^{-4}$ *M*	[123]
K^{+}, Na^{+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, NH_4^{+}	5 m*M* imidazole, 6.5 m*M* HIBA, 0.55 m*M* 18-crown-6, 20% CH_3OH, pH 4.5 60 cm (–)×75 μm, 20 kV	Indirect UV at 214 nm	[123]
Cs^{+}, Rb^{+}, NH_4^{+}, K^{+}, Ca^{2+}, Na^{+}, Mg^{2+}, Mn^{2+}, Sr^{2+}, Cd^{2+}, Ba^{2+}, Li^{+}	5 m*M* DHBP, 6 m*M* glycine 2 m*M* 18-crown-6, 2% CH_3OH, pH 6.52 57 cm (50 cm)×75 μm, 25 kV	Indirect UV at 280 nm $7\cdot10^{-6}$–$6\cdot10^{-5}$ *M* atmospheric aerosol	[124]
NH_4^{+}, K^{+}, Na^{+}, Li^{+}, Mg^{2+}, Ca^{2+}, Cr^{3+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}	5 m*M* imidazole, 6.5 m*M* HIBA, 20% CH_3OH, 0.53 m*M* 18-crown-6, pH 4.5 60 cm (–)×75 μm, 20 kV	Indirect UV at 214 nm $3\cdot10^{-5}$–$9\cdot10^{-5}$ *M*	[125]

(*continued on next page*)

Table 4 (*continued*)

Analyte	Conditions (running electrolyte, pH, capillary length, length to the detector, inner diameter, voltage)	Detection, concentration range and sample type	Ref.
K^+, Ba^{2+}, Sr^{2+}, Ca^{2+}, Na^+, Mg^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Li^+, Cr^{3+}	15 m*M* 2-aminopyridine, acetic acid, pH 5.0 80 cm (–)×75 μm, coated, 25 kV	Indirect UV at 214 nm $3\cdot10^{-7}$–$5\cdot10^{-6}$ *M*	[126]
K^+, Ba^{2+}, Ca^{2+}, Na^+, Mg^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Li^+, Cr^{3+}, lanthanoids	15 m*M* 2-aminopyridine, 3.5 m*M* HIBA, acetic acid, pH 5.0 60 cm (–)×75 μm, coated, 30 kV	Indirect UV at 214 nm $1\cdot10^{-5}$–$8\cdot10^{-5}$ *M*	[126]
K^+, Ba^{2+}, Ca^{2+}, Na^+, Mg^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Li^+, Cr^{3+}	15 m*M* 2-aminopyridine, acetic acid, pH 5.0 80 cm (–)×75 μm, 25 kV	Indirect UV at 214 nm $3\cdot10^{-6}$–$2\cdot10^{-3}$ *M*	[127]
Ni^{2+}, Co^{2+}, Fe^{2+}	20 m*M* Na_2SO_4, 4 m*M* sodium phosphate, 1 m*M* EDTA, 5.35 m*M* Polybrene, pH 8.0 60 cm (46 cm)×50 μm, −20 kV	Indirect Vis at 490 nm $1\cdot10^{-5}$ *M*	[128]
NN_4^+, K^+, Ca^{2+}, Na^+, Mg^{2+}, Zn^{2+}	10 m*M* histidine, 2 m*M* 18-crown-6, 8 m*M* lactic acid, pH 4.0 65 cm (–)×75 μm, 15 kV	Indirect UV at 214 nm $1\cdot10^{-4}$–$2\cdot10^{-3}$ *M* air particulate matter	[129]
Rb^+, K^+, Na^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Cd^{2+}, Li^+	10 m*M* lactic acid, 8 m*M* UV Cat-1, 15% CH_3OH, pH 4.9 60 cm (40 cm)×50 μm, 20 kV	Contactless conductivity $1\cdot10^{-4}$ *M*	[70]
Rb^+, K^+, Na^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Cd^{2+}, Li^+	20 m*M* MES, 20 m*M* histidine, pH 6 58 cm (45 cm)×50 μm, 20 kV	Contactless conductivity $4\cdot10^{-4}$ *M*	[70]
Ca^{2+}, Na^{2+}, Mg^{2+}, Ni^{2+}, Cd^{2+}	5 m*M* CH_3COOH, pH 5.0 70 cm (–)×75 μm, 14 kV	End-column conductivity $5\cdot10^{-5}$ *M*	[101]
Tl^+, Pb^{2+}, Cd^{2+}, Cu^{2+}	5 m*M* DBA, 6.5 m*M* HIBA, CH_3COOH, pH 4.90 60 cm (–)×25 cm, 30 kV	Electrochemical $1\cdot10^{-6}$–$1\cdot10^{-5}$ *M*	[71]
Se^{4+}, Se^{6+}	200 m*M* HPO_4^{2-}, $H_2PO_4^-$, pH 6 150 cm (–)×50 μm, −15 kV	ICP-MS	[79]
Se^{4+}, Se^{6+}	10 m*M* Na_2CO_3, KOH, pH 11.5 30 cm (–)×50 μm, 18 kV	ICP-MS $1\cdot10^{-7}$–$3\cdot10^{-7}$ *M*	[80]
Pt^{2+}, Pt^{4+}	50 m*M* NaH_2PO_4, Na_2HPO_4, pH 6.0 150 cm (–)×50 μm, 10 kV	ICP-MS $2\cdot10^{-6}$–$4\cdot10^{-6}$ *M*	[81]
Mn^{2+}, Ni^{2+}, Co^{2+}, La^{3+}	20 m*M* CH_3COONH_4, pH 7.0 50 cm (–)×50 μm, 10 kV	ICP-MS $3\cdot10^{-4}$–$1\cdot10^{-4}$ *M*	[82]
As^{3+}, As^{5+}	50 m*M* NaH_2PO_4, Na_2HPO_4, pH 6.0 66 cm (–)×100 μm, 15 kV	ICP-AES $1\cdot10^{-3}$ *M*	[78]
(C) Lanthanoids and uranium			
Lanthanoids	4 m*M* HIBA, 10 m*M* UV Cat-1, acetic acid, pH 4.4 36.5 cm (–)×75 μm, 30 kV	Indirect UV at 210 nm $7\cdot10^{-6}$–$3\cdot10^{-5}$ *M*	[24]
Lanthanoids	4 m*M* HIBA, 5 m*M* UV Cat-1, pH 4.3 60 cm (–)×75 μm, 30 kV	Indirect UV at 214 nm	[27]
Lanthanoids	4 m*M* HIBA, 9 m*M* benzylamine, 20 m*M* CH_3COOH, pH 4.60 60 cm (–)×75 μm, C_{18} bonded, 28 kV	Indirect UV at 214 nm $1\cdot10^{-4}$ *M*	[54]
U^{6+}, lanthanoids	25 m*M* Arsenazo III, 15 m*M* citric acid, 20 m*M* Tris, pH 4.3 60 cm (52 cm)×75 μm, −30 kV pre-conditioned with Carbowax 20M	Vis at 654 nm $1\cdot10^{-5}$–$2\cdot10^{-5}$ *M*	[68]
Lanthanoids	20 m*M* $Na_2B_4O_7$, 1 m*M* CDTA, pH 11.1 50 cm (42 cm)×75 μm, 15 kV	UV at 214 nm	[130]
Lanthanoids	30 m*M* creatinine, 8 m*M* HIBA, pH 4.8 0.9 m*M* malonic acid, 2-ethylbutyric acid 40 cm (27.7 cm)×75 μm, 10 kV	Indirect UV at 220 nm $3\cdot10^{-4}$ *M*	[131]

HEDTC	Bis(2-hydroxyethyl)dithiocarbamate
HIS	Histidine
HIBA	α-Hydroxyisobutyric acid
HMB	Hexamethoniumbromide
HTAB	Hexadecyltrimethylammoniumbromide
HQS	8-Hydroxyquinoline-5-sulfonic acid
ICP	Inductively coupled plasma
mHEC	Methylhydroxyethylcellulose
MES	Morpholinoethanesulfonic acid
METOL	4-Methyl-amino-phenol-sulfate
MOPS	Morpholinopropanesulfonic acid
MS	Mass spectrometry
NTA	Nitrilotriacetic acid
PAR	4-(2-pyridylazo)resorcinol
SDS	Sodium dodecyl sulfate
Sulfonazo III	3,6-Bis(2-sulfophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfomic acid
TBAB	Tetrabutylammoniumbromide
TEAOH	Tetraethylammonium hydroxide
Tris	Tris(hydroxymethyl)aminomethan
TTAB	Tetradecyltrimethylammoniumbromide
TX-100	Triton X-100
UV Cat-1	Trademark of Waters (4-methylbenzylamine)
UV Cat-2	Trademark of Waters

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