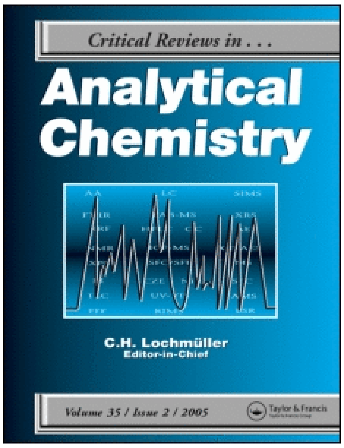

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Speciation of Metal Ions by Capillary Electrophoresis

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ABSTRACT: The speciation of metal ions by capillary electrophoresis is an important area for environmental chemists. The speciation of metal ions by capillary electrophoresis in different matrices is reviewed. Various aspects of speciation such as sample pretreatment, metal ion complexation, detection, detection limit, choice of electrolytes, etc. have been described. Suggestions to improve the application of CE for the speciation of metal ions are given. The future scope of this technique has also been discussed.

KEY WORDS: metal ions, speciation, capillary electrophoresis.

List of abbreviations:

AAS:	Atomic absorption spectrometer
BGE:	Background electrolyte
CDTA:	Cyclohexane-1,2-diaminetetraacetic acid
CE:	Capillary electrophoresis
CHES:	2-(*N*-Cyclohexylamino)ethanesulfonic acid
CN^-:	Cyanide
CTAB:	Cetyltrimethylammonium bromide
CZE:	Capillary zone electrophoresis
DTPA:	Diethylenetriaminepentaacetic acid
DzS:	Dithizone sulfonate
EDTA:	Ethylenediaminetetraacetic acid
EOF:	Electroosmotic flow
EtOH:	Ethanol
GC:	Gas chromatography
HMB:	Hexamethonium bromide
HPLC:	High performance liquid chromatography

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HTMAB:	Hexadecyltrimethylammonium bromide
IC:	Ion chromatography
ICP:	Inductively coupled plasma
ICP-MS:	Inductively coupled plasma-mass spectrometer
KHP:	Potassium hydrogenphthalate
NTA:	Nitrilotriacetic acid
PAR:	4-(2-Pyridylazo)resorcinol
RSD:	Relative standard deviation
SDS:	Sodium dodecyl sulfate
NaCN:	Sodium cyanide
NaOH:	Sodium hydroxide
TTAOH:	Tetradecyl-trimethylammonium hydroxide
TTHA:	Triethylenetetraminehexaacetic acid
UV:	Ultraviolet
Visb.:	Visible

I. INTRODUCTION

The concept of speciation was first introduced by Goldberg[1] in 1954 and generally, used to differentiate the different oxidation states of an element or metal ion. Metal ions are the most toxic pollutant in the environment, nonbiodegradable and highly toxic leading to carcinogenesis.[2,3] It has also been reported that the toxicity of the metal ions may be different for the different oxidation states.[4–7] The toxicity of As(II) and Sb(III) is higher than their pentavalent state,[4,5] Cr(III) is essential, while Cr(VI) is highly toixic.[8] Similarly, the species of other metal ions differ in the toxicity point of view. Most of the species of organometallic compounds are more toxic than the inorganic species with the exception of arsenic metal. It is interesting to note that the valency state of an element plays a crucial role for the uptake, sorption, and dynamics behavior of the elements in the biological and environmental matrices. Therefore, the diverse groups of people ranging from the regulators to the material industries, clinicians and nutritional experts, agriculture and environmentalists are now demanding specitation data rather than total elemental concentrations of metal ions.[9] Due to the importance of the analysis of the speciation of metal ions, several publications have been published on this issue. Figure 1 indicates the growth of publications on the speciation from 1980 to 1998.[9] Of course, this growth is impressive and affects the quality and traceability of speciation analysis.[10] The speciation analysis will become more important each year as the regulators start specifying the limits and controls on individual elemental species.

The most advance techniques such as high-performance liquid chromatography (HPLC), ion chromatography (IC), gas chromatography (GC), atomic absorption spectrometry (AAS), inductively coupled plasma spectrometry (ICP), and other UV-Visb spectrometric methods have been developed for the speciation of metal ions.[7,11–13] However, still the speciation of metal ions is a challenging job. In the last decade, a newly developed technique, capillary electro-

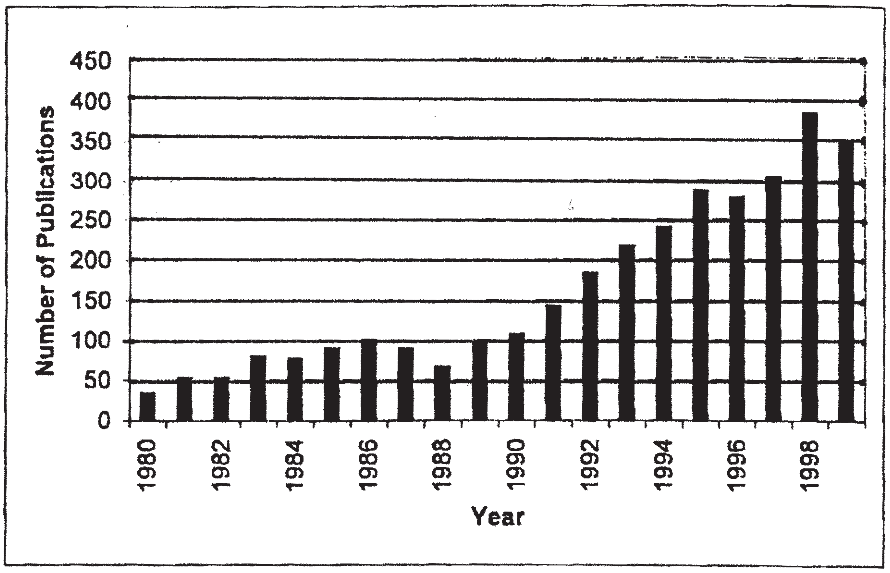

FIGURE 1. Number of papers published on the speciation from 1980 to 1989.[9]

phoresis (CE), has been used as one of the tools for the speciation of metal ions. The CE has certain advantages compared with the other techniques. The advantages of CE include simplicity, high speed of analysis, greater separation efficiency, unique selectivity, and a high degree of matrix independence, all of which make it ideal for the speciation of metal ions. Due to the importance of metal ions speciation and the ease of CE, it has been of interest to review and discuss the status of the speciation of metal ions by CE. In this review, the sample preparation, detection, metal ions complexation and separation efficiency aspects for the metal ions speciation by CE have been discussed

II. PRINCIPLE OF METAL IONS SPECIATION BY CE

The mechanism of separation/speciation of metal ions in CE is based on the difference in the electrophoretic mobility of the metal ions. Under the CE conditions, the migration of the metal ions is controlled by the sum of intrinsic electrophoretic mobility (μ_{ep}) and electroosmotic mobility (μ_{eo}), due to the action of electroosmotic flow (EOF). The observed mobility (μ_{obs}) of metal ions is related to μ_{eo} and μ_{ep} by the following equation.

$$\mu_{obs} = \mu_{eo} + \mu_{ep} \qquad (1)$$

The electrophoretic mobility of cation (μ_{obs}) can be related to the limiting ionic equivalent conductivity, λ_{ekv}, by the following equation.

$$\mu_{obs} = \lambda_{ekv}/F = q_i/6\pi\eta r_i \qquad (2)$$

where F is the Faraday constant (F = 9.6487 × 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 μ_{ep} values can be calculated from the experimental data, the mobility of the cation (μ_{obs}), and the mobility of the electroosmotic flow μ_{eo}, according to the following equation.

$$\mu_{ep} = \mu_{obsp} - \mu_{eo} = [1/t_{m(ion)}-1/t_{m(eo)}][l_T.L_d/V] \qquad (3)$$

where $t_{m(ion)}$, $t_{m(eo)}$, l_T, L_d and V are migration time of the cation (seconds), migration time of the EOF (seconds), the overall capillary length and the length, of the capillary to the detector (cm) and voltage (kV), respectively. Thus, the controlling of EOF plays an important role in CE separations.

III. APPLICATION OF CE FOR THE SPECIATION OF METAL IONS

Contrary to the large molecules, small cations have higher charge-densities (q_i/r_i) ratio and hence larger ionic mobilities (Equation 1). As a principally striking electrophoretic property, it should lead to rapid separation of high efficiency. However, in practice, it seldom occurred unless a special precautions are taken. The mobilities of the cations are almost equal (except alkali metals) due to their similar size, but the cations in different oxidation states have different sizes, and hence this may be considered as the advantage of speciation in CE. Moreover, the different charges on the cations may again be an advantage of their speciation in CE as the migration of cations in CE is controlled by the charges on the cations. The speciation of metal ions can be carried out by several modes of CE, but, mostly, CZE has been used for the speciation of metal ions.

Due to accute toxicity of arsenic metal ion, the speciation of arsenic was carried out extensively.[14–28] Further, the speciation of arsenic and selenium species has been studied by using EOF modifier to simultaneously separate inorganic and organometallic species.[21,29–32] Pozdniakova et al.[33] have also used phenanthroline and CDTA as the chelating agents for the speciation of iron Fe(II) and Fe(III). Other ligands such as PAR,[34] 5-Br-PAPs,[35] and CN^-[36] were also used for the speciation of metal ions. Timerbaev et al.[37,38] added excess of CDTA in the sample solution containing chromium species, that is, Cr(III) and Cr(VI), and analyzed using phosphate buffer. Jung et al.[39] used CTBA as the ligand for chromium speciation and obtained sharp peaks with short analysis time. Padarauskas and Schwedt[40] described chromium speciation by using DTPA as the chelating agent. Further, they used DTPA as the complexing agent for the speciation of vanadium. V(IV) and V(V) were speciated as their EDTA complexes with HTMAB as the modifier.[41] Medina et al.[42] speciated inorganic mercury and organomercury species. Further, the improvement in mercury speciation was carried out by Carro-Dias et al.[43] DzS complexes of mercury were prepared and speciated by Hardy.[44] Wuping and Hian[45,46] described the simultaneous method of speciation for lead, mercury, and selenium using NTA and TTHA as the ligands. Further, the selectivity of speciation was increased by using SDS. Silva da Rocha et al.[47] have developed a method for the speciation of inorganic and organic mercury species. The detection was carried out by coupling CE with ICP-MS. The speciation of metal ions by CE is summarized in Table 1. The typical electropherograms of the speciation of arsenic species is shown in Figure 2.[21]

IV. SAMPLE TREATMENT AND DETECTION IN METAL IONS SPECIATION

A search of the literature conducted and discussed herein indicates that most of the speciation of metal ions analysis was carried out in the laboratory synthesized samples.[16–25] However, some reports are also available for metal ions speciation in real samples. A little attention has been paid to the sample treatment in CE speciation of metal ions. The samples containing high ionic matrix cause problems in CE. The high ionic strength imparts a low electric resistance, resulting in a very poor and a broad shape to peaks. In addition, EOF in the capillary can be altered by the influence of the sample matrix, resulting in poor resolution. Additionally, the detector baseline

Table 1. Application of Capillary Electrophoresis for the Speciation of Metal Ions

Metal Ions	Sample Matrix	Electrolytes	Detection	Detn .Limit	Ref.
Arsenic species	Drinking water	0.025 mM Phosphate buffer, pH 6.8	Direct UV 190 nm	<2 mg/L	14
	Water	50 mM CHES, 20 mM LiOH	Conductivity	0.4 mg/L	15
	Tin mining process water	15 mM phosphate buffer, 1 mM CTAB 50 mM CHES, 0.03% triton X-100 20 mM LiOH, pH 9.4	Conductivity	0.4 mg/L	15
As(III) & As(V)	--	Chromate-NICE-Pak OFM anion-BT, pH10.0	Indirect UV 254 nm	---	16
	--	5 mM Chromate 0.25 mM cetyltrimethyl ammonium bromide , pH 10.0	Indirect UV 254 nm	10^{-4} M	17
	---	5 mM $K_2Cr_2O_4$, 0.25 mM CTAB, pH 10.0	Indirect UV 254 nm	10^{-4} M	17
As(III), As(V) & dimethyl arsenic acid	--	60 mM Calcium chloride (pH 6.7) cetyltrimethyl ammonium bromide, pH 10.0	ICP-MS	1 ppb	18
As(III), As(V), monomethyl & dimethyl arsenic acid	--	75 mM Na_2HPO_4 - 25 mM $Na_2B_4O_7$, pH 7.8	Direct UV	0.8 ppm 195 nm	19
As(III), As(V) & dimethylarsenic acid	--	75 mM Na_2HPO_4-25 mM $Na_2B_4O_7$, pH 7.8	Direct UV 190 nm	0.8-3.7 ppm	20
As(III), As(V), monomethyl & dimethyl arsenic acid	--	6 mM Chromate-NICE-Pak OFM anion-BT, pH 8.0	Indirect UV 274 nm	0.4 ppm	21
As(III), As(V), monomethyl & dimethyl arsenic acid	--	2.3 mM Pyromellitic acid-6.5 NaOH-1.6 mM triethanolimine-75 mM hexamethonium bromide, pH 7.7	ICP-MS	20-100 ppt	22
As(III), As(V), monomethyl & dimethyl arsenic acid	--	10 mM Dodecyltrimethylammonium phosphate, pH 8.0	Direct UV 190 nm	15-90 ppb	23
As(III), As(V), monomethylarsonic acid, dimethylarsenic acid & monophenylarsonic acid	--	7 mM Na_2HPO_4-NaH_2PO_4 pH 5.8	Direct UV 190 nm	---	24
As(III), As(V), monomethylarsonic acid, dimethylarsenic acid & monophenylarsonic acid	--	25 mM Na_2HPO_4-NaH_2PO_4 pH 6.8	Direct UV 190 nm	---	15

Table 1 (continued)

As(III), As(V), monomethylarsonic acid, dimethylarsenic acid & monophenyl-arsonic acid	--	15 mM Na_2HPO_4-NaH_2PO_4 pH 5.8	Direct UV 190 nm	---	25
As(III), As(V), hexafluoroarsenate, dimethylarsinic acid, p-aminobenzenearsonic acid & monophenylarsonic acid	--	15 mM Na_2HPO_4 pH 6.5	Direct UV 200 nm	60-90 ppb	15
As(III), As(V), hexafluoroarsenate, dimethylarsinic acid, p-aminobenzenearsonic acid & monophenylarsonic acid	--	50 mM 2-(Cyclohexyl-amino)-ethanesulfonic acid -0.03% triton X-100-20 mM LiOH, pH 9.4	Conductivity 200 nm	40-76 ppb	15
As(III), As(V), monomethylarsonic acid, dimethylarsinic acid, arsenobetaine & arsenocholine	Urine & sewage sludge	----	ICP-MS	15 µg/L	28
Arsenic & selenium species	Drinking water	20 mM KHP, 20 mM Boric acid (pH 9.03) hydrodynamically modified EOF	Hydride generation ICP-MS	6 ng/L	26, 27
	Tap & drinking waters	75 mM Dihydrogen phosphate 25 mM, tetraborate (pH 7.65)	Direct UV 12 µg/L 195 nm	---	19
Co(III) & Co(IV)	---	NaAc, 0.12 mM 5-Br-PAPS, pH 4.9	Indirect UV 550 nm	10^{-8} M	35
	---	20 mM Na_2HPO_4, 5 mM DTPA, pH 8.0 or 8.5	Indirect UV 214 nm	10^{-6} M	40
Cr(IV) & Cr(VI)	Rinse water from chromium platings	1 mM CDTA, 10 mM formate buffer (pH 3.8)	Direct UV 214 & 254 nm	10 µg/L	37, 38
	Chromium plating water	10 mM Formate buffer, 1 mM CDTA (pH 3.0)	Direct UV 214 nm	10 ppb	37, 38
	---	10 mM Phosphate buffer, 0.5 mM HTMAB, 30 mM NaAc, 5 mM Na_2SO_4, pH7.0	Idirect UV 254 nm	15 ppm	39,
	Electro plating water	10 mM Formate buffer, pH 3.0)	Indirect UV 214 nm	50 ppb	38
	Waste water	20 mM Na_2HPO_4, 0.05 mM TTAOH,	Direct UV 214 & 254 nm	---	40
	Chromium plating water	10 mM HCOOH, 1 mM CDTA, NaOH, pH 3.0	Indirect UV 214 nm	!0^{-3} M	38
Fe(II) & Fe(III)	Electroplating Waters	20 mM Phosphate buffer (pH 7.0)	Direct UV 214 nm	10^{-5} M	52
	---	1 mM Ammo. phosphate buffer, 75 mM SDS, 0.1 mM MPAR, pH 8.0	Indirect UV 254 nm	10^{-7} M	34

Table 1 (continued)

Fe(II) & Fe(III)	---	NaAc, 0.12 mM 5-Br-PAPS, pH 4.9	Indirect UV 550 nm	10^{-8} M	35
	---	100 mM Borate buffer, pH 9.2	Indirect UV 214 nm	10^{-6} M	71
	---	20 mM Borate buffer, 1 mM CDTA, 0.5% EtOH, pH 9.0	Indirect UV 214 nm	10^{-5} M	72
	---	100 mM Borate buffer, pH 9.0	Indirect UV 185-214 nm	ppb level	64
	---	100 mM Borate buffer 1 mM CDTA, pH 9.0	Indirect UV 254 nm	0.6 ppm	73
	Envtl. samples	20 mM Phosphate buffer, 2 mM NaCN, pH 9.4	Indirect UV 214 nm	25 ppb	73
	---	7.5 mM Salicylic acid, 0.5 mM EDTA, 0.2 mM HTMAB, pH 4.0	Indirect UV 200 nm	10^{-4} M	75
	---	20 mM Na_2HPO_4, KH_2PO_4, 2 mM NaCN, pH 9.4	Indirect UV 214 nm	10^{-7} M	74
	---	5 mM Na_2HPO_4, 5 mM triethanolimine, 0.8 mM hexamethonium bromide	Indirect UV 214 nm	10^{-7} M	36
Hg(II), CH_3Hg^+ & CH_3CH_2Hg+	--	25 mM $Na_2B_4O_7.10\ H_2O$, pH 9.3	ICP-MS	81-275 ppb	47
Hg(II) & phenyl-Mercury (II)		Na_2HPO_4-$Na_2B_4O_7$, 2.5 mM TTHA, 2.0 mM SDS, pH 7.5	Indirect UV 220 nm	ppb level	46
Ir(II) & Ir(III)		4 mM H^+, 23 mM Cl^-, PH 2.4	Indirect UV 214 nm	---	76
Pb(II), triethyl lead (IV), trimethyl lead (IV) & diphenyl lead (IV)		Na_2HPO_4-$Na_2B_4O_7$, 2.5 mM TTHA, 2.0 mM SDS, pH 7.5	Indirect UV 220 nm	ppb level	46
Pt(II) & Pt(IV)		4 mM H^+, 23 mM Cl^-, PH 2.4	Indirect UV 214 nm	---	76
	Soil	50 mM Phosphate buffer (pH 6.0)	ICP-MS	1 µg/L	55
Se(IV) & Se(V)	Thermal water	Chromate, 0.5 mM TTAOH (pH 10.5)	Indirect UV 254 nm	10 µg/L	49
	--	5 mM Chromate-0.25 mM cetyltrimethylammonium bromide, pH 10.0	Indirect UV 254 nm	10^{-4} M	17
	--	75 mM Na_2HPO_4-25 mM $Na_2B_4O_7$, pH 7.8	Direct UV 195 nm	1.9-202 ppm	19
	--	2.3 mM Pyromellitic acid-6.5 mM NaOH-1.6 mM triethanolamine-75 mM hexamethonium bromide, pH 7.7	ICP-MS	100-300 ppt	22
	--	50 mM 2-(Cyclohexylamino)-ethane-sulfonic acid-0.03% triton X-10020 mM LiOH, pH 9.4	Conductivity	65-85 ppb	15
	--	200 mM $HPO^{-}{}_{4}^{2}$, $H_2PO_4^-$ pH 6.0	ICP-MS	10^{-7} M	29

Table 1 (continued)

Se(IV) & Se(V)	--	10 mM Na_2CO_3, KOH pH 11.5	ICP-MS	10^{-7} M	30
Se (IV), phenyl-selenium (II) & diphenyl selenium (II)	---	Na_2HPO_4-$Na_2B_4O_7$, 2.5 mM TTHA, 2.0 mM SDS, pH 7.5	Indirect UV 220 nm	ppb level	46
Se(IV), Se(VI) & selenocystine & selelenomethionine	---	80 mM Na_2HPO_4-2 mM tetra-decyltrimethylammonium bromide	Direct UV 200 nm	---	15,51
V(IV) & V(V)	Electroplating bath	20 mM Na_2HPO_4, 5 mM DTPA, pH 8.0 or 8.5	Indirect UV 214 nm	10-6 ^{M}	40

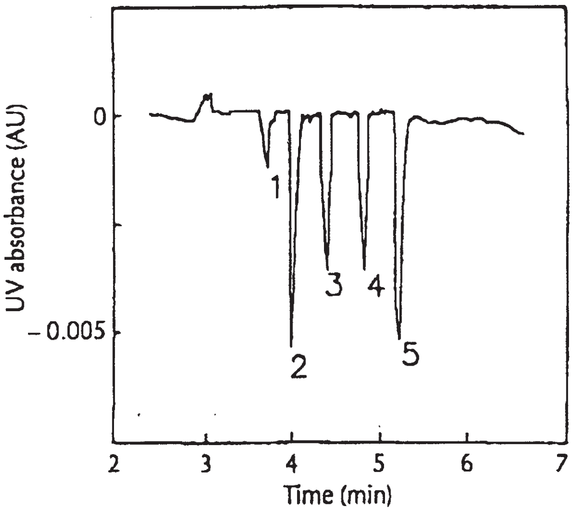

FIGURE 2. Speciation of arsenic species by capillary electrophoresis using 6 m*M* chromate solution with NICE-Pak OFM Anion-BT (1:40, v/v) as electrolyte with 28 kV potential and UV detection (274 nm).[21]

Peaks: 1 = Unidentified, 2 = As(V), 3 = monomethylarsonate, 4 = dimethylarsenate and 5 = As(III) usually pertubed when the pH of the sample differ greatly from the pH of BGE. The samples containing UV-absorbing materials are also problematic in the detection of metal ions. Due to all of these, some of the authors have applied the clean up and sample preparation prior to load onto CE. Lin et al.[21] described the extraction procedure for the arsenic species from fly ash coal samples. The detection limits have been increased by using preconcentration methods.[48]

Despite the use of many detectors in CE for metal ions speciation, the sensitivity of the detection of metal ions is still a challenging problem. The most common method with which to solve this problem is indirect UV detection.[16,17,21,49] The main advantages of indirect UV detection is its universal application, and thus it is most commonly used for the speciation of metal ions. The complexation of metal ions with ligands also increased the sensitivity of detection. However, the indirect detection shows poor sensitivity for organomatallic compounds.[50] The UV visualization agents (probe) have also been used to increase the sensitivity of detection in UV mode. In addition, to achieve a high sensitivity in indirect detection, the cations peak width should be minimized. The interaction of the cations and visualization agent with the capillary wall should be suppressed. The visualization agents should exhibit a mobility close to that of the cations, and its UV absorbence should be as high and the detector noise as small as possible. In addition, the direct UV detection has also been used for the speciation of metal ions.[14,15,19,20,23-25,37,38,40,51,52] To overcome the problem of detection in CE, many other workers have used inductively coupled plasma mass spectrometry (ICP-MS) as the method of detection of choice.[18,22,26-30,47,53-56] The use of conductivity detector shows a slight improvement in detection compared with the photometric mode.[15] The conductivity detection has also been used for the speciation of metal ions. From the literature available and discussed herein, it is clear that the speciation efficiency of metal ions is not good compared with HPLC and IC, because the detection limits varied from ppm to ppb levels only.

V. VALIDATION OF METHODS

There are only a few studies dealing with the method validation of metal ions speciation by CE. However, some authors have demonstrated the application of their developed methods for the speciation of metal ions. The accuracy determination of arsenic species has been reported by Lin et al.[21] They have also reported their method as reproducible with a detection limit of 3.5 pg for As(III). Liu et al.[22] have reported the detection of arsenic species at ppb and ppt levels. Aguilar and co-workers[52] described CE as the powerful tool for environmental samples analysis. CE as an attractive method than IC or HPLC, for metal ions speciation, has been described by Silva da Rocha and co-workers.[47] Wuping and Hian[46] have reported RSD 2.67 to 5.49% for the speciation of lead, mercury, and selenium species. Further, they claimed the applicability of their method for the speciation of these metal ions in real samples. Several other studies have also shown a reliable results with recoveries close to 100% or good agreements with the results obtained by other methods. Despite this, the precision linearity, sensitivity, and reproducibility of CE methods for metal ions speciation are not superior than ion chromatography and other chromatographic methods.

VI. CONCLUSION

As discussed above, the speciation of metal ions is very important and essential from a health point of view. Despite the development of several chromatographic, electrophoresis, and atomic absorption spectrometric methods, it is still a challenging job. A search of the literature, as discussed in this review, indicates the very limited application of CE for the speciation of metal ions, and hence CE could not achieve great success in this area. The reasons for this are the poor detection of metal ions and the lack of reproducibility of CE methods. The precision linearity, sensitivity, and reproducibility of CE methods for metal ions speciation are not superior to the other chromatographic methods. Various workers[19,50,57–65] have suggested different modifications and alternatives to make the CE a method of choice for the analysis of metal ions in different matrices. In addition, to get the good sensitivity and reproducibility, the selection of the capillary wall chemistry, pH and ionic strength of BGE, complexing and visualizing agents, detectors and optimization of BGE have also been described and suggested.[66–70] Similar approaches may be utilized to improve the speciation of metal ions by CE.

In addition to the above points discussed for the improvement of speciation of metal ions by CE, some other aspects should also be addressed to improve the working of CE. This include the development and wide use of fluorescent and radioactive complexing agents as the detection by fluorescent and radioactive detectors is more sensitive and reproducible with low limit of detection. To make the CE application more reproducible, the background electrolyte should be developed in such a way that physical and chemical properties remain unchanged during the experimental run. The nonreproducibility of the CE method may be due to the heating of BGE after a long run of the CE machine. Therefore, to keep the temperature constant through out the experiments, a cooling device should be included in the machine. It seems that in future CE will be realized as widely recognized method of choice for the speciation of metal ions. All the capabilities and possibilities of CE have not been fully explored still but they are underway. Briefly, there is a lot to be developed for the advancement of CE for the speciation of metal ions. Definitely, CE will prove itself as the best technique for the speciation of metal ions after a few years and will achieve the status of the technique of routine analysis in most of the environmental laboratories.

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