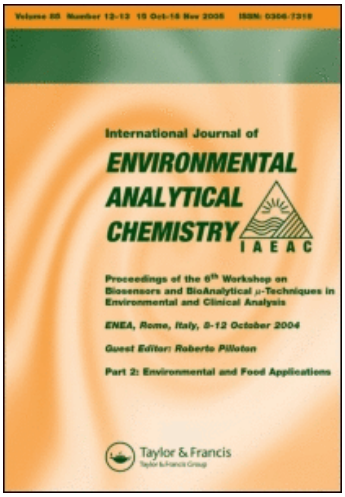

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Speciation of Tin, Lead, Mercury, Arsenic and Selenium Compounds by Capillary Electrophoresis

Baoguo Sun[a]; Miroslav Macka[a]; Paul R. Haddad[a]
[a] Australian Centre for Research on Separation Science, School of Chemistry, University of Tasmania, Hobart, Tasmania, Australia

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SPECIATION OF TIN, LEAD, MERCURY, ARSENIC AND SELENIUM COMPOUNDS BY CAPILLARY ELECTROPHORESIS

BAOGUO SUN, MIROSLAV MACKA and PAUL R. HADDAD*

Australian Centre for Research on Separation Science, School of Chemistry, University of Tasmania, GPO Box 252-75, Hobart, Tasmania 7001, Australia

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Capillary electrophoresis (CE) methods published over the period 1992–2000 for the speciation of tin, lead, mercury, selenium and arsenic are reviewed, with emphasis on the determination of the metallorganic species. Analytical conditions and detection techniques suitable for the determination of these species are discussed. The electrolytes covered by the review include both non-micellar and micellar solutions. Although direct UV detection is still the predominant detection method for speciation by capillary electrophoresis, ICPMS has been gaining in significance because of its sensitivity and selectivity in elemental analysis. Further, ways of increasing the concentration sensitivity are outlined and discussed. Apart from the use of more sensitive detectors, this can be accomplished either by derivatisation of the analytes to form highly absorbing or fluorescent species or thorough leading a higher total amount of the analytes into the capillary. The latter aim can be achieved by preconcentration using solid-phase extraction (SPE), or using various on-capillary stacking methods. Finally, an overview of applications to speciation analysis is presented, organized according to the particular element being determined.

Keywords: Capillary electrophoresis; Tin; Lead; Mercury; Arsenic; Selenium; Speciation

INTRODUCTION

Significance of the target analytes

Arsenic, mercury, selenium, lead and tin (henceforth referred to as target elements) can exist in many forms and as inorganic or organometallic species. The major species are listed in Table I, together with their structures

*Corresponding author. Fax: +61-3-62262858. E-mail: paul.haddad@utas.edu.au

TABLE I Structures and pKa values of the inorganic and organic forms of the target elements

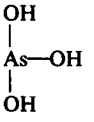
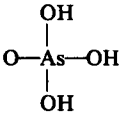
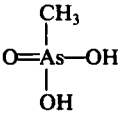
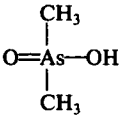
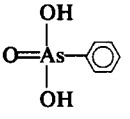
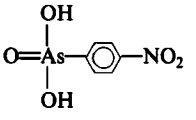
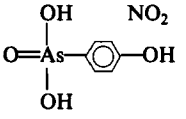
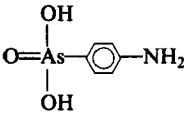
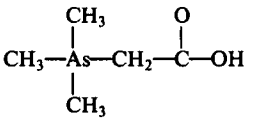
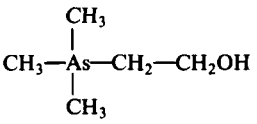
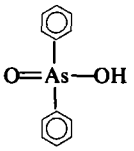
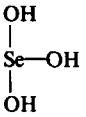
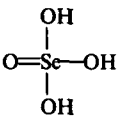
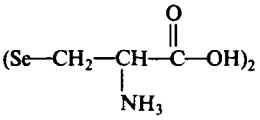
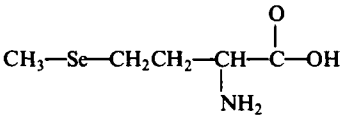
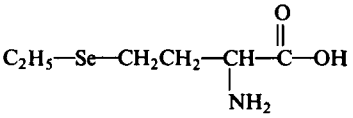
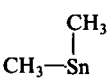
Name	*Abbreviation*	*Structure*	*pK values*
As			
Arsenite	As(III)		9.2
Arsenate	As(V)		2.3 6.9 11.4
Monomethylarsonic acid	MMA		3.6 8.2
Dimethylarsinic acid	DMA		1.3 6.2
Phenylarsonate	PAA		3.6 8.8
4-nitrophenylarsonic acid	4-NPAA		NA
3-nitro-4-hydrophenylarsonic acid	Roxarsone		NA
p-aminobenzenearsonate	PABA		1.9 4.1 9.2
Arsenobetaine	AsB		2.2

TABLE I (Continued)

Name	*Abbreviation*	*Structure*	*pK values*
Arsenocholine	AsC		NA
Diphenylarsonic acid	DPA		NA
Se			
Selenite	Se(IV)		8.3
Selenate	Se(VI)		< 2
Selenium carrying glutathione	GSSeSG	$H_2NCH(COOH)CH_2CH_2CO\text{-}NH$ $CH(CH_2SH)CONHCH_2\text{-}COOH$	NA
Selenocystamine	SeCM	$NH_2CH_2CH_2SSCH_2CH_2NH_2$	NA
Selenocystine	SeC		1–2.1 8.02–8.71
Selenomethionine	SeM		2.28, 9.21
Selenoethnionine	SeE		NA
Hg			
Phenylmercuric acetate	PMA		NA
Methyl mercury	MeHG	$CH_3—Hg$	NA
Ethyl mercury	EtHg	$C_2H_5—Hg$	NA
Sn			
Dimethyltin	DMT		NA

(*Table I Continued*)

TABLE I (Continued)

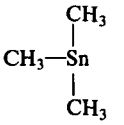
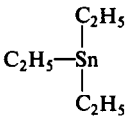
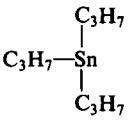
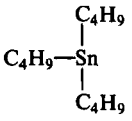
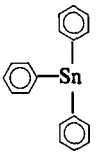
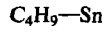
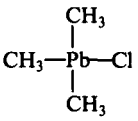
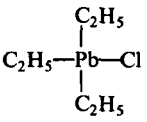
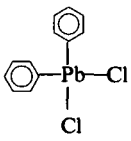
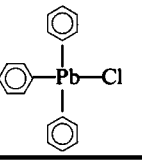
Name	*Abbreviation*	*Structure*	*pK values*
Trimethyltin	TMT		NA
Triethyltin	TET		NA
Tripropyltin	TPT		NA
Tributyltin	TBT		NA
Triphenyltin	TPhT		NA
Monobutyltin	MBT		NA
Pb Trimethyl-lead chloride	TMLC		NA
Triethyl-lead chloride	TELC		NA
Diphenyl-lead chloride	DPLC		NA

TABLE I (Continued)

Name	*Abbreviation*	*Structure*	*pK values*
Triphenyl-lead chloride	TPLC		NA

and pKa values (where applicable). Once the target elements have entered the environment, their physical and chemical properties, toxicities, mobilities and biotransformations are controlled to a large extent by their chemical form [1].

Arsenic is widely distributed in the environment and since different arsenic species have a wide range of toxicities, speciation of this element is of particular interest to environmental and biological chemists [2]. Humans may be exposed to arsenic compounds occupationally and through food, tobacco smoke, ambient air and water. Inorganic As(III) and As(V) species are highly toxic, whereas methylated As species are generally considered as less toxic and arsenobetaine (AsB) and arsenocholine (AsC) are believed to be non-toxic because they are not metabolised [2]. Selenium is both a toxic element and an essential element for human beings and as such it plays an important role in environmental analysis and in human health studies. Excess Se intake can cause toxic reactions in living organisms and the toxicity of selenium is to a large extent dependent on its chemical form [3]. On the other hand, Se takes part in the biological selenium cycle and is incorporated into proteins [4] and selenium supplementation may aid in the prevention of some diseases.

Organometallic compounds of mercury, lead and tin are much more toxic than the ions of the corresponding inorganic compounds because of their greater biological compatibility. Organomercury compounds have a strong tendency to accumulate as they pass through the food chain [4]. This biomagnification is particularly large in marine ecosystems and leads to potential human exposure through seafoods [1]. Organotin compounds are widely used as stabilisers in the plastics industry and as insecticides, fungicides and biocides in agriculture. The most important organotin compounds in the aquatic environment are tetrabutyltin (TBT), the active ingredient in antifouling paint, and triphenyltin (TPT), used as a non-selective pesticide [5]. Because organotins with alkyl- or aryl-groups are among the most toxic compounds and their annual production is growing steadily,

there is increasing concern over their presence in the environment. Organolead compounds have been shown to be carcinogenic. They are disseminated into the environment by mining, refining, paints and as antiknock additives in gasoline. Tetraalkyllead, which are the most commonly used organolead compounds, undergo photochemical and metabolic dealkylation to form trialkylead compounds, which are reactive and thermally sensitive [1].

The determination of the total concentration of the target elements does not reflect the important information of distinguishing between the different species in which the elements can exist. Speciation analysis, defined as the determination of the individual physico-chemical forms of an element, plays an increasingly important role in environmental analysis [6] and often presents a major challenge for analysts.

Analytical methods used for speciation

When speciation is needed, a separation method is usually necessary. The most commonly used separation technique in speciation of the target elements is gas chromatography (GC) [7–10] which offers a high separation power and can be connected to very sensitive and selective detectors, such as flame photometric detection (FPD), electron capture detection (ECD), atomic absorption spectrometric (AAS) or atomic emission spectrometric (AES) detection. In order to enhance the volatility and detectability of ionic species, sample derivatisation is typically necessary before GC analysis. Further drawbacks of GC are that it is often performed at temperatures that can cause thermal degradation of the compounds of interest, and sample cleanup procedures are often very tedious. High performance liquid chromatography (HPLC) has also been employed for speciation of the target elements [8–11]. Although complicated derivation procedures are often not required for HPLC methods, the separation power of this technique is not as high as that of GC. In addition, many of the target element species lack UV chromophores, so the use of direct UV detection is precluded.

Capillary Electrophoresis (CE) is generally recognised to have a higher resolution power than HPLC and has evolved as an alternative technique for speciation analysis, especially applied to those target element species which cannot be analysed by GC. Since Morin *et al.* established a CE method for the determination of organic As species in 1992 [12], there have been 69 further studies on the separation of organic As, Se, Hg, Sn and Pb species using CE methods (see Fig. 1). Several review papers have

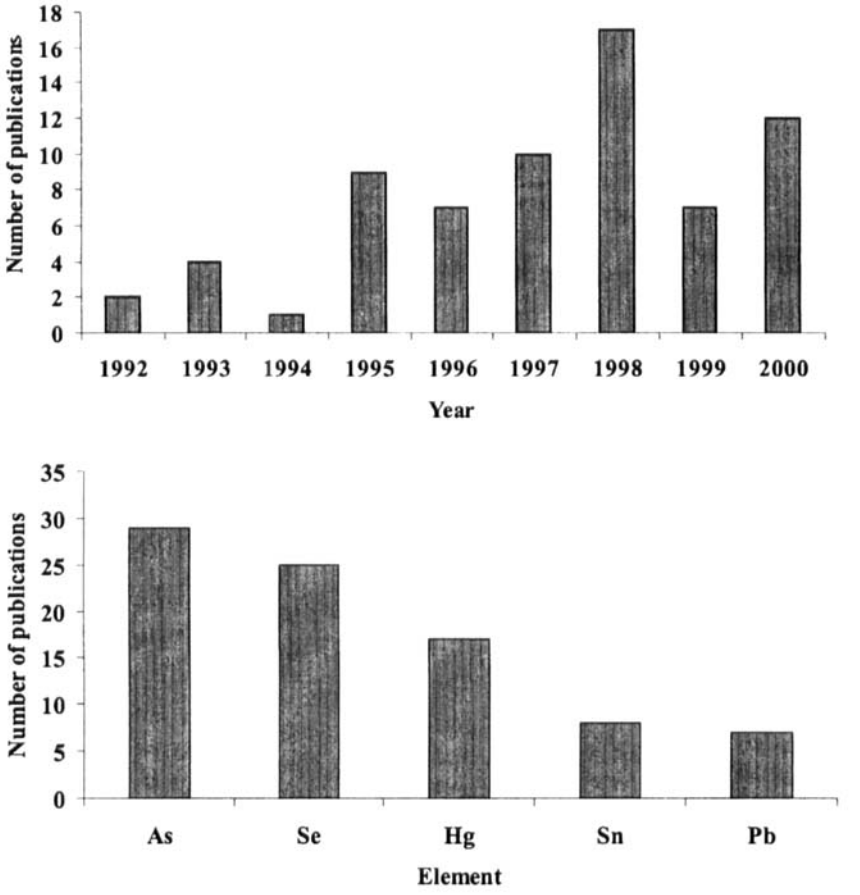


FIGURE 1 Scientometric analysis of the publication numbers for the target analytes: (a) total number of publications per year, and (b) number of publications per element.

briefly covered early developments of speciation analysis by CE, especially of the inorganic forms of the target elements [13–18]. In the present review, we focus on CE methods for the determination of inorganic and organometallic forms of As, Se, Hg, Sn and Pb compounds. The review is organised into the following sections (i) separation conditions, (ii) detection conditions, (iii) approaches to increase sensitivity, and (iv) a review of papers according to the individual elements determined. Table II summarises the literature cited in this review and presents information on the analytes determined, together with experimental details covering the injection method, the type of capillary used, the nature of the background electrolyte (BGE), the detection method, and the detection limit achieved.

TABLE II Experimental details of published CE methods (1992–2000) for the speciation of the target elements

Analyte	*Sample*	*Capillary, separation voltage, injection voltage*	*Electrolyte*	*Detection*	*Detect Limt*	*Ref.*
As(III), As(V), MMA and DMA	NA	Fused silicon capillary (FS.) 72 cm × 30 μm. 10 to 40 kV at 40°C	phosphate buffer, pH range of 4.5–6.5	UV, 190 nm	40 pg. As(V)	12
Dimethyltin, tributhyltin, dibuthyltin	NA	FS. 60 cm × 75 μm, 20 kV	PH 2.65, containing CTAB	Indirect UV 254 nm	NA	20
Trimethyl-, triethyl-, tripropyl-, tributyl- and triphenyltin	NA	FS. 64 cm × 50 μm, 300 V/cm, injection at 18 kV	70 mM HEPES and 1 mM-6-aminoquinoline pH4	Indirect Fluorescence	0.95–2.1 mg/L	21
Se(VI), Se(IV), As(V), Te(IV), MMA, SeC, SeM, Te(VI), As(III), Sb(V), DMA	Soil	FS. 60 cm × 75 μm Hydrostatically or electromigratively (−10 kV, 20 s) injection, Stacking; −20 V	5 mM-Na_2CrO_4 containing 0.5 mM-tetradecyltrimethyl-ammonium hydroxide (pH 11.2)	UV, 254 nm	13 μg/L Se(VI) with stacking	22
Se(VI), Se(IV), As(III), DMA and As(V)	Tin ore processing plant	FS. 70 cm × 75 μm, CTAB dynamic coating, Electrokinetic injection for 12 s, −25 kV	0.03% Triton X-100 and 50 mM-2-(cyclohexylamine)-ethanesulfonic acid, adjusted to pH 9.4 with LiOH;	Conductivity	40, 76, 70, 85, 65 μg/L for As(V), As(III), DMA, Se(VI) and Se(IV)	23
As(III), As(V), DMA, MMA, PAA, AsB and AsC	NA	FS. 72 cm × μm and 70 cm × 50 μm, 50 and 25°C for As and Se, respectively	NA	UV, AS: 190 nm, Se: 200 nm	pg range	24
As(III), As(V), DMA, MMA, PAA, Se(VI), Se(IV), SeC and SeM	NA	FS. 72 cm × 50 μm, 25 kV or TTAB coated capillary, −12 kV	25 mM-Phosphate buffer of pH 6, or 80 mM phosphate buffer of pH 8 containing 2 mM TTAB	UV, 190 nm	Simpler and more efficient than HPLC but less sensitive	25
Phenylarsonic, methylarsonic, and arsenic acids	NA	FS. 44 cm × 75 μm. 50 s injection, −20 kV Stacking: 165 s, 80% of the column volume	TTAB 0.4 mM in 20 mM-phosphate buffer, pH 6	UV, 195 nm	30- to 40-fold improvement of sensitivity	26

Organoselenium	NA	FS. 75 cm × 50 μm, − 25 kV	2% acetic acid of pH 2., coaxial sheath liquid (acetic acid/H_2O/ methanol = 1 : 2 : 17)	ESI MS	1–5.5 mg/L	27
As(III), As(V), MMA, DMA, PAA, PABA, Roxarsone, 4-NPAA and PAO	Lake water	PDDAC coated capillary, 60 cm × 50 μm, 18 kV. Stacking, up to 80% capillary, − 18 kV	20 mM carbonate buffer, pH 10	UV 192 nm	1.38, 3.75, 2.50, 0.63, 0.99, 0.27, 3.30, 0.66, 7.51 mg/L for As(III), As(V), MMA, DMA, PAA, PABA, Roxarsone, 4-NPAA, PAO, respectively	28
As(III), As(V), MMA and DMA	Potable water	Polyimide-coated capillary, 85 cm × 75 μm, electrokinectic injection	20 mM-potassium hydrogen phthalate/20 mM-borate buffer, pH 9.03	ICPMS (with hydride generation)	Arsenite, arsenate, MMA and DMA were 0.025, 0.006, 0.009 and 0.058 μg/L*	29
Se(IV), Se(VI), GSSeSG, SeM, SeC and SeCM	Human milk, blood serum	FS. 150 cm × 50 μm, + 18 kV	10 mM-Na_2CO_3 (adjusted to pH 11.5 with KOH)	ICPMS	30–50 μg/L	30
Se(IV), Se(VI), As(III), As(V), MMA, DMA, PAA, PABA, Benzeneselenium	NA	polymer-coated capillary, 27 cm × 50 μm, Large-volume stacking with matrix removal	20 mM Phosphate buffer, pH 10.5-	UV, 190 nm	μg/L, level with stacking	31
Organic Hg	Fish tissues	FS. 60 cm × 100 μm, coated with polyacrylamide, on-line derivatisation. − 25 kV	10 mM-sodium acetate, pH5, 5 mg/L dithizone sulfonate	Vis, 480 nm	~ μg/L with stacking	32
TELC, diphenyllead, Se, Hg	NA	FS. 65 cm × 50 μm, 20 kV stacking, reach 95% capillary, − 10 kV, 2 min	2.5 mM-TTHA/2 mM SDS 40 mM phosphate/borate, pH 7.5	UV, 200 nm	0.3–2 μg/L	33
TMLC, TELC, TMT and TBT	NA	FS. 55 or 60 cm × 75 μm, 20 kV, SPE with use of an Empore C18 silica disc	0.05 M-SDS in 15 mM-borate-30 mM-phosphate buffer of pH 7.65, Diethyldithiocarbamate derivatisation	UV, 200 nm	Trimethyl-lead, triethy-lead, trimethyltin and tributyltin 22.4, 17.2, 42.1 and 15.5 pg	34

(Table II Continued)

TABLE II (Continued)

Analyte	*Sample*	*Capillary, separation voltage, injection voltage*	*Electrolyte*	*Detection*	*Detect Limt*	*Ref.*
As(III), As(V), DMA, MMA, DPA, PAA, PABA and PAO	As compounds in spiked urine	FS. 70 cm × 75 μm, 35°C, 25 kV, 6 s injection	15 mM-phosphate solution adjusted to pH 6.5 containing SDS	UV, 200 nm	~ mg/L	35
Organolead, organomercury and organoselenium	NA	FS. 65 cm × 50 μm, 20 kV, pre-capillary derivatisation with nitrilotriacetic acid (NTA)	40 mM-SDS, 5 mM-NTA in phosphate/borate, pH 7	UV, 200 nm	10–310 μg/L 0.2–5.31 μg/L with stacking	36
TMLC, TELC, diphenylselenide and phenylselenyl chloride	Waters from a car-park drain	FS. 44 cm × 50 μm, 15 kV	50 mM-SDS and 5 mM-beta-cyclodextrin in 25 mM-phosphate/borate at pH 6.0	UV, 210 nm	20, 8, 9 and 18 pg for TMLC, TELC, diphenyl selenide and phenylselenyl chloride, respectively	37
SeM, SeC and SeCM	NA	FS. 70 cm × 75 μm	5% acetic acid	ICPMS and ESI MS	30–50 μg/L, 10–24 pg	38
As(III), As(V), PABA, PAA, DMA	NA	FS. 57 cm × 75 μm at 25°C. Stacking procedures, − 15 kV and detect at 10–15 kV	15 mM-phosphate buffer at pH 8.5, sample solutions containing 40% methanol	UV, 192 nm	350 μg/L As(III), 275 μg/L DMA, 479 μg/L As(V), 16 μg/L PABA and 11 μg/L PAA	40
As(III), As(V), DMA, MMA, AsB and AsC	Urine and sewage sludge	FS. 150 cm × 50 μm, 18 kV	20 mM-Na_2HPO_4/NaH_2PO_4 of pH 5.6/acetonitrile (1:1)	ICPMS	15 μg/L As for As(III), As(V), DMA and MMA and 65 μg/L as for AsB and AsC	41
Se(IV), Se(VI), SeC and SeCM	NA	FS. 70 cm × 50 μm, − 18 kV. 3–10 s injection	30 mM-phospate, pH 8.5, containing 1.3 mM-TTAB	UV, 200 nm	1 mg/L	42
Asenic species	NA	FS. 60 cm × 50 μm. 20 s injection	40 mM-borate, containing 0.4 mM-CTAB, at pH 8.2	UV, 197 nm	arsenite and arsenate were 27 and 85 pM,	43

MMA, AsB, AsC	Mineral water, human urine and soil	FS. 88 cm × 75 μm, −25 kV	20 mM-borate buffer (pH 9.4) containing 2% of Anion-BT osmotic flow modifier as electrolyte	ICPMS	As(III), MMA, DMA and As(V) were 1.3, 1.6, 1.7, and 2.1 μg/L	44
Organomercury species	Fish and crab	FS. 65 cm × 100 μm, internally coated with polyacrylamide, −25 kV	10 mM-sodium acetate, pH 4.5, 5 mg/L dithizone sulfonate	Vis, 480 nm	2 μg/kg methylmercury	45
Methylmercury	Tuna	FS. 65 cm × 100 μm, coated with polyimide, 15 kV	0.2 M sodium borate pH 8.11	UV, 200–400 nm	2 pg	46
Triorganotin species	Water	HPLC: Partisil SCX-1D (25 cm × 4.6 mm) CE: FS 60 and 100 cm × 75 μm, 20 kV	LC: 70% methanol in 10 mM acetate/2 mM-benzyltrimethylammonium chlorine (BTMA) CE: 20 mM-tartaric acid/ methanol (4:1)/ 1 mM-BTMA	Indirect UV LC: 262 nm, CE: 210 nm	CE: ~ μg/L, preconc. with SPE	47
Triorganotin species	NA	FS. 70 cm × 75 μm. Preconc. with XAD-2 resin SPE	20 mM-tartaric acid/methanol (4:1) and 4 mM-butyltrimethylammonium	Indirect UV	~ μg/L, preconc. with SPE	48
Triorganotin species	Sediment	FS. 60 cm × 75 μm, 300 V/cm	5 mM acetate and 3 mM-4-aminopyridine pH 4.5,	Indirect UV	0.24–2.4 mg/L	49
As(III), As(V), MMA, DMA and PAA	Ground water	FS. 60 cm × 50 μm, is 15 kV	1.5 mM-fluorescein of pH 9.8	LIF	0.04–0.16 mg/L As	50
As(III), As(V), MMA, DMA, Se(IV) and Se(VI)	NA	FS. 85 cm × 75 μm, Se(VI) was reduced to Se(IV)	20 mM-potassium hydrogen phthalate/20 mM-borate buffer of pH 9.03	MS	10 pg for Se(IV) and 24 pg for Se(VI) (values for As species not given)	52
As(III), As(V), DMA, MMA and AsB	NA	FS. 80 cm × 75 μm, 25 kV	4.4 mM sodium chlromate pH 8.2 with 1:50 dilution with OFM Aion BT	Indirect UV and ICPMS	0.44–1.9 mg/L for UV, 53–280 μg/L for ICPMS	54

(*Table II Continued*)

TABLE II (Continued)

Analyte	*Sample*	*Capillary, separation voltage, injection voltage*	*Electrolyte*	*Detection*	*Detect Limt*	*Ref.*
As(III), As(V), AsB, AsC, DMA, MMA, TMLC, TELC	NA	FS. 55 cm × 75 μm, 30 kV	4 mmol/L, Borate buffer pH 9.3	ICPMS	NA	55
methyl- and inorganic Hg	Bio-certified reference materials	FS. 75 cm × 75 μm, 21 kV	25 mM-calcium chloride with pH of 7	ICPMS	13.6 μg/L for methyl mercury and 6.0 μg/L for mercury(II)	63
Methyl-, ethyl and inorganic Hg	NA	FS. 110 cm × 100 μm, 17 kV	50 mM-carbonate buffer with pH 11, 20 mM SDS and 0.2% (m/v) L-cysteine	ICPMS	80–170 μg/L	65
Methyl- and inorganic Hg	NA	FS. 100 cm × 75 μm, 20 kV, stacking	20 mM-sodium tetraborate decahydrate buffer with pH 9.3	ICPMS	7 μg/L for methyl mercury and 4 μg/L for mercury(II)	66
Methyl- and inorganic Hg	NA	FS. 100 cm × 75 μm, 20 kV, stacking	20 mM-sodium tetraborate decahydrate buffer with pH 9.3	ICPMS	7 μg/L for methyl mercury and 4 μg/L for mercury(II)	68
As(III), As(V), DMA and MMA	Chinese herbal medicine	FS. 65 cm × 75 μm, 18 kV	25 mM-phosphate of pH 6.5	ICPMS	0.6, 0.41, 0.42 and 0.34 μg/L for As(III), DMA, MMA and As(V), respectively	73
As(III), As(V), MMA, DMA, PAA, AsB and AsC	NA	FS. 78 cm × 40 μm, electrokinetic injection	5 mM-ammonium acetate/ acetic acid buffer of pH 6.8	MS	0.5–3.3 mg/L. 100–200 μg/L for AsB and AsC with preconcentration	76
As(III), As(V), MMA, PAA, AsB and AsC	NA	FS. 78 cm × 50 μm, 30 kV, Stacking	5 mM-ammonium acetate/acidic acid buffer of pH 6.8	MS	0.5–3.3 mg/L 100–200 μg/L for AsB and AsC with stacking	77
As(III), As(V), MMA, DMA	NA	FS. 66 cm × 100 μm, 15 kV, 400 nl injection	50 mM-phosphate buffer of pH 6	ICP AES	0.32 mg/L for As(III), As(V) and MMA and 0.35 mg/L for DMA	78

Methyl and ethyl mercury	NA	FS. 65 cm × 50 μm, 25 kV	0.1 M-creatinine at pH 4.6	Amperometric detection	Methylmercury 25 μg/L, ethyl mercury 150 μg/L	79
As(III), As(V), MMA, DMA, Se(IV) and Se(VI)	Tap water Mineral water	FS. 50 cm × 50 μm, 20 kV, Stacking: 10 kV and 48 cm sample	75 mM-NaH_2PO_4 and 25 mM-sodium borate	UV, 195 nm	Below 25 μg/L for the various Se and As species with stacking	85
MMA, DMA and arsenic acids	NA	FS. 70 cm × 75 μm, Polarity switching Stacking with −25 kV, +25 kV for the separation	20 mM-Na_2HPO_4 at pH 6	UV, 195 nm	10- to 20-fold improvement of sensitivity	88
TELC, DPS, TMLC, PSC, DPLC, Pb(II), Se(IV), PMA	NA	FS. 65 cm × 50 μm, 20 kV, precapillary derivatisation with EDTA	40 mM-SDS, 5 mM-EDTA in phosphate/borate pH7	UV, 200 nm	1700 fold enhance with stacking technique	90
Methyl-, ethyl, phenyl Hg	Marine sample	FS. 50 cm × 75 μm, 18 kV	0.1 M sodium borate pH 8.35	UV, 200 nm	10 pg	92
Methylmercury	Environmental waters	FS. 100 cm × 75 μm, 30 kV	0.2 M sodium borate pH 8.24	UV, 200–400 nm	12 μg/kg with stacking	93
As(III), As(V), MMA, DMA, AsC and AsB	NA	FS. 60 cm × 75 μm, 10 kV, hydrostatically or electromigration injection	2.5 mM-phosphate buffer at pH 10	UV, 186 nm	100 μg/L for As(III), 150 μg/L for As(V) and 400 μg/L for DMA. with stacking	96
As(III), As(V), MMA and DMA	NA	FS. 72 cm × 50 μm 30°C and −25 kV, 20 s injection	10 mM-dodecyltriethylammonium dihydrogenphosphate of pH 8	UV, 190 nm	14–20 pg As. No interference from other anions	97
As_2O_3, As_2O_5, MMA and DMA	Spiked drinking water	FS. 122 cm × 50 μm and 20–25 kV	25 mM-phosphate buffer at pH 6.8, PAA as internal standard	UV, 190 nm	The calibration graphs were linear for 2–14 mg/L of As2O5, MMA and DMA	98
As(III), As(V), DMA and DPA, PAA, PABA and o-aminophenyl arsonic acid	NA	FS. 64.5 cm × 50 μm, −20 kV	50 mM-borate with pH 9.2 containing 0.5 mM CTAB	UV, 200 nm	~ mg/L	99

(Table II Continued)

TABLE II (Continued)

Analyte	*Sample*	*Capillary, separation voltage, injection voltage*	*Electrolyte*	*Detection*	*Detect Limt*	*Ref.*
As(III), DMA	Water	FS. 72 cm × 50 μm, 25 kV, 10 s injection	5 mM-chromate buffer of pH 8 containing 0.5 mM-EOF modifier as the running buffer	UV, 254 nm	0.5, 0.1 and 0.1 mg/L for As(III), As(V) and DMA, respectively	100
As(III), As(V) and DMA	NA	FS. 57 cm × 50 μm, 25 kV, 50 s injection	20 mM-phosphate buffer of pH 7–10.8. CAPS and NaCl added to the sample solution	UV, 200 nm	0.15, 1.1 and 1.3 mg/L	101
As(III), As(V), MMA and DMA	NA	FS. 75 cm × 50 μm, −28 kV	6 mM-chromate solution of pH 10 containing NICE-Pak OFM Anion-BT (1 : 40)	UV, 274 nm	5.2, 3.5, 15.6 and 15.6 pg for arsenate, arsenite, MMA and DMA, respectively	102
Selenate, selenite, selenocystine and selenomethionine	NA	FS. 150 cm × 50 μm, −25 kV, Electrokinetic injection at −5 kV for 30 s	1) 5 mM-dodecyltrimethyl-ammonium phosphate in borate buffer of pH 9; 2) 0.25 mM-hexadecyltrimethylammo-nium bromide in 2.5 mM-sodium chromate of pH 9;	UV 1) 190 nm 2) 254 nm	1) 200 μg/L 2) 5 fold improved	105
Selenate, selenite, selenocystine and selenomethionine	Human milk	FS. 150 cm × 50 μm, 12 kV	20 mM-phosphate, pH 5.6; leading electrolyte 20 mM-sodium hydroxide; make-up buffer pH 2.3, 20 mM-phosphate	ICPMS	~ μg/L	106
DMA, MMA and selenomethionine	NA	FS. 150 cm × 50 μm, +18 kV, 100 mM Phosphate buffer pH 2.3 for stacking, 375 nl	100 mM Phosphate buffer pH 6	ICPMS	~ 1 μg/L	107

SEPARATION CONDITIONS

Capillaries

Among the CE methods reviewed in this paper, fused-silica capillaries of 50–100 μm I.D were the most frequently used. The inner wall of the capillary is in contact with BGE (typically aqueous in composition) and is negatively charged at pH values above approx. 3 because of the presence of silanols on the surface. However, for some analytes (especially multiply charged cationic or hydrophobic cationic analytes) adsorption onto the capillary surface due to coulombic and hydrophobic interaction is a problem during the separation, resulting in poor peak shape and/or complete loss of the analyte peak. Interactions between the analyte and the capillary wall can often be suppressed by coating the capillary using either a "permanent coating" or a dynamic coating method. Permanent coating involves pre-treatment of the capillary with a suitable reagent designed to permanently modify the surface, and the reagent is then not included in the BGE during analysis. Dynamic coating involves adding the coating reagent to the BGE in order to establish an equilibrium concentration of the reagent on the capillary surface, often as a homogeneous layer which changes the chemical nature of the capillary surface and usually also suppresses or reverses the electroosmotic flow (EOF). The coating may act to retard the adsorption of cationic or acidic analytes, leading to significant improvements in separation efficiency and peak symmetry.

Hydrophilic polymers or surfactants are often used for the dynamic coating method [19], with alkyltrimethylammonium bromide compounds such as cetyltrimethylammonium bromide (CTAB) [20] and tetradecyltrimethylammonium bromide (TTAB) [26,42] being commonly used as EOF modifiers. Lee and Whang [21] have claimed that zwitterionic Good's buffers such as HEPES were adsorbed on the capillary wall and as a result the EOF was suppressed but still maintained the same direction of electrophoretic mobility as cationic analytes, resulting in co-EOF separations of these analytes. An additional advantage of these zwitterionic buffers was that they generate a low electrophoretic current. Dynamic coatings have been also applied successfully in fast separations of As and Se species [22–25], most of which are negatively charged. Cationic surfactants or polymers have been added to the BGE to reverse the EOF, so that the separation was run in co-EOF mode and considerable reductions in the separation time. Dynamic capillary coating has also been applied in large volume stacking injection methods for arsenic speciation without polarity switching [26] (see section on Stacking).

Permanently coated capillaries have found use for the CE separation of the target elements [27–32]. In capillary electrophoresis–mass spectrometry (CE–MS) or capillary electrophoresis–inductively coupled plasma mass spectrometry (CE–ICPMS) methods, permanently coated capillaries remove the need to use EOF modifiers in the BGE which prevents the interference of these modifiers with the detection [27,29]. In capillary isoelectric focusing (cIEF) used for selenium speciation, permanently coated capillaries are used to suppress the EOF and to allow the pH gradient established in the capillary to separate the analytes [30]. Also Vanifatova *et al.* [31] used a polymer-coated capillary with a large volume stacking technique to separate eight arsenic and selenium species, but the unstable coated layer caused the EOF mobility to be changeable. Poly(diallyldimethylammonium chloride) (PDDAC) was permanently coated onto the fused silica capillary for arsenic speciation by Sun *et al.* with good resolution and very stable baselines [28].

Background electrolytes

The composition of the BGE plays a central role in CE methods as it determines the fundamental migration behaviour of the analytes. A good BGE must guarantee suitable electrophoretic behaviour of all individual analytes, resulting in satisfactory resolution and overall ruggedness of the system, and must not interfere with the detection. In speciation methods, it is often necessary to separate a large number of analytes in a single run, usually at low concentration. Optimisation of the BGE system is required to achieve the best resolution and peak shape, so that in most studies listed in Table II, numerous BGE parameters have been considered. These include the solubility and stability of the analytes in the BGE, degree of ionisation of the analytes, influence of the anions and cations present in the BGE on the electromigration of the solutes, effect of pH, effects of organic modifiers and other additives, and the dissipation of heat generated in the electrolyte.

In all cases of CE speciation methods, aqueous BGEs were applied with acetate, phosphate and borate (see Table II) being the most commonly used buffers. Often, sodium dodecylsulphate (SDS) was added into the BGE as a micellar surfactant [33–35] to enable neutral analytes to be separated by micellar electrokinetic chromatography (MEKC), sometimes also called micellar electrochromatography (MEC). MEKC is the predominant mode for the speciation of Pb [33,34,36,37] and it has also been used for As speciation [35]. β-cyclodextrin was also added to the BGE in an early study in an attempt to improve peak shapes [37].

The degree of ionisation of analytes in the BGE depends primarily on the pH of the solution. Both the separation efficiency and separation time may be affected by the electrolyte pH. Usually the optimum pH of the separation system is related to the values of protonation dissociation constants (pKa) of the analytes. For a fused silica capillary, typical pH ranges of BGEs used for the speciation of the target elements are: weakly acidic (2.65–4.5) for Sn, neutral (~7) for Pb, around neutral (4.6–8.35) for Hg, weakly acidic to weakly alkaline (4.5–10) for As and weakly alkaline for Se. Optimised separation systems were employed for multi-element speciation so that all species could be separated [33,34,36,37]. Six Se species could be separated at pH 11.5, while the same aim could be achieved at pH 2 when a permanently coated capillary was used [27,38].

Some analytes which are not normally soluble in aqueous solution could be separated by adding organic solvents to the BGE in order to improve their solubility in the separation system. Organic solvents are also known to reduce the EOF, which may result in better resolution at the expense of a longer analysis time. The influence of organic modifier concentration on plate number in MEKC was discussed thoroughly by Seals [39]. For the speciation analysis of As, acetonitrile and methanol were used to suppress the conductivity of the sample matrix, so that a sensitivity enhancement could be achieved by stacking [40,41]. The separation result depends to a large extent on the EOF of the separation system, and this can be controlled by a careful selection of the BGE composition. Many EOF modifiers, such as alkyl trimethylammonium [22,42,43], Anion-BT [44] and Triton X-100 [26], have been coated onto the capillary wall to suppress or reverse the EOF. Complexing additives are sometimes used both for pre-capillary complexation of analytes prior to injection as well as being employed as BGE additives during the separation [32,36,45,46]. Finally, indirect UV detection is commonly used in speciation, with various indirect detection probes (absorbing co-ionic substances) being added to the BGE [21,47–49].

DETECTION TECHNIQUES

The detection techniques used in CE speciation analysis of the target analytes are listed in Table III, together with typical limits of detection and references to individual papers arranged according to the element determined.

TABLE III Detection methods used in speciation of the target elements by CE

	UV			*Indirect fluorescence*	*ICPMS*	*MS*	*ECD*	*AES*	*Stacking*
	Direct UV detection	*Derivatisation prior to UV detection*	*Indirect UV*						
Typical LODs (μg/L)	1000–10000	10–300	1000–10000	40–160 (LIF)	1–50	1000–6000	40–70	~300	10–100 fold improvement
Organoarsenic	12, 22, 24, 25, 26, 28, 42, 85, 88, 96, 97, 98, 99, 100, 101, 102	–	54, 102	50(LIF)	29, 40, 41, 44, 52, 54, 55, 56, 57, 58, 71, 72, 73, 107	29, 38, 76, 77	23(c)	78	26, 28, 31, 40, 76, 77, 85, 88, 96, 107
Organoselenium	24, 31, 37, 42, 85	33, 36, 94	105	–	30, 38, 41, 56, 57, 58, 59, 60, 71, 72, 74, 106, 107	27, 75	23(c)	–	31, 33, 36, 85, 107
Organomercury	–	33, 36, 45, 46, 32, 92, 104, 109		–	63, 65, 66, 68	63	79(A)	–	33, 36, 46, 93
Organotin	–	34	20, 47, 48, 49	21	–	–	–	–	–
Organolead	37	33, 34, 36, 94		–	55	–	–	–	33, 36, 55

A: Amperometry C: Conductivity.

On-capillary UV-photometric and fluorimetric detection

On-capillary direct photometric detection in the UV region is the most commonly used detection method, even though its predominant position in speciation has been increasingly challenged by CE–ICPMS. Among a total of 68 studies in this area during the period from 1992 to 2000, there are 34 papers using UV detection, compared to 22 papers using ICPMS detection. Unfortunately, UV detection suffers from poor sensitivity because of the short light path lengths of 50–100 μm (depending on the internal diameter of the capillary), compared to 5–10 mm for a standard HPLC detector. This loss of sensitivity can be only partly compensated for by the very high efficiencies of CE separations. Indirect photometric detection, which is based on the principle of displacement of a visualisation probe by the analyte to yield a decrease in the background signal, is used to detect analytes which have no strong absorption bands in UV region. Although this universal-detection approach is capable of determining a large number of analytes, the sensitivity and detection limits are often inadequate for most environmental applications.

Fluorimetric detection, in particular laser-induced fluorimetry (LIF), has become popular in CE because of its very high sensitivity. However, the drawbacks of this detection mode are the need to derivatise most of the analytes because only a few show native fluorescence, and the choice of available excitation wavelengths of LIF is rather limited. An alternative to derivatising non-fluorescent analytes is the use of indirect fluorimetric detection. In this case, the choice of the fluorophore added to the BGE is very important. To date, there has been only one paper for organoarsenic analysis by CE–LIF [50]. A commercial fluorimeter, built with a xenon lamp as the excitation source, has been used for indirect fluorimetric determination of organotin using 6-aminoquinoline as the indirect fluorimetric detection probe [21].

ICPMS detection

ICPMS can be coupled with CE as an extremely sensitive, element specific, multi-element detector. Donard *et al.* [51] reviewed the development of commercial ICPMS in speciation. Combined with the separation power of CE, ICPMS plays an increasingly important role in element speciation because of its excellent sensitivity and selectivity. It can detect species at the μg/L level without preconcentration [52]. Since ICPMS was first coupled with CE by Olesik *et al.* [53] in 1995, its applications in speciation have increased

sharply. Though ICPMS has many advantages compared to conventional detection, the number of papers reporting the coupling of CE to ICPMS remains limited because of the cost of ICPMS and until recently, the lack of commercially available interfaces.

Designing an efficient interface to connect the end of the CE separation capillary with the plasma is critical to the success of any coupled CE–MS technique. A successful interface construction for CE–ICPMS coupling should satisfy three main requirements: First, the interface must provide an electrical connection and a stable electrical current for reproducible electrophoretic separations. Second, the interface must be able to adapt the electroosmotic flow inside the CE capillary to the flow-rate of the nebulizer. Third, the interface should prevent pressure-induced flow inside the CE capillary resulting from a pressure difference at the end of the capillary caused by the nebulizer. In all cases of speciation with CE–ICPMS, an electrolyte liquid sheath flow has been applied as a make-up solution to complete the electrical circuit. To eliminate the pressure-induced flow inside the capillary, the make-up solution also has the function of controlling the nebulizer suction. The flow-rate of the make-up solution is usually optimised either using a reciprocating pump or by self-aspiration using the nebulizer [54,55].

Michalke and Schramel designed and manufactured a modified Meinhard nebulizer to meet the requirements of the CE–ICPMS interface [56–58]. Special care was needed to optimize the positioning of the capillary end and to ensure reliable closure of the CE electrical circuit during nebulisation. An additional Ar/H_2 gas stream was directed to the ICPMS torch and coated the inner surface of the spray chamber. This avoided an aerosol condensation at the walls of the chamber and gave complete transport of the aerosol into the plasma [see Fig. 2]. Good sensitivity and selectivity was achieved in the speciation of Se and As with this type of interface [59,60].

Liu *et al.* [61] modified a commercial Microneb 2000 DIN system as a CE–ICPMS interface. The direct injection nebulizer (DIN) is a microconcentric pneumatic nebulizer without a spray chamber which nebulises the liquid sample directly into the central channel of the ICP torch with make-up solution. As shown in Fig. 3 the Microneb DIN torch insert is fitted with a polyetheretherketone (PEEK) cross connector. The CE capillary is inserted concentrically inside the fused-silica DIN sample introduction capillary. A pulse-free make-up solution through the DIN sample transfer capillary establishes the CE electrical contact at the grounding terminus of the CE capillary. The make-up solution flow, merged with the flow generated inside the CE capillary by the EOF, is nebulized by the DIN directly into the ICP torch. Utilising the same principle, two concentric

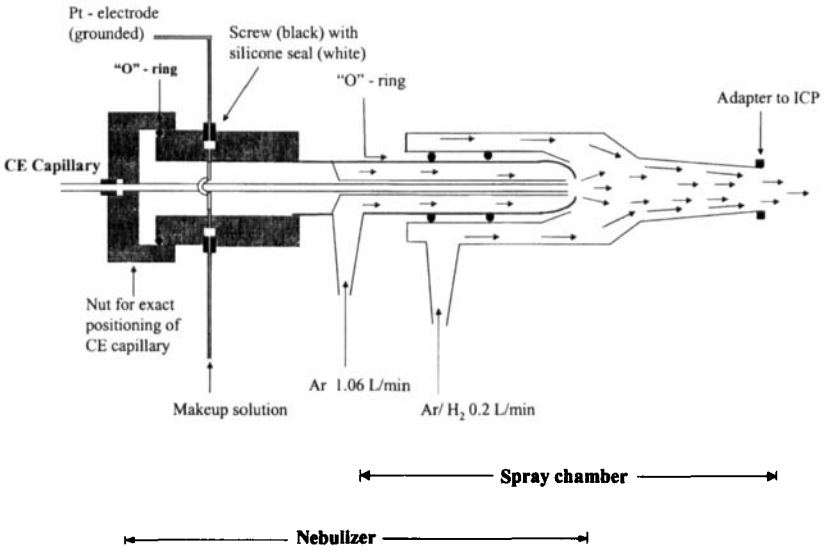


FIGURE 2 Scheme of the modified nebulizer and the new spray chamber is shown. The CE capillary is fixed to a nut. Reprinted with permission from ref. [57].

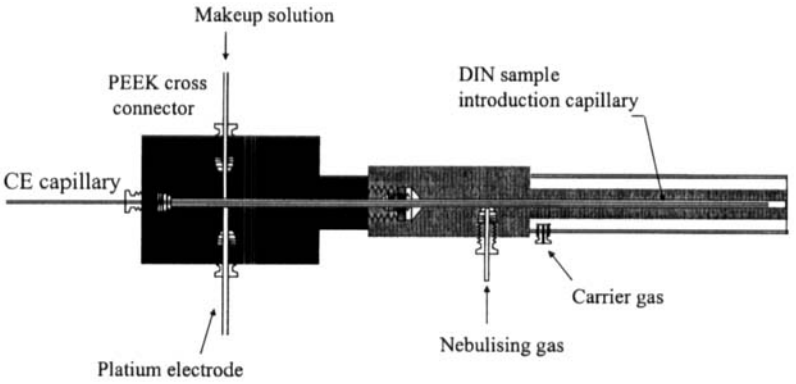


FIGURE 3 Scheme of the DIN CE–ICPMS interface. Reprinted with permission from ref. [61].

nebulizer interfaces of simpler construction were designed for Holderbeke [44]. Tangen *et al.* [62] discussed new nebulizer technology exclusively designed for nebulisation of microflows and designed various CE–ICPMS nebulizer tips for different liquid flow-rate working ranges.

Most recent studies in this area have adopted either a standard cross-flow nebulizer with a Scott spray chamber [63–68] or a micro-concentric

nebulizer (MCN-100) with a cyclone spray chamber [63,65,67]. Tu *et al.* [64] compared two kinds of interfaces and demonstrated that the first offered a shorter analysis time, better resolution and ruggedness, while the second provided better detection limits. Baker [67] achieved similar results. A simple design which adopted a commercial spray chamber was made by Majidi and Miller-Ihli [63] but the electropherograms showed that the resolution was compromised because of the simple design. A new interface design recently reported by Schaumloffel and Prange [55] divided the interface construction into two parts, namely the nebulizer capillary and the CE capillary. The CE capillary was not inserted into the nebulizer capillary and this prevents any pressure-induced flow in the CE capillary, while the make-up solution is transporated by self-aspiration of the nebulizer. This type of design was developed by combining a commercial connecting unit and a spray chamber and was recently applied in mercury speciation by Lee and Jiang [65]

An interface based on an ultrasonic nebulizer has been described by Lu *et al.* [69] and Caruso *et al.* [70]. Although this construction has the advantage that the nebulizer does not cause any suction, it gives a higher background noise level than pneumatic nebulizers. Finally, a hydride generation CE–ICPMS interface has been designed by Magnuson *et al.* and consists of a polytetrafluoroethylene (PTFE) cross, a PTFE reaction manifold and isolating peristaltic pump. The electrolyte from the CE capillary is not directed into the ICPMS torch but to a hydride generator [71–73]. The gaseous analytes and excess H_2 migrate across the membrane of a gas–liquid separator into an argon carrier gas, which is then introduced directly into the central channel of the ICP torch.

Other detection techniques

Electrospray ionization–mass spectrometric detection (ESIMS) is a powerful detection technique providing selective detection and also structural information for organic substances. This approach has been employed for the determination of organoselenium species, but is lacking in concentration sensitivity when coupled with CE [27,63,74,75]. Demesmay and Rocc [76,77] developed a CE–MS method for the determination of seven As species with detection limits of 1–6 mg/L. Electrokinetic injection technique could be used to further lower the detection limits by a factor of around 10.

Atomic absorption spectrometry (AAS), atomic emission spectrometry (AES) and atomic fluorescence spectrometry (AFS) are powerful detectors

for element-specific analysis but they have not been connected with CE in an operationally effective manner. Similarly, there has been only one application of inductively coupled plasma atomic emission spectroscopy (ICPAES) for arsenic speciation published to date [78]. Electrochemical and conductivity detectors have been used commonly with HPLC but have been applied only rarely for CE for the target elements, with only one paper on speciation analysis appearing for each detection technique [23,79]. However, their detection sensitivities are somewhat better than UV detection (see Table III).

APPROACHES USED TO INCREASE DETECTION SENSITIVITY

As discussed earlier, on-capillary UV photometric detection is available on all commercial CE equipment but suffers from poor sensitivity due to the short path length, the small amounts of sample injected and the low absorptivities of most of the target analytes. Detection limits are usually only in the low mg/L range, which is inadequate for most environmental samples. Thus, the most severe drawback limiting the application of CE to trace element speciation is the lack of a general, sensitive and commonly available detection system.

To overcome this problem, either a greater amount of the sample has to be introduced into the capillary, or the detection sensitivity has to be increased. Several strategies can be adopted to achieve either or both of these goals. These include increasing the analyte concentration by sample preconcentration using off-line, on-line or in-line chromatographic methods (such as solid phase extraction, SPE), increasing the volume of the analyte introduced into the capillary followed by some form of on-capillary zone compression (or 'stacking'), and increasing the concentration sensitivity of the detection method.

Despite the fact that SPE has been increasingly applied for preconcentration of analytes when using chromatography or electrophoretic separation methods [80,81], there have been only two reports on SPE (off-line) applied to tin speciation with CE [47,48]. The results obtained demonstrate that the use of SPE with octadecylsilica sorbent or cation-exchange sorbents improves the detectability of both chromatographic and CE determination by about three orders of magnitude [47,48]. This offers the possibility of practical application of SPE to the environmental analysis of real water samples, except sea water because of its high ionic strength. However, the studies above were conducted with artificial samples and were not applied

to any real samples. For on-line SPE, the further problem is that it is difficult to combine with CE.

Increasing the detection sensitivity is a straightforward way of increasing the overall method sensitivity. For UV photometric detection, special capillaries designed to increase the path length can be used to enhance the sensitivity, typically by a factor of 3–10 times [82,83]. However, as the baseline noise often increases as well, the improvements in signal-to-noise and LOD values are rather modest and the specially manufactured capillaries or extended path length detection cells are quite expensive. As a result, there have been no applications of this technique to the target elements. Derivatisation of the analyte(s) is another possibility and can be realised by complexation of the analytes with appropriate ligands to obtain highly UV absorbing compounds.

Stacking

Stacking of an injected sample plug is an on-line preconcentration technique which is unique to CE. In a normal CE method, the sample plug must be short enough so that the separation is performed in diffusion-controlled zones of the individual analytes in order to maintain the separation efficiency. To increase the concentration sensitivity, the technique of sample stacking, or field-amplified sample injection, has been proposed by Chien and Burgi [84]. This technique operates on the basis of the lower conductivity of the sample solution with respect to the BGE solution. When the separation potential is applied to the capillary, a higher field strength is created in the lower conductivity sample zone, which causes the analytes ions to move faster and stack at the boundary of the sample and the BGE zones. The stacked analytes are then separated as usual within the BGE solution. As a result, the injected sample plug length can be increased without loss of resolution and the sensitivity can be considerably increased. Injection stacking was applied not only with UV detection but also with ICPMS detection [41].

Large volume sample stacking (LVSS) techniques have been used commonly in As and Se speciation with CE, where most of the analytes are negatively charged [85–88]. There are two modes for LVSS, namely with or without polarity switching. The former mode (LVSS with polarity switching) is conducted according to the following steps (shown the Fig. 4): First, (Fig. 4(a)) the analytes in a low-conductivity electrolyte are introduced hydrodynamically or electrokinetically into the capillary. Second, a high

voltage that is reversed in polarity compared to that used for the separation is applied and causes stacking of the analyte ions at the interface between the sample and BGE. Next, (Fig. 4(b)) as the sample zone stacking continues, the analyte ions will stay at this boundary forming a sharp band, while the plug of the sample solvent is pumped out of the capillary by the EOF moving in the direction towards the injection side. Finally, (Fig. 4(c)) once most of the sample plug has left the capillary, the polarity of the applied voltage is reversed, bringing the conditions back to normal for the separation and detection of the stacked ions. This technique allows the injection of a sample up to the full volume of the capillary, which permits maximum sensitivity to be obtained. However, polarity switching may lead to poorly reproducible results. The critical point in the polarity switching stacking procedure is the monitoring of the current that passes through the capillary. At the beginning of the stacking, the current is much lower than the usual separation current because the sample plug has a very low conductivity. During the stacking step the low conductivity sample solution is being replaced by the more conductive BGE, so the current gradually increases. When the sample plug has been completely removed, the current rapidly increases to the normal value corresponding to that of the BGE solution. The polarity should be reversed just before this normal value of the current is reached in order to avoid loss of the anionic analytes. With this strategy, the volume of the injected sample can be as large as whole capillary volume, hence the detection limit can be improved more than 100 times [85]. To remove the polarity switching step (i.e. to establish LVSS without polarity switching), EOF modifiers can be added to the BGE to dynamically coat the fused-silica capillary, or alternatively permanently coated capillary can be used to suppress the EOF. As a result, large volume sample stacking can be realised without polarity switching [87], and the stacking and separation procedure for anionic analytes can be presented as shown in Fig. 5. The important steps are as follows. First, (Fig. 5(a)) the analytes are introduced as a low-conductivity solution and a high voltage of the same polarity as used in the separation is applied. In this situation, the conductivity of the electrolyte is much higher than that of the sample, thus the electrophoretic mobilities of the analytes in the sample are much higher than those in the electrolyte because of the higher field strength in the sample plug. The negatively charged analyte ions in the sample region will be stacked against the boundary between the sample region and the electrolyte region. As the sample zone stacking continues (Fig. 5(b)), the analyte ions will stay at this boundary forming a sharp band, while the plug of the sample solvent is pumped out of the capillary by

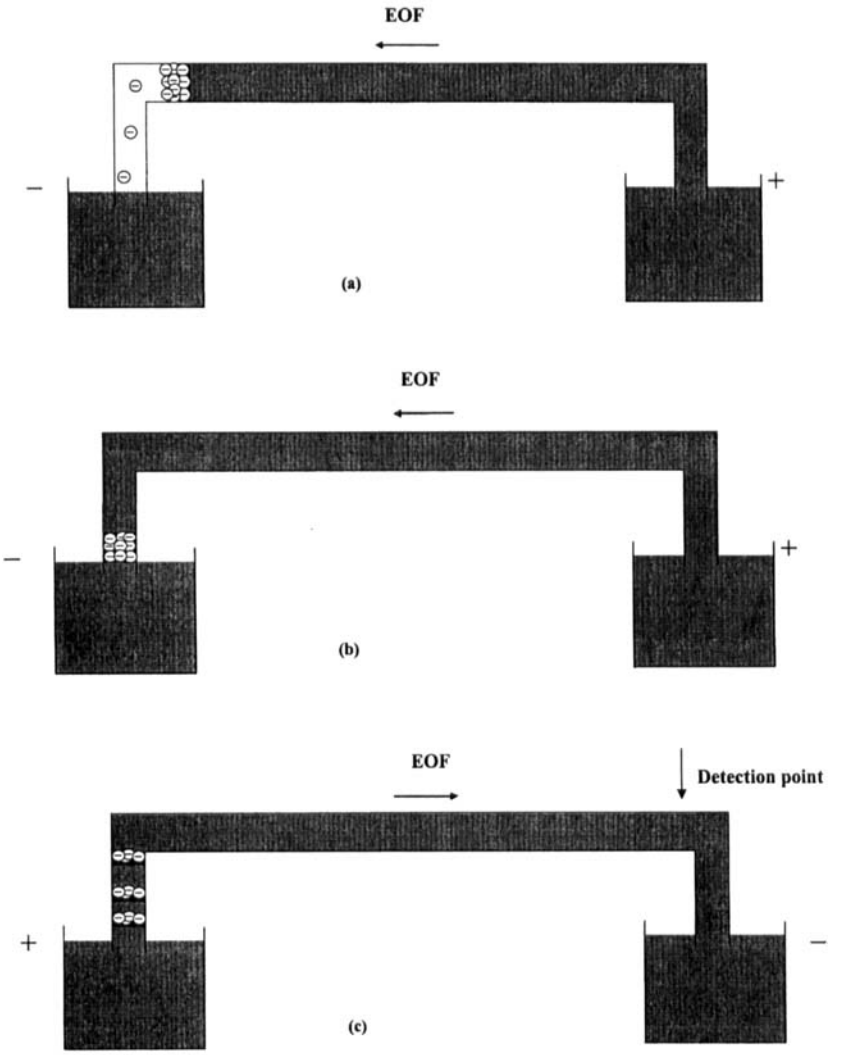


FIGURE 4 Large Volume Sample Stacking with polarity switching. (a) Analytes are introduced in a low-conductivity electrolyte, then reversed voltage is applied and the analytes undergo a process of stacking to form a band at the boundary between the sample electrolyte and the electrolyte. (b) The EOF pushes the analyte back to the cathode while sample plug is being removed. (c) Voltage polarity changed to normal, the stacked ions are separated and detected.

the EOF moving in the direction towards the injection side. Once most of the sample plug has left the capillary (Fig. 5(c)), the field strength in the electrolyte which now fills the whole capillary, increases sharply and the ions begin to migrate towards the detector and separate. In this case, the EOF

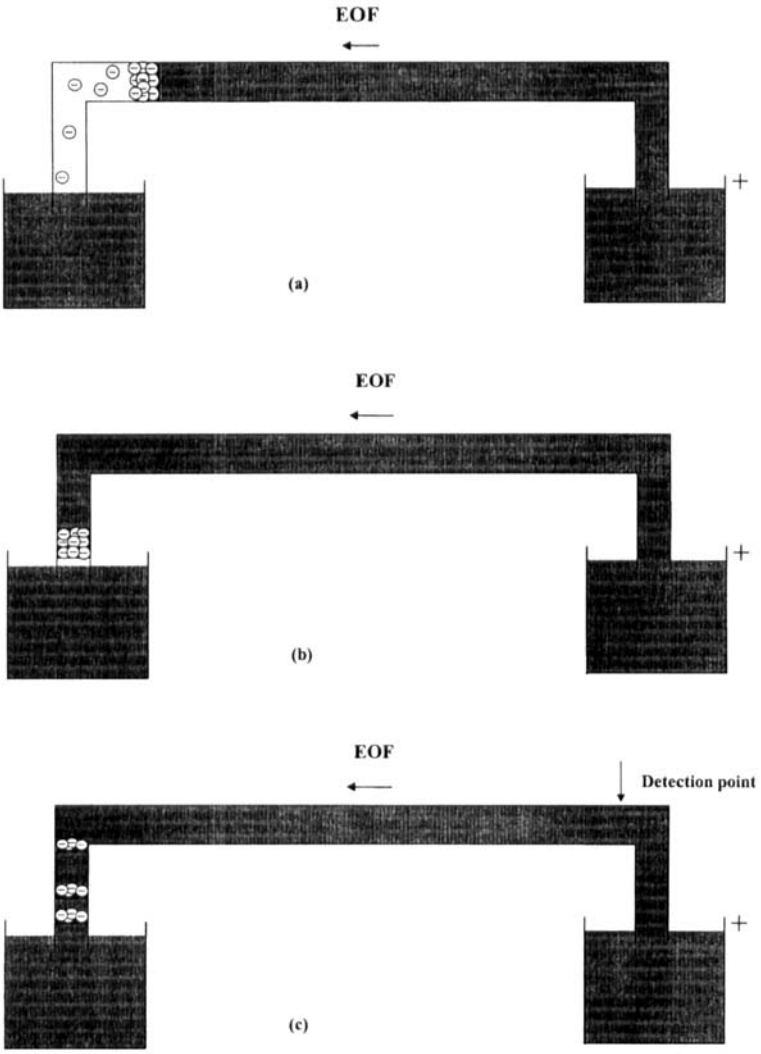


FIGURE 5 Large Volume Sample Stacking without polarity switching. (a) Analytes are introduced in a low-conductivity electrolyte, then normal polarity voltage is applied and the analytes undergo a process of stacking to form a band at the boundary between the sample electrolyte and the electrolyte. (b) The sample plug leaves the capillary and the ions are stacked in a narrow band. (c) The analyte ions are separated and detected.

modifier concentration, the volatage, and the injection volume should be considered carefully in order to prevent the slow-moving analyte anions from being pushed out of the capillary, and also to maintain the efficiency of the stacking procedure. Albert *et al.* [26] applied stacking without polarity

switching with tetradecyltrimethyl ammonium bromide (TTAB) as EOF modifier for the separation of As species and they achieved a sensitivity enhancement of 30–40 fold and a quantitative relationship between peak area and analyte concentration. Vanifatova *et al.* [31] obtained similar results with a permanently polymer-coated capillary.

When the sample ions are stacked under the amplified field, co-ionic impurities will also be simultaneously concentrated. In the analysis of a real sample, it is important to separate the impurities and sample matrix from the analytes [40]. A large volume sample stacking of positively charged analytes in CE without polartity switching was achieved by employing a low pH BGE containing a cationic surfactant [89], but has not yet been applied to the speciation of the target elements. However, this approach should be applicable to the positively charged species. Stacking methods are not applicable to neutral species of the target elements because they are unaffected by the electric field. However, Liu *et al.* have successfully preconcentrated trimethyllead chloride (TMLC), triethyllead chloride (TELC), phenylmercuric acetate (PMA) and other metal species using stacking injection after complexing these species with suitable reagents, such as nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), triethylenetetraminehexaacetic acid (TTHA), to give anionic products [33,36,90]. In the MEKC mode, charged and also uncharged analytes can be stacked [91], but the stacking techniques are complex in comparison to CE and have not yet been applied to the target analytes. There have been no applications of stacking techniques combined with indirect UV detection for speciation of the target elements and again this approach offers possibilities for sensitive and universal detection.

Derivatisation

To enhance their UV absorptivity, some analytes can be derivatised by complexation prior to the CE separation. Normally the analytes are extracted from samples with an organic solvent and their re-extracted by an aqueous solution containing a suitable derivatisation reagent. There are several derivatisation methods for the target elements. Cysteine was the first off-line derivatisation reagent used by Medina *et al.* [92]. Organomercury species were extracted from the sample and formed stable cysteine-organomercury-OK complexes before being injected. This derivatisation technique was later validated and developed further using stacking injection by Carro-Diaz *et al.* [46,93]. Dithizone has been one of the most studied chelating agents since it forms intensely coloured and very stable

complexes with a wide range of organometallic species [94]. However, most dithizone complexes with a wide range of organomettalic species [94]. However, most dithizone complexes are uncharged and insoluble in water so that they are unsuitable for CE separation. To overcome this, Tanaka *et al.* [95] described the synthesis of water-soluble dithizone sulfonate (DzS), which has been shown to be a suitable chelating reagent for CE methods. With this reagent, direct detection could be applied in the visible region and consequently the background noise could be reduced dramatically. Sodium diethyldithiocarbamate, which is a traditional chelation reagent for tin and lead, has also been employed to derivatise organolead and organotin species before a MEKC separation [34]. The complexation reagent was added to the extraction solvent to form UV-absorbing chelates and has also used as a BGE additive to improve the resolution in the CE separation. Liu *et al.* [36,33,90] employed NTA, TTHA and EDTA as complexation reagents in the BGE to simultaneously determine lead, mercury and selenium species. Combined with stacking injection, these methods can improve the sensitivity by a factor of up to several hundred times compared to common CE methods.

DISCUSSION OF CE SPECIATION METHODS FOR INDIVIDUAL ELEMENTS

Arsenic

Arsenic speciation using CE has been a very active research area. Normally, direct UV detection at 190–200 nm after separation in a phosphate electrolyte at pH 4.5–10 has been applicable for the determination of the most common arsenic species, such as arsenite, arsenate, and some other environmentally interesting As(V) forms, including monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) [12,25,42,96–100]. However, this detection mode is not very sensitive and the arsenic concentrations that can be detected are generally at mg/L levels in aqueous solutions. Morin *et al.* [12] applied CE to inorganic arsenic and organoarsenic analysis for the first time and DMA and MMA were separated successfully. CE methods applying EOF reversal are commonly used to speed up the separation [20,22,28,43,97]. Several surfactants, such as 3-[cyclohexyiamino]-1-propanesulfonic acid (CAPS) [101], tetradecyltrimethylammonium hydroxide [22], Anion BT [20], PDDAC [28], CTAB [43] and dodecyltriethylammonium dihydrogenphosphate [97] have been used to modify the EOF for

As speciation. Separation of nine As species has been optimized by Sun *et al.* who applied both normal and reversed EOF to improve the separation and large volume sample stacking techniques to improve the sensitivity [28]. Greschiong *et al.* [35] separated nine arsenic species with MEKC. There are several studies on the usage of stacking techniques to improve the detection limit down to the μg/L range [25,26,38,31,76,77,85,88,101]. Albert *et al.* [26,88] theoretically discussed large-volume stacking for quantitative analysis of anions with and without polarity switching. However, for the analysis of real samples which required the removal of sample matrix components, the polarity switching method was more often applied [28,40,85].

CE coupled to ICPMS has been applied increasingly to arsenic speciation [29,41,44,52,54–58,71–73]. Magnuson *et al.* [29] determined four arsenic and two inorganic selenium species with CE coupled to ICPMS. Hydrodynamically assisted EOF and on-line hydride generation were employed and almost quantitative transport of the gaseous hydride into the ICP without interference from the sample matrix was achieved. Tian *et al.* [73] applied this method to arsenic speciation in Chinese herbal medicine. CE–ICPMS combined with a sample stacking technique was used by Michalke to separate and detect six As species of common interest [30,41]. A phosphate buffer was employed as BGE in an uncoated capillary, together with a special two-step injection technique derived from capillary isoelectric focusing which was used for sample stacking and gave detection limits of 15 μg/L As for DMA and MMA and 65 μg/L As for arsenobetaine and arsenocholine. A similar study was made by Van Holderbeke *et al.* [44], who used 20 mM borate buffer (pH 9.4) containing 2% of Anion-BT EOF modifier as BGE and achieved better detection limits (1.3–2.1 μg/L). The method was applied to the speciation of As in mineral water, human urine and soil leachate. Arsenic species and organolead have also been separated by MEKC and detected by ICPMS with a 4 mM borate buffer pH 9.3 used as the BGE, with detection limits at the μg/L level [55].

Day *et al.* [54] separated five arsenic species by both indirect UV absorbance and ICPMS detection. Reversed polarity and a chromate BGE containing an EOF modifier were applied. Indirect UV detection for inorganic arsenic analysis has also been described with detection limits in the same order of those obtained with direct UV detection [54,102]. Tian *et al.* [78] described a CE–ICPAES method where the effluent from the CE capillary was mixed with KBH_4/tartaric acid (1 : 3) in a hydride generator and the Ar carrier gas flow analysed for As by ICPAES. The detection limits were 0.32 and 0.35 mg/L for MMA and DMA, respectively, which are similar to those obtainable with direct UV detection. A conductomeric

detection method was established for arsenic and selenium specification by Schlegel *et al.* [23], which improved the sensitivity slightly with a detection limit of 40–70 μg/L. Huang and Whang [50] developed an indirect LIF method for arsenic speciation in which five arsenic species were separated in 8 min (See Fig. 6). The detection limits were in the range 40–60 μg/L. Seven arsenic species have also been separated and detected at ~mg/L levels with CE–MS, and use of a stacking technique enabled further reduction of the detection limits by approximately one order of magnitude [76,77].

Selenium

The identification and determination of the many chemical forms of selenium in environmental and biological systems is a major challenge for the analytical chemist. Of particular importance is the need to minimise interactions of analyte species with the stationary and mobile phases which may cause decompositional changes of the analytes [103,104]. Thus CE, which operates without any stationary phase, offers a considerable advantage for these analyses compared to liquid chromatography [85,103].

The first method for organoselenium analysis by CE was set up by Ng *et al.* [37], who used a MEKC system with β-cyclodextrin added to BGE. Albert *et al.* used TTAB to control the EOF and separated organoselenium species at a voltage of − 18 kV, achieving detection limits of around 1 mg/L [24,42]. After optimisation of CE parameters for selenium speciation, Hagege [105] reported that indirect direction of 254 nm gave better detection limits than direct detection at 190 nm. Liu and Lee [33,36,90] developed a method for the simultaneous determination of ten inorganic and organic species of Pb, Hg and Se following pre-capillary derivatisation with NTA, TTHA [See Fig. 7] and EDTA. The detection limits of the analytes were improved by stacking, down to the sub-μg/L Level.

A conductivity detection method was established by Schlegel *et al.* [23] The separation conditions involved electrokinetic injection onto a fused silica capillary pretreated with 1 mM hexadecyltrimethylammonium bromide for 20 min at the start of each day and for 0.5 min before each analysis, and a BGE containing 0.3% Triton X-100 and 50 mM 2-(cyclohexylamine)-ethanesulfonic acid, adjusted to pH 9.4 with LiOH. Several CE–ESIMS methods could be used to separate selenomethionine, selenocystamine and selenocystine, but the absolute sensitivity was poor (low mg/L level) [27]. CE–ICPMS has been used commonly for the speciation of selenium [56–60,106]. Michalke *et al.* [30,107] developed a capillary isoelectric focusing

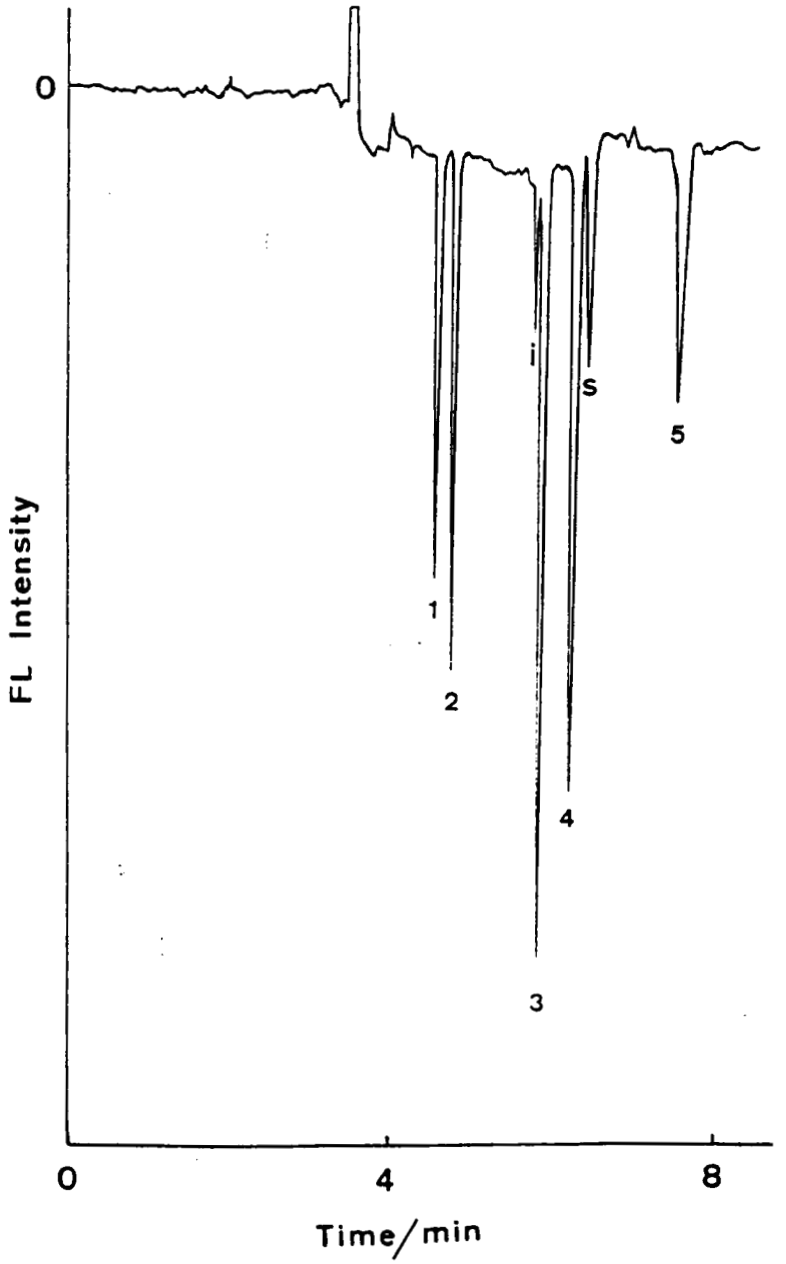


FIGURE 6 Electropherogram of five arsenic compounds with indirect fluorescence detection. Peak identities: 1, As(III); 2, DMA; 3, PhA; 4, MMA; 5, As(V); each at 4 mg/L. Conditions: 1.5 mM fluorescein, pH 9.8; applied voltage, 15 kV; electromigration injection, 2s at 15 kV; LIF detection $\lambda_{ex} = 488$ nm, $\lambda_{em} = 520$ nm. Reprinted with permission from ref. [50].

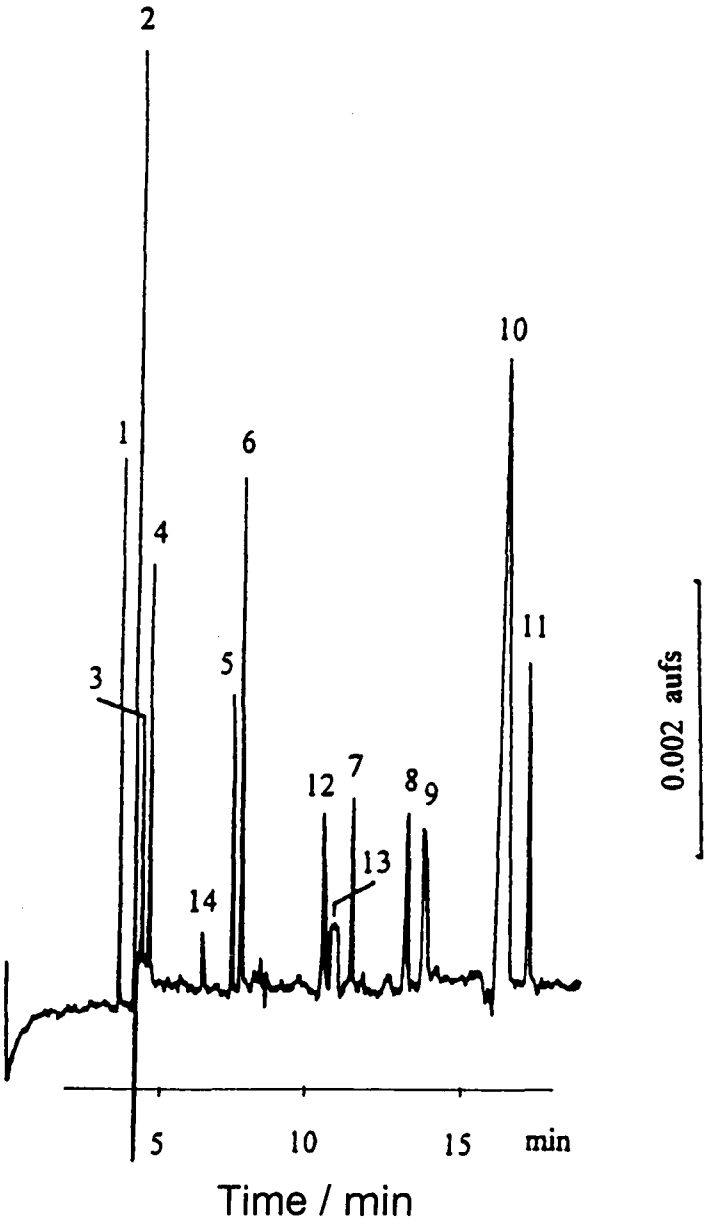


FIGURE 7 Electropherogram of selenium, lead and mercury species by complexation with TTHA in MEKC mode. Peak identities (concn, mg/L) 1, TELC (0.37); 2, MeOH; 3, DPS (12.5); 4, TMLC; 5, PSC (0.35); 6, DPLC (0.16); 7, Pb(II); 8, Se(IV) (0.32); 9, PMA (0.12); 10, TTHA; 11, Hg(II) (0.082); 12, Mg(II); 13, Ca(II); 14, Na(I). Conditions: TTHA/2 mM SDS 40 mM phosphate/borate pH 7.5; stacking voltage were +/− 10 kV, applied volatage during separation was 20 kV. Reprinted with permission from ref. [33].

method for separating Se(IV), Se(VI), selenium-carrying glutathione, selenomethinonine, selenocystine and selenocystamine using 10 mM Na_2CO_3 (pH 11.5) as BGE. The separation was stopped after 10 min and detection was carried out by pressure-assisted forcing of the separated analyte bands into the ICP nebulizer. Detection limits were in the 10–20 μg/L and 30–50 μg/L ranges for inorganic and organic forms of Se, respectively. The same authors also developed, for the first time, a CE–ICPMS method for the simultaneous separation of all six Se species in the same electropherogram. The detection limits were 10–50 μg/L [57] [See Fig. 8]. Compared to CE–ESIMS, CE–ICPMS has 10^2 to 10^3 times better sensitivity and provides a shorter analysis time [38].

Mercury

Analytical methods for mercury speciation published up to 1994 have been reviewed previously [108]. There are two approaches for the speciation of mercury: selective reduction and chromatographic methods. Selective reduction methods have a major drawback in that they only distinguish between inorganic and organic mercury, and not between the individual organic species. On the other hand, chromatographic methods can determine individual organomercury compounds directly.

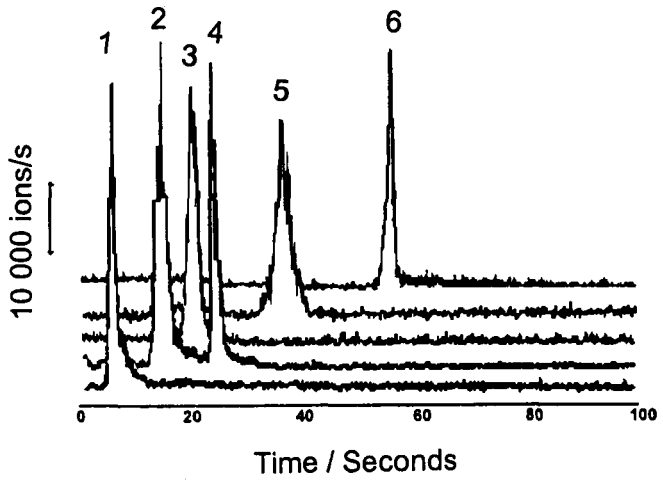


FIGURE 8 Electropherograms of six selenium species with CE–ICPMS. Peak identiies: 1, SeCM; 2, Se(VI); 3, SeC; 4, Se(IV); 5, SeM; 6, GSSeSG; each at 0.5 mg/L. Conditions: 10 mM Na_2CO_3, pH 11.5; applied volatage 18 kV. Reprinted with permission from ref. [57].

Carro-Diaz *et al.* [109,110] reviewed the up-to-date applications of chromatographic methodology for the speciation of organomercury compounds in food analysis, and compared the methods of GC with ECD, GC with AES detection, and CE with diode-array detection. GC with ECD was used commonly for the detection of the organomercuric halides. The problems of GC methods lie in irreversible interactions of organomercuric compounds with the chromatographic support, but these can been solved to some extent by using capillary columns and careful conditioning procedures. HPLC methods have also been developed using a variety of detection systems. Like organotin, organomercury compounds have no strong absorption in the UV region so it is impossible to establish a sensitive CE method based on spectrophotometric detection. Therefore, indirect UV methods and derivatisation methods have to be applied. The most common detection method for organomercury compounds in based on pre-capillary or on-capillary derivatisation to form strongly UV absorbing mercury complexes. In general, mercury forms very stable complexes, particularly with sulfur-containing ligands.

Medina *et al.* [92] found that the cysteine complexes were stable during electrophoretic separation and could be detected with reasonable sensitivity in the low UV region. The complexes of organomercuric compounds were cysteine were separated by CE using a BGE comprising 100 mM sodium borate at pH 8.35, and UV detection at 200 nm. The mercury species ethylmercury, methylmercury, and phenylmercury and inorganic mercury were well resolved in 12 min. For methylmercury, the detection limit was 10 pg. The method was applied to the analysis of seafood and the results were compared with those obtained by GC. This technique has been further investigated with respect to sample stacking by Carro-Diaz *et al.* [93] With the stacking techniques, the detection limit was up to 12 μg/kg (as methylmercury in the sample). Since many inorganic and organic substances absorb strongly in the low-UV region, interferences and unstable baselines troubled the detection. Therefore, Jones and Hardy [32] developed a different derivatisation method using dithizone sulfonate which allowed the detection of organomercuric compounds at 480 nm. Electrophoresis was carried out at −25 kV in a capillary internally coated with polyacrylamide. Sample solutions containing the pre-formed dithizone sulfonate complexes were injected hydrostatically into the cathodic end with a BGE of 10 mM sodium acetate at pH 5 containing 5 mg/L dithizone sulfonate. The method was able to separate the complexes of inorganic mercury, methylmercury, ethylmercury and phenylmercury in 7 min, with detection limits at the μg/L level. Complexes with other metals at up to 10 mg/L did not interfere

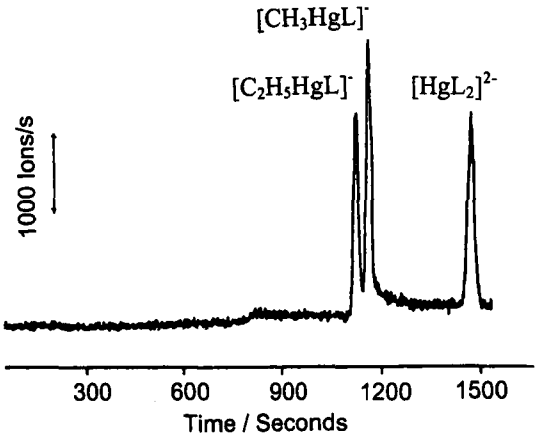


FIGURE 9 Electropherograms of three organomercury species with CE–ICPMS; each at 10 mg/L. Conditions: 10 mM Na_2CO_3, pH 11 containing 20 mM SDS; applied voltage 15 kV. Reprinted with permission from ref. [65].

because of their lower stability during electrophoresis. The method was applicable to the analysis of fish and crab tissues [32,45]. As discussed above, NTA, EDTA and TTHA derivatisation methods were also used for the determination of PMA [33,36,90] and excellent detection limits could be achieved by stacking injection techniques.

Methylmercury and ethylmercury have been separated by CE with amperometric detection by Lai *et al.* [79]. They applied electrokinetic injection, 100 mM creatinine at pH 4.6 as the BGE and amperometric detection at -0.2 V vs. Ag/AgCl (Au working electrode, Pt counter electrode). The detection limits for methylmercury(II) and ethylmercury(II) were 25 and 150 μg/L, respectively.

CE coupled with ICPMS has been recently developed for the speciation of mercury [64–66,68]. In the same manner as described by Tu *et al.* [64], the Hg compounds were separated as Hg-cysteine complexes by CE in a fused-silica capillary at 20 kV and using a 20 mM borate buffer (pH 9.3), and detected on-line with both quadrupole and double-focusing ICPMS. The detection limits were 13.6 μg/L for methylmercury and 6.0 μg/L for mercury(II), corresponding to absolute detection limits of 2.3 pg and 1.0 pg, respectively. Rocha *et al.* applied a similar separation mode, but when coupled with stacking techniques, the detection limits could be as low as 4 and 7 μg Hg/L for inorganic mercury and methylmercury, respectively [66,68].

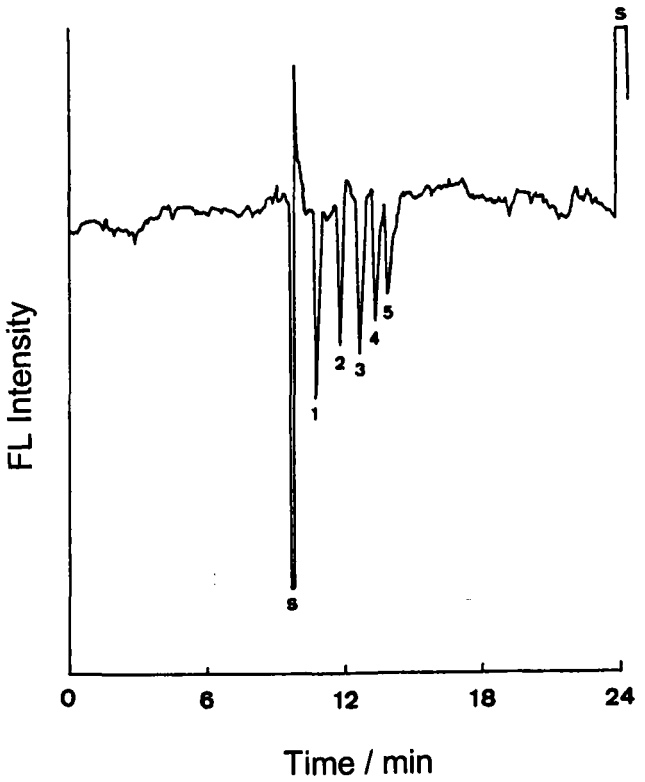


FIGURE 10 Electropherograms of five triorganotin compounds with indirect fluorescence detection; each CE–ICPMS; Peak identities: 1, TMT (17.8 mg Sn/L); 2, TET (11.9 mg Sn/L); 3, TPT (8.78 mg Sn/L); 4, TBT (6.53 mg Sn/L); 5, TPhT (4.75 mg Sn/L). Conditions: 70 mM HEPES, pH 4.0 containing 1 mM 6-AQ; applied voltage 300 V/cm. Detection $\lambda_{ex} = 404$ nm, $\lambda_{em} = 515$ nm. Reprinted with permission from ref. [21].

Tin

Several methods have been proposed to separate and quantify organotin compounds. The most commonly used separation technique is GC with flame photometric detection (FPD), electron capture detection (ECD) or atomic emission detection (AED). Although CE is a potential alternative method for tin speciation, GC methods are clearly prevailing for this task because of the much higher detection sensitivity compared to CE. There have not been any papers for the application of ICPMS detection or stacking techniques for the analysis of organotin compounds.

Direct detection or organotin compounds by UV photometry of fluorimetry is difficult for CE methods because most organotin analytes do not

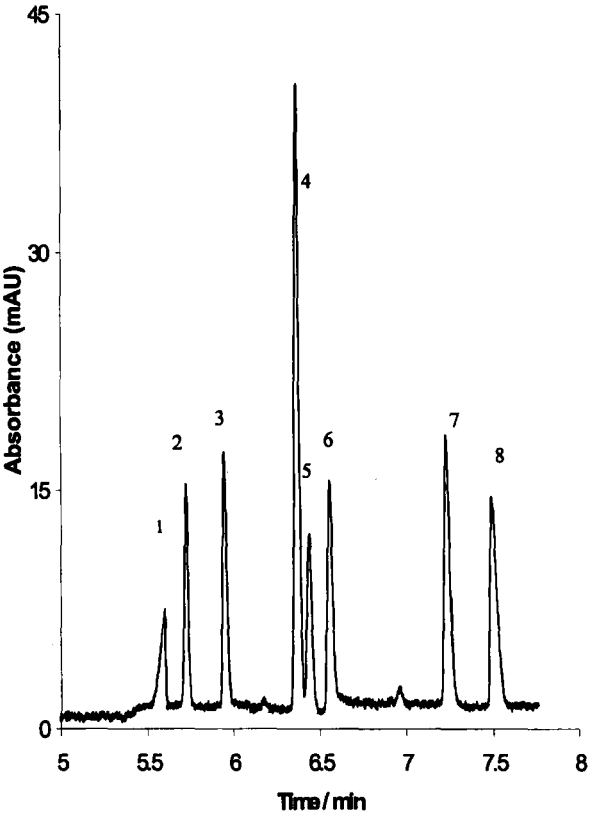


FIGURE 11 Standard electropherogram of arsenic species in reversed EOF mode. Peak identities: 1, AS(V); 2, Roxarsone; 3, MMA; 4, PAA; 5, 4-NPAA; 6, PABA; 7, As(III); 8, DMA. 0.4 mg As/L for aromatic species and 2 mg As/L for others. Injection: 160 s × 50 mbar. Separation Conditions: 50 μm × 60 cm PDDAC coated capillary, −25 kV, 20 mM carbonate buffer pH 10.0.

possess good chromophores or fluorophores. Therefore, indirect detection is usually employed [20,21,47,48]. Han *et al.* [20] used pyridine as the UV absorbing probe, CTAB as EOF modifier, and the BGE was adjusted to pH 2.65.

TBT, dibutyltin and dimethyltin in aqueous solutions were separated successfully. Whang *et al.* [49] set up an indirect UV method with 4-aminopyrindine (4-AP) as the UV-absorbing probe. Five triorganotin cations were efficiently separated by CE in 10 min with 5 mM acetate BGE at pH 4.5 containing 3 mM 4-AP. Resolution of the various organotin species can be significantly enhanced by the inclusion of α-cyclodextrin in the BGE. The concentration limits of detection for the organotin compounds

studies were in the range 0.24–2.4 mg Sn/L. Pobozy *et al.* [47] employed solid-phase extraction to preconcentrate TMT, TET, TBT and TphT in a water sample, followed by separation using 20 mM-tartaric acid containing 20% methanol/2 mM-BTMA at pH 2.6 as BGE, with indirect UV detection at 210 nm. This method was used to determine organotin compounds in water at the μg/L level. After comparing five different commercially available sorbents, XAD-2 resin was regarded as the best for solid-phase extraction of TBT and TPT. Co and Cr complexes and organotin in environmental sample can also be detected by a similar method [48]. Lee and Whang [21] developed an indirect fluorescence detection for triorganotin. 70 mM HEPES at pH 4.0 was used as BGE, with 1 mM 6-aminoquinoline (6-AQ) being added as the electrolyte fluorophore. Indirect fluorescence detection was performed using a non-laser-based fluorometer. The concentration limits of detection for the five triorganotin compounds were in the range 0.95–2.1 mg Sn/L, which are similar to the results obtained with indirect UV detection.

An MEKC method using direct UV detection and with SPE was developed by Li *et al.* [34]. Two triorganotin and two triorganolead compounds were derivatised with sodium diethyldithiocarbamate. SPE was used with Empore C_{18} silica discs, and the adsorbed analytes were eluted with methanol. The BGE was 0.05 M-SDS in 15 mM borate–30 mM phosphate at pH 7.65. The detection limits were 15.5 pg and 42.1 pg for trimethyltin and tributyltin, respectively.

Lead

The most common technique for the speciation of organolead species is gas chromatography with AAS detection [111,112]. Major disadvantages of this technique are the need for this highly specialized detector and the requirement for purification steps to remove interferences from other forms of organic and inorganic compounds. More recently. HPLC has been used for the determination of these compounds but it does not offer better sensitivity than GC [113].

The CE methods for the determination of organolead are very limited in number. Most published papers have used MEKC with UV detection. Ng *et al.* [37] established a MEKC method for the determination of organolead in conjunction with organoselenium. β-cyclodextrin was used to improve the peak shapes and on-capillary UV detection was performed at 210 nm. This method was applied to the analysis of trialkyllead and organoselenium compounds in spiked distilled water and environmental samples. The detection

limits were 20 pg and 8 pg for trimethyllead and triethyllead, respectively. A further direct UV detection MEKC method by Li *et al.* [34] was applied to the separation of two triorganotin and two triorganolead species after derivatisation with sodium diethyldithiocarbamate. SPE was performed off-line with Empore C_{18} silica discs and the analytes were eluted with methanol. The detection limits were 22.4 pg and 17.2 pg for trimethyllead and triethyllead, respectively.

Liu and Lee [33,36,90] developed a simultaneous method for the determination of ten inorganic and organic species of Pb, Hg and Se following precapillary derivatisation with NTA, TTHA or EDTA. The derivatisation was performed with 5 mM NTA in phosphate/borate buffer at pH 6 and the BGE consisted of 40 mM SDS and 5 mM NTA in phosphate/borate buffer at pH 7, with detection at 200 nm. A theoretical model was presented relating the migration behaviour of the analytes to the BGE composition. The detection limits were 40 and 100 μg/L for TELC and diphenyllead chloride (DPLC), respectively, using hydrodynamic injection and 2.48 μg/L for DPLC with stacking [36]. Triethlyllead, diphenyllead, organomercury and organoselenium were separated in a BGE containing 2.5 mM TTHA, 2 mM SDS and 40 mM phosphate/borate buffer at pH 7.5. With polarity-switching field-amplified stacking injection techniques, detection limits of 2.0 and 0.3 μg/L were obtained for triethyllead and diphenyllead, respectively [33]. Better sensitivity was achieved when EDTA was employed as the derivatisation reagent, with sub-μg/L detection limits being reported [90].

CE–ICPMS has been applied for the detection of organolead compounds. Trimethyllead, triethyllead and arsenic species have been separated by MEKC and detected by ICPMS using a borate BGE, with detection limits in the μg/L range [55].

CONCLUSIONS

In this paper, developments in the area of speciation analysis of tin, lead, mercury, arsenic and selenium by CE between 1992–2000 have been reviewed. In this period, CE has developed as a viable method for speciation analysis and plays an increasingly important role. Solid-phase extraction, injection stacking techniques, derivatisation, and the use of highly sensitive ICPMS detection are the approaches used to enhance the method sensitivity and to make it applicable to environmental analysis. ICPMS has become the method of choice for Se and As speciation because of its high sensitivity and selectivity, although more applications to real samples are yet to come.

Because of the environmental importance of the speciation of the target elements, further intense research activity in this area is to be expected.

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LIST OF ABBREVIATIONS

AAS	atomic absorption spectrophotometry
AES	atomic emission spectrophotometry
AFS	atomic fluorescence spectrophotometry
AsB	arsenobetaine
AsC	arsenocholine
BGE	background electrolyte
BTMA	benzyltrimethylammonium chloride
CAPS	3-(cyclohexylamino)-propanesulfonic acid
CE	capillary (zone) electrophoresis
cIEF	capillary isoelectric focusing
Co-EOF	co-electroosmotic flow
CTAB	cetyltrimethylammonium bromide
DETA	diethylenetriamine
DIN	direct injection nebulizer
DMA	dimethylarsinic acid
DMT	dimethyltin
DPA	diphenylarsonic acid
DPLC	diphenyl-lead chloride
ECD	electron capture detector
EDTA	ethlenediamine tetraacetic acid
EOF	electroosmotic flow
ESI MS	electrospray ionisation–mass detection
EtHg	ethyl mercury
FPD	flame photometric detection
FS	Fused silica capillary
GC	gas chromatography
GSSeSG	selenium carrying glutahione
HEPES	N-2-hydroxyethylpiperazine-N′-2-ethane sulfonic acid

HPLC	High performance liquid chromatography
ICPAES	inductively coupled plasma
ICPMS	inductively coupled plasma mass spectrometry
LIF	Laser induction fluorescence
MBT	monobutyltin
MeHg	methyl mercury
MEKC	micellar electrokinetic chromatography
MGLS	membrane gas–liquid separator
MMA	monomethylarsonic acid
NTA	nitrilotriacetic acid
PAA	ployacrylamide
PABA	*p*-aminobenzenearsonate
PDDAC	Poly(diallyldimethylammonium chloride)
PEEK	polyetheretherketone
PMA	phenylmercuric acetate
PSC	Phenyl selenium chloride
PTFE	polytetrafluoroethylene
SDS	sodium dodecylsulphate
SeC	selenocystine
SeCM	selenocystamine
SeE	Selenoethnionine
SeM	selenomethionine
SPE	Solid phase extraction
TBT	tributyltin
TELC	triethyl-lead chloride
TET	trimethyltin
TMLC	trimethyl-lead chloride
TMT	trimethyltin
TPhT	triphenyltin
TPLC	triphenyl-lead chloride
TPT	tripropyltin
TTAB	tetradecyltrimethyl ammonium bromide
TTHA	triethylenetetraminehexaacetic acid

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